

Karl Blum

# Density Matrix Theory and Applications

*3rd Edition*



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Karl Blum

# Density Matrix Theory and Applications

Third Edition

With 31 Figures

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# Preface to the Third Edition

The main change in this edition is the addition of the new Sect. 3.6, which explores one of the most puzzling aspects of quantum mechanics, the non-separability or entanglement of correlated systems. Because of its inherent difficulties the basic concepts are explained and reexplained in various ways, and illustrated by examples. The discussion concentrates on two-particle spin-1/2 systems. The reason for this is twofold. Firstly, correlated spin-1/2 particles represent an excellent model system which allows to develop the theory in a transparent way close to possible experiments. Secondly, the discussion will provide us with additional examples illuminating the general density matrix theory developed in the preceding chapters. The discussions are kept on an introductory level. The new Sect. 3.6 can be read immediately after Sects. 1.1, 3.1, and 3.2.

Furthermore, five additional appendices have been included that clarify some points raised in the main text, or provide supplementary material.

Finally, I would like to thank Priv.-Doz. Dr. Bernd Lohmann for his expert technical assistance in preparing the manuscript. I have profited from his many helpful comments and suggestions, and from his knowledge of quantum information theory.

Münster  
July 2011

*Karl Blum*



# Preface to the Second Edition

Since publication of the first edition, many studies on oriented and aligned systems have been performed, ranging from atomic collision physics to molecular processes, and to interactions with surfaces. No attempt has been made in the present volume to cover all these developments. Rather, a few topics have been selected.

In Chap. 4 a section on the “natural system,” popular in atomic collision physics, is included. In Sect. 4.6.5 a description of shape and spatial orientation of atomic charge distributions is given in order to obtain a deeper insight into the geometrical significance of state multipoles. Two new sections in Chap. 6 deal with the interactions of atomic charge clouds and external fields. Neither of these sections attempts to give a complete survey of the many experimental and theoretical results obtained in this field. Rather, the emphasis is on pointing out the essential features by studying simple cases.

The main addition is the new Chap. 7, in which the previously developed methods are extended to cover oriented and aligned molecules. The bulk of this chapter can be read after Sect. 4.5. The first sections contain a detailed treatment of angular momenta and axes distributions of linear rotors and symmetric tops. Since the angular momenta are often sufficiently high, semiclassical approximations apply and have been used throughout this chapter to illustrate quantum mechanical results. The techniques developed in these sections are then extended in order to include electronic orbital orientation and alignment, which are related, for example, to shape and spatial directions of electronic orbital lobes. A systematic treatment of these topics is attempted in Sect. 7.7. The basic definitions are introduced and illustrated with some simple examples, and the theory is then gradually developed. In Sect. 7.8 the formalism is applied to some topics in the rapidly expanding field of “dynamical stereochemistry.” The main purpose of this chapter is to introduce methods which allow coverage of a broad range of phenomena in a systematic and coherent way.

Smaller additions have been made throughout the book in order to relate their material presented here to more recent experimental and theoretical results. As in the first edition, no attempt has been made to present a complete list of references. Because this book is meant as an introduction, references are preferentially made to

monographs and reviews. As a rule, original papers are only cited if the results are used in the text or if no review is available.

I have many debts I would like to acknowledge. First I wish to thank Prof. J. Kessler and Prof. H. Kleinpoppen for continual encouragement and help over many years. Discussions with Dr. K. Bartschat, Dr. D. Thompson, and many colleagues from Queen's University in Belfast, and the University of Münster have helped to clarify many passages. In particular, I would like to thank my co-workers, K. Bonhoff, A. Dellen, R. Fandreyer, R. P. Nordbeck, S. Nahrup, B. Lohmann, J. Lehmann, C. Ostrawsky, A. Raeker, G. Wöste, and U. Kleinmann, each of whom has added a more or less mosaic piece to this book in the form of a Diploma- or Ph.D. thesis. I also acknowledge their help in preparing the figures and checking the equations. In addition, I wish to express my appreciation to Mrs. Volmer and Mrs. Oenning for carefully and patiently typing and correcting the many versions of this manuscript.

*Karl Blum*

# Preface to the First Edition

Quantum mechanics has been mostly concerned with those states of systems that are represented by state vectors. In many cases, however, the system of interest is incompletely determined; for example, it may have no more than a certain probability of being in the precisely defined dynamical state characterized by a state vector. Because of this incomplete knowledge, a need for statistical averaging arises in the same sense as in classical physics.

The density matrix was introduced by [von Neumann \(1927\)](#) to describe statistical concepts in quantum mechanics. The main virtue of the density matrix is its analytical power in the construction of general formulas and in the proof of general theorems. The evaluation of averages and probabilities of the physical quantities characterizing a given system is extremely cumbersome without the use of density matrix techniques. The representation of quantum mechanical states by density matrices enables the maximum information available on the system to be expressed in a compact manner and hence avoids the introduction of unnecessary variables. The use of density matrix methods also has the advantage of providing a uniform treatment of all quantum mechanical states, whether they are completely or incompletely known.

Until recently the use of the density matrix method has been mainly restricted to statistical physics. In recent years, however, the application of the density matrix has been gaining more and more importance in many other fields of physics. For example, in modern atomic physics, density matrix techniques have become an important tool for describing the various quantum mechanical interference phenomena which are of importance in scattering theory, quantum beat spectroscopy, optical pumping, and laser physics. This book proposes to introduce the reader to the methods of density matrix theory with an emphasis on their application in atomic (and nuclear) physics. It is aimed at beginners and not experts. All the basic concepts are therefore discussed in detail and all the steps in the calculations are explained. As background, a standard one-year course in quantum mechanics is assumed, as is knowledge of the elements of statistical mechanics. Some background in modern atomic physics and scattering theory would also be helpful. For Chaps. 4–6 the reader should have a working knowledge of angular momentum theory. Otherwise the treatment is begun

from the lowest level possible. Some topics of contemporary interest are covered in sufficient detail to make the book also useful to those readers engaged in research in the fields of atomic or nuclear physics, laser physics, and physical chemistry.

The book can be divided into three main parts. In the first three chapters the basic concepts and methods of density matrix theory are introduced. In order to do this, some of the fundamental ideas of quantum mechanics and statistics are discussed. In particular, a clear understanding of pure and mixed quantum mechanical states is important. This is best achieved by considering simple systems. For this reason Chap. 1 is restricted to a discussion of the polarization states of spin-1/2 particles and photons, which enables all the basic concepts to be introduced in a simple way. The density matrix is first introduced as the counterpart of the distribution function of classical statistical mechanics, that is, by considering how many systems are in an ensemble with given wave functions. Then, after some of its basic properties are discussed, another aspect of the density matrix is considered: By introducing a convenient parametrization it is shown that the density matrix is the most convenient way of collecting all parameters of interest for a given experimental setup and of describing their behavior from an operational point of view.

In Chap. 2 these results are generalized to systems with more than two degrees of freedom and the basic properties of the density matrix derived in a more systematic way. The concept of coherence, which will be of central importance for the discussion of quantum mechanical interference phenomena in the following chapters is introduced. The properties of the time evolution operators are then reviewed and the basic equations of motion for statistical mixtures derived and illustrated with some examples.

In Chap. 3 another important aspect of the density matrix is introduced. Often, one is only interested in a few of many degrees of freedom of a quantum system, for example, when only one of several interacting systems is observed. In Sects. 3.1 and 3.2 it is shown that, in general, it is impossible to find a wave function which depends only on the variables of the system of interest and not on those of all other systems as well. By averaging over all unobserved degrees of freedom a density matrix is obtained which describes the behavior of the system of interest. It is then shown that this “reduced” density matrix is the most general description of an open quantum mechanical system. The consequence of these general results are illustrated in Sects. 3.3 and 3.4 with particular emphasis on the quantum mechanical theory of coherence. Finally, in Sect. 3.5 the reduced density matrix of atoms excited by electron impact is constructed and discussed in detail.

The subjects discussed in this chapter are related to the quantum mechanical theory of measurement. The questions raised here have attracted a great deal of interest from physicists in recent years.

The second part of the book (Chaps. 4–6) is devoted to the application of the irreducible tensor method in density matrix theory. Quantum mechanical calculations for systems having symmetry can be divided into two parts. The first part consists of deriving as much information as possible from the symmetry requirements. The second part consists of calculating the dynamical quantities for which no information can be obtained from symmetry considerations. Often these two parts

are tangled. The irreducible tensor method is designed to separate dynamical and geometrical elements and to provide a well-developed and efficient way of making use of the symmetry.

In Sects. 4.2 and 4.3 the basic properties of tensor operators are discussed and the irreducible components of the density matrix (state multipoles, statistical tensors) are introduced. Sects. 4.4–4.6 give various applications of the method, while Sect. 4.7 is devoted to a discussion of the time evolution of state multipoles in the presence of external perturbations.

The formalism developed up to this point is then applied in Chaps. 5 and 6 to various problems of relevance to modern atomic spectroscopy, including the theory of quantum beats, electron-photon angular correlations, and the depolarization of the emitted radiation caused by fine and hyperfine interaction and magnetic fields. Throughout these chapters the discussion of quantum interference phenomena in atomic physics is based on the concept of “perturbation coefficients” developed by nuclear physicists in order to describe perturbed angular correlations. This formalism allows a very economic interpretation of experiments.

The last part of the book (Chap. 7) can be read independently of Chaps. 4–6 (except some parts of Sects. 7.5 and 7.6). In this chapter we discuss the density matrix approach to irreversible processes relating reversible and irreversible dynamics via generalized Master equations. Throughout this chapter the Markoff approximation is used. In Sect. 7.1 the fundamental concepts are introduced and the basic equations derived by considering the interaction between a “small” dynamic system and a “large” one (“heat bath”). Irreversibility is introduced by assuming that the bath remains in thermal equilibrium at constant temperature, irrespective of the amount of energy and information diffusing into it from the dynamic system. The special case of rate equations (Pauli’s Master equation) is considered in Sect. 7.2. The formalism is then applied to some simple examples in radio- and microwave spectroscopy. In order to illustrate the use of Master equation techniques in quantum electronics we consider the interaction between electromagnetic fields and two-level atoms. The corresponding Master equation is discussed in detail and the effects of relaxation interactions on the emitted line are described. In Sect. 7.4, the Bloch equations are derived and applied to magnetic resonance phenomena. It is shown that the density matrix method enables both longitudinal and transverse relaxation to be treated in a natural way, thereby avoiding the shortcomings of semiclassical theories. The usefulness of the Bloch equations for a description of the interaction between atoms or molecules and laser or maser fields is briefly considered.

The discussion of the general formalism is then continued by deriving the general properties of the relaxation matrix in Sect. 7.5. The discussion of the Liouville formalism in Sect. 7.6 is restricted to the basic concepts. Finally, in Sect. 7.7, the response of a quantum system to an external field is considered. Here, an expression is derived by approximating the exact equation of motion of the density matrix in retaining only terms linear in the field strength. This method is closely related to the theory of retarded Green’s functions and is of importance for the investigation of transport phenomena.

The theory and application of the density matrix have been well summarized by various authors. Here, we mention in particular the review papers by [Fano \(1957\)](#) and [ter Haar \(1961\)](#). Some textbooks on quantum mechanics outline the formalism ([Messiah 1965](#); [Roman 1965](#); [Gottfried 1966](#)). These sources (and many others which are acknowledged in the appropriate places) were used in writing this book. Because of the introductory nature of this book we refer as a rule to monographs and reviews of the subject and only to those original papers whose results are used in the text.

Over the years my understanding of the theory and applications of the density matrix has benefited from many discussions with my colleagues at the Universities of Stirling and Münster. I am especially grateful to Prof. H. Kleinpoppen, who first aroused my interest in atomic physics, for his constant encouragement. I am indebted to Prof. J. Kessler for reading parts of the manuscript and making helpful suggestions for revisions in the first and second drafts. Dr. H. Jakubowicz has read the complete manuscript and made many improvements, and K. Bartschat has checked most equations. Finally, I wish to thank Mrs. Queen and Mrs. Raffin for their help in preparing the manuscript.

*Karl Blum*

NOTE TO THE READER: The Chap. [7](#) outlined here is Chap. [8](#) in this volume.

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# Chapter 1

## Basic Concepts

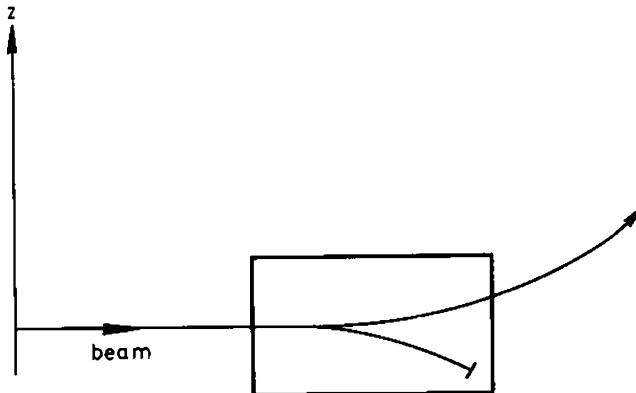
### 1.1 Spin States and Density Matrix of Spin-1/2 Particles

#### 1.1.1 Pure Spin States

In order to become familiar with the basic concepts of density matrix theory we will begin by considering the problem of describing the spin states of spin-1/2 particles. First of all we will review some results of the quantum mechanical theory of experiments with Stern–Gerlach magnets and then in the following sections we will reinterpret the results and discuss them in more detail.

Consider a beam of spin-1/2 particles (for example, hydrogen atoms) which passes through a Stern–Gerlach magnet which has its field gradient aligned along the  $z$  direction with respect to a fixed coordinate system  $x$ ,  $y$ ,  $z$  (Fig. 1.1). In general the beam will split vertically into two parts each of which corresponds to one of the two possible eigenvalues of the component  $S_z$  of the spin operator  $\mathbf{S}$  ( $m = \pm 1/2$ ). If one of the beams is eliminated, for example, the lower one as in Fig. 1.1, then the emerging particles will be in a state which corresponds to only one of the eigenvalues; in the case of the apparatus in Fig. 1.1 this would be  $m = +1/2$ . Similarly, if the apparatus is rotated in such a way that its field gradient points in the direction  $z'$ , the emerging particles will be in a state which is described by the quantum number  $m' = +1/2$ , where  $m'$  is the eigenvalue of the operator  $S_{z'}$ , the component of  $\mathbf{S}$  in the  $z'$  direction.

If the incident beam is such that it contains particles which are in a state with  $m = +1/2$  only, then the beam will pass through the apparatus shown in Fig. 1.1 without any loss of intensity. In all other cases part of the beam will be blocked off and the emerging beam will be less intense than the incident one. However, by tilting the apparatus at various angles about  $z$  it may be possible to find an orientation of the magnet which allows the whole beam to be transmitted. For example, if an incident beam contains only a spin component corresponding to  $m' = +1/2$  in the frame  $z'$ , it would be attenuated by the Stern–Gerlach apparatus in Fig. 1.1. If the



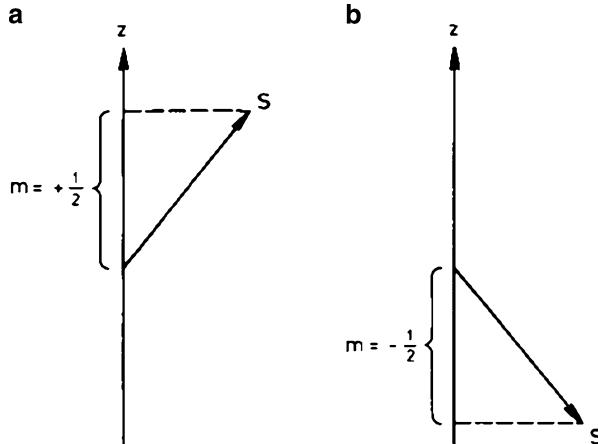
**Fig. 1.1** Stern–Gerlach filter

magnet were rotated so that its field gradient lay along  $z'$ , then the beam would be completely transmitted. In this case all particles are deflected in the same way; they behave identically in this particular experiment. This enables the following (preliminary) definition to be made:

- If it is possible to find an orientation of the Stern–Gerlach apparatus for which a given beam is *completely* transmitted, then we will say that the beam is in a *pure spin state*.

In terms of the semiclassical vector model a beam of particles with definite quantum number  $m = +1/2$  can be described by considering the spin vector of each particle to precess around the direction of the  $z$  axis such that its projection on the  $z$  axis has the value of  $+1/2$  (Fig. 1.2a). In this case the particles are said to have “spin up.” A similar interpretation holds for the case of  $m = -1/2$  (Fig. 1.2b) and the spins of particles in eigenstates of the operator  $S_z$  will, by analogy, precess around the  $z'$  direction. In the case of a pure spin state the spin vectors of the particles precess around a unique direction which is parallel to the direction of alignment of the Stern–Gerlach apparatus when it allows the beam to pass through unattenuated.

*If the state of a given beam is known to be pure then the joint state of all particles can be represented in terms of one and the same state vector  $|\chi\rangle$ .* This is an important point and we will illustrate it with some examples. If a beam of particles passes completely through a Stern–Gerlach apparatus oriented in the  $z$  direction then we will say that *all* particles in the beam are in identical spin states with quantum number  $m = 1/2$  with respect to  $z$ , or that all particles have spin up with respect to  $z$ . We describe this state by assigning the state vector  $|\chi\rangle = | + 1/2 \rangle$  to the *whole* beam. Similarly, a beam of particles with  $m = -1/2$  will be characterized by  $|\chi\rangle = | - 1/2 \rangle$ . In the usual Pauli representation the state vectors are represented by two-dimensional column vectors,



**Fig. 1.2** (a) Spin “in the  $z$  direction”; (b) spin “in the  $-z$  direction”

$$\left| +\frac{1}{2} \right\rangle = \begin{pmatrix} 1 \\ 0 \end{pmatrix}; \quad \left| -\frac{1}{2} \right\rangle = \begin{pmatrix} 0 \\ 1 \end{pmatrix} \quad (1.1a)$$

and the adjoint states by the row vectors

$$\left\langle +\frac{1}{2} \right| = (1, 0); \quad \left\langle -\frac{1}{2} \right| = (0, 1) \quad (1.1b)$$

In general, for a beam that emerges from a Stern–Gerlach apparatus which has its magnet pointing in the  $z'$  direction, all particles in the beam are in a state with definite spin quantum number  $m' = 1/2$  defined with respect to  $z'$  as quantization axis. The joint state of all particles will be described by the state vector  $|\chi\rangle = |+\frac{1}{2}, z'\rangle$ .

A general spin state  $|\chi\rangle$  can always be written as a linear superposition of two basis states, for example, the states  $|\pm 1/2\rangle$ :

$$|\chi\rangle = a_1 \left| +\frac{1}{2} \right\rangle + a_2 \left| -\frac{1}{2} \right\rangle \quad (1.2)$$

In the representation (1.1) this is equivalent to

$$|\chi\rangle = \begin{pmatrix} a_1 \\ a_2 \end{pmatrix} \quad (1.3a)$$

The adjoint state is represented by the row vector

$$\langle \chi | = (a_1^*, a_2^*) \quad (1.3b)$$

where the asterisk denotes the complex conjugate.

The state  $|\chi\rangle$  is normalized such that

$$\langle\chi|\chi\rangle = |a_1|^2 + |a_2|^2 = 1 \quad (1.4)$$

A pure spin state can be characterized either by specifying the direction in which the spins are pointing (for example, by giving the polar angles of this direction in our fixed coordinate system) or, alternatively, by specifying the coefficients  $a_1$  and  $a_2$  in the expansion (1.2). In the following section we will discuss the relation between these two descriptions and derive an explicit representation for the coefficients  $a_1$  and  $a_2$ .

An apparatus of the type shown by Fig. 1.1 acts as a *filter*, because irrespective of the state of the beam sent through it, the emerging beam is in a definite spin state which is defined by the orientation of the magnet. Passing a beam through the filter can therefore be regarded as a method of preparing a beam of particles in a pure state.

### 1.1.2 The Polarization Vector

In order to discuss the description of pure spin states in greater detail we will now introduce a vector  $\mathbf{P}$ , called the *polarization vector*, which has components defined as expectation values of the corresponding Pauli matrices:

$$P_i = \langle\sigma_i\rangle \quad (1.5)$$

( $i = x, y, z$ ). In the case of a pure state these expectation values are defined by the relations.

$$\langle\sigma_i\rangle = \langle\chi|\sigma_i|\chi\rangle \quad (1.6)$$

In the representation (1.1) the Pauli matrices have the form

$$\sigma_x = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}, \quad \sigma_y = \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix}, \quad \sigma_z = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} \quad (1.7)$$

The expectation values (1.6) may then be calculated by applying (1.3a), (1.3b), and (1.7), treating the row and column vectors as one-dimensional matrices and applying the rules of matrix multiplication. In order to see the significance of the polarization vector we will now consider a few examples.

A beam of particles in the pure state  $|+1/2\rangle$  has a polarization vector with components

$$P_x = (1, 0) \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} \begin{pmatrix} 1 \\ 0 \end{pmatrix} = 0$$

$$P_y = (1, 0) \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix} \begin{pmatrix} 1 \\ 0 \end{pmatrix} = 0 \quad (1.8a)$$

$$P_z = (1, 0) \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} \begin{pmatrix} 1 \\ 0 \end{pmatrix} = 1$$

Similarly we find for an ensemble of particles in the pure state  $| - 1/2 \rangle$  the polarization vector has components

$$P_x = 0, \quad P_y = 0, \quad P_z = -1 \quad (1.8b)$$

Thus the states  $| + 1/2 \rangle$  and  $| - 1/2 \rangle$  are characterized by polarization vectors of unit magnitude pointing in the  $+z$  and  $-z$  directions, respectively. The states  $| + 1/2 \rangle$  and  $| - 1/2 \rangle$  can therefore be said to be states of opposite polarization.

Consider now the general pure state (1.2). It will be convenient to give first of all a parametrization of the coefficients  $a_1$  and  $a_2$ . These are complex numbers corresponding to four real parameters specifying the magnitudes and phases. The overall phase of the state (1.2) has no physical significance and can be chosen arbitrarily, for example by requiring  $a_1$  to be real. From this condition and the normalization (1.4) it follows that the general pure spin state (1.2) is completely specified by two real numbers. It will therefore be convenient to introduce two parameters  $\theta$  and  $\delta$  defined by

$$a_1 = \cos \frac{\theta}{2}, \quad a_2 = e^{i\delta} \sin \frac{\theta}{2} \quad (1.9)$$

where  $\delta$  is the relative phase of the coefficients. Using (1.9), (1.3a) becomes

$$|\chi\rangle = \begin{pmatrix} \cos \frac{\theta}{2} \\ e^{i\delta} \sin \frac{\theta}{2} \end{pmatrix} \quad (1.10)$$

In order to see the physical significance of the parameters  $\theta$  and  $\delta$  consider the polarization vector associated with the state (1.10). We obtain

$$\begin{aligned} P_x &= \left( \cos \frac{\theta}{2}, e^{-i\delta} \sin \frac{\theta}{2} \right) \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} \begin{pmatrix} \cos \frac{\theta}{2} \\ e^{i\delta} \sin \frac{\theta}{2} \end{pmatrix} \\ &= \sin \theta \cos \delta \end{aligned} \quad (1.11a)$$

$$P_y = \sin \theta \sin \delta \quad (1.11b)$$

$$P_z = \cos \theta \quad (1.11c)$$

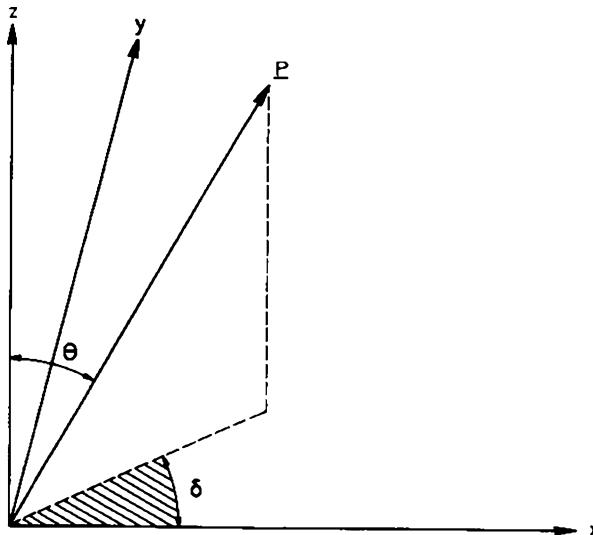


Fig. 1.3 Direction of  $\mathbf{P}$

The polarization vector (1.11) has unit magnitude

$$|\mathbf{P}| = (P_x^2 + P_y^2 + P_z^2)^{1/2} = 1 \quad (1.12)$$

From (1.11) it follows that the parameters  $\theta$  and  $\delta$  can be interpreted as the polar angles of  $\mathbf{P}$ :  $\theta$  is the angle between  $\mathbf{P}$  and the  $z$  axis and the relative phase  $\delta$  specifies the azimuth angle of  $\mathbf{P}$  (Fig. 1.3).

A second coordinate system  $x'$ ,  $y'$ ,  $z'$  can be chosen in such a way that the  $z'$  axis is parallel to  $\mathbf{P}$ . Taking  $z'$  as quantization axis we have in the primed system  $P_{x'} = 0$ ,  $P_{y'} = 0$ ,  $P_{z'} = 1$ ; that is, all particles have spin up with respect to  $z'$ . The direction of the polarization vector is therefore the direction “in which the spins are pointing.” If we send the beam through a Stern–Gerlach filter oriented parallel to  $\mathbf{P}$  the whole beam will pass through.

Equations 1.10 and 1.11 enable explicit spin functions to be constructed for any pure state. For example, a given beam of particles may be in a pure state with spins pointing in the  $x$  direction of our fixed coordinate system. In this case the corresponding polarization vector points in the  $x$  direction and, consequently, has polar angles  $\theta = 90^\circ$ ,  $\delta = 0$ . From (1.10) the state vector can be seen to be

$$\left| +\frac{1}{2}, x \right\rangle = \frac{1}{2^{1/2}} \begin{pmatrix} 1 \\ 1 \end{pmatrix} \quad (1.13a)$$

A beam of particles with “spin down” with respect to the  $x$  axis has a polarization vector pointing in the  $-x$  direction and is characterized by the angles  $\theta = 90^\circ$ ,

$\delta = 180^\circ$ . The state vector is represented by

$$\left| -\frac{1}{2}, x \right\rangle = \frac{1}{2^{1/2}} \begin{pmatrix} 1 \\ -1 \end{pmatrix} \quad (1.13b)$$

Similarly, the state vector of particles with “spin up” (“spin down”) with respect to the  $y$  axis is represented by the column vectors

$$\left| +\frac{1}{2}, y \right\rangle = \frac{1}{2^{1/2}} \begin{pmatrix} 1 \\ i \end{pmatrix} \quad (1.13c)$$

and

$$\left| -\frac{1}{2}, y \right\rangle = \frac{1}{2^{1/2}} \begin{pmatrix} 1 \\ -i \end{pmatrix} \quad (1.13d)$$

It should be noted that the four states (1.13) are constructed by superposing the states  $| + 1/2 \rangle$  and  $| - 1/2 \rangle$  with the same magnitude  $|a_1| = |a_2| = 1/2^{1/2}$  but with different relative phases. The corresponding polarization vectors have the same angle  $\theta$  but different azimuth angles depending on the relative phase existing between the states  $| \pm 1/2 \rangle$ .

### 1.1.3 Mixed Spin States

Pure spin states are not the most general spin states in which an ensemble of particles can be found. Suppose, for example, that two beams of particles have been prepared *independently*, one in the pure state  $| + 1/2 \rangle$  and the other one in the pure state  $| - 1/2 \rangle$ . By “independently” we mean that no definite phase relation exists between the two beams (this point will be clarified later). The first beam may consist of  $N_1$  particles, the second one of  $N_2$  particles. If the polarization state of the combined beam is investigated by sending it through a Stern–Gerlach filter in various orientations it will be found that it is not possible to find such an orientation of the filter which allows the whole beam to be transmitted. It follows that, by definition, the joint beam is not in a pure spin state.

- States which are not pure are called *mixed states* or *mixtures*.

We now have to consider the problem of describing the state of the joint beam. Clearly, it is not possible to characterize the state of the beam in terms of a single state vector  $|\chi\rangle$  since associated with any of these states there is necessarily a direction in which *all* spins are pointing: the direction of the polarization vector. If the Stern–Gerlach filter were placed in this orientation the whole beam would have to be transmitted. Since no such orientation exists it is not possible to describe a mixture by a single state vector.

In particular, the mixture cannot be represented by a linear superposition of the states  $| + 1/2 \rangle$  and  $| - 1/2 \rangle$  representing the two constituent beams. In order to construct such a linear superposition it is necessary to know the magnitudes and relative phase  $\delta$  of the relevant coefficients  $a_1$  and  $a_2$ . The absolute squares  $|a_1|^2$  and  $|a_2|^2$  are probabilities  $W_1$  and  $W_2$  of finding a particle in the state  $| + 1/2 \rangle$  and  $| - 1/2 \rangle$ , respectively. In the case of the mixture under discussion these probabilities are known ( $W_1 = N_1/N$  and  $W_2 = N_2/N$  with  $N = N_1 + N_2$ ) and can be used to determine the magnitudes of the coefficients ( $W_1 = |a_1|^2$ ,  $W_2 = |a_2|^2$ ). The important point is that the constituent beams have been prepared independently. So there is no definite phase relation between the two beams, and without a definite phase  $\delta$  it is not possible to construct a well-defined state vector  $|\chi\rangle$  describing the joint beam.

A mixture has to be described by specifying the way in which it has been prepared. For example, the joint beam under discussion is characterized by saying that  $N_1$  particles have been prepared in the state  $| + 1/2 \rangle$  and  $N_2$  in the state  $| - 1/2 \rangle$  independently of each other. This statement contains all the information we have obtained about the mixture.

Let us continue discussion of our example by calculating the polarization vector associated with the total beam.  $\mathbf{P}$  is obtained by taking the statistical average over the separate beams:

$$P_i = W_1 \left( \frac{1}{2} |\sigma_i| \frac{1}{2} \right) + W_2 \left( -\frac{1}{2} |\sigma_i| - \frac{1}{2} \right)$$

which gives

$$P_x = 0, \quad P_y = 0, \quad P_z = W_1 - W_2 = \frac{N_1 - N_2}{N} \quad (1.14)$$

It should be noted that the polarization vector (1.14) has a magnitude which is less than 1 and is proportional to the difference of the population numbers of the two states,  $| + 1/2 \rangle$  and  $| - 1/2 \rangle$ .

More generally, if a beam is prepared by mixing  $N_a$  particles in the state  $|\chi_a\rangle$  and  $N_b$  in the state  $|\chi_b\rangle$  then the components of the polarization vector are given by the statistical average over the independently prepared beams:

$$P_i = W_a \langle \chi_a | \sigma_i | \chi_a \rangle + W_b \langle \chi_b | \sigma_i | \chi_b \rangle \quad (1.15)$$

$$= W_a P_i^{(a)} + W_b P_i^{(b)} \quad (1.16a)$$

with  $W_a = N_a/N$ ,  $W_b = N_b/N$ , and where  $P_i^{(a)}$  and  $P_i^{(b)}$  are the polarization vectors associated with the constituent beams [see, (1.6)]. Equation 1.15 can be rewritten in vector notation as

$$\mathbf{P} = W_a \mathbf{P}^{(a)} + W_b \mathbf{P}^{(b)} \quad (1.16b)$$

Since  $|\mathbf{P}^{(a)}| = 1$ ,  $|\mathbf{P}^{(b)}| = 1$  the magnitude of  $P$  is determined by

$$\begin{aligned}
 P^2 &= (W_a \mathbf{P}^{(a)} + W_b \mathbf{P}^{(b)})^2 \\
 &= W_a^2 (P^{(a)})^2 + W_b (P^{(b)})^2 + 2W_a W_b \mathbf{P}^{(a)} \cdot \mathbf{P}^{(b)} \\
 &\leq W_a^2 + W_b^2 + 2W_a W_b \\
 &= (W_a + W_b)^2 = 1
 \end{aligned} \tag{1.17}$$

since the scalar product  $\mathbf{P}^{(a)} \cdot \mathbf{P}^{(b)}$  of two different unit vectors is less than 1.

The equality sign in (1.17) applies if  $\mathbf{P}^{(a)} \cdot \mathbf{P}^{(b)} = 1$ , that is, if the two beams have identical polarization vectors. In this case both constituent beams are in the same spin state described by (1.10) and (1.11) and the joint beam is in a pure state. Vice versa, if two beams are mixed in identical spin states the resulting beam consists of particles in identical spin states and is therefore characterized by a polarization vector of unit magnitude. The above arguments may be easily generalized to cases of mixtures which consist of more than two beams.

We therefore have the following result: The magnitude of the polarization vector is bounded such that

$$0 \leq |\mathbf{P}| \leq 1 \tag{1.18}$$

*The maximum possible value  $|\mathbf{P}| = 1$  is obtained if (and only if) the beam under consideration is in a pure state, whereas mixtures necessarily have a polarization vector of less than unit magnitude.*

This result once more illustrates the basic property of a pure spin state: all the particles are in identical states with *all* the spins pointing in the same direction, the direction of  $\mathbf{P}$ .

Henceforward we will refer to states with  $|\mathbf{P}| > 0$  as *polarized* and to beams with  $|\mathbf{P}| = 0$  as *unpolarized*. Pure states ( $|\mathbf{P}| = 1$ ) will be called *completely polarized*.

### 1.1.4 Pure Versus Mixed States

Before proceeding further with any analysis it is important to have a clear understanding of the concepts of pure and mixed states. We will therefore consider both types of states again from a different viewpoint. Consider the following problem. A beam of particles which is completely polarized in the  $y$  direction and hence can be represented by the state vector (1.13c)

$$\left| +\frac{1}{2}, y \right\rangle = \frac{1}{2^{1/2}} \left( \left| +\frac{1}{2} \right\rangle + i \left| -\frac{1}{2} \right\rangle \right) \tag{1.19a}$$

is sent through a Stern–Gerlach filter oriented in the  $z$  direction. What will happen? It is a familiar result of quantum mechanics that, although we know that any particle

in the beam is in the state  $| + 1/2, y \rangle$ , it is impossible to predict whether a given single particle will pass through the filter. This is because a system which is to be measured is in general disturbed by the act of measurement. In this case the measuring apparatus (the filter) changes in a completely uncontrollable way the state of the incident particles; that is, it is only possible to predict the probability that a particle will be admitted by the filter (and emerge in the state  $| + 1/2 \rangle$ ) or be blocked off. From (1.19a) it can be seen that the probability is 1/2 for each case. The only case in which it is possible to predict with complete certainty whether a given particle will pass through a filter is that where the filter is oriented in the  $y$  direction all particles will pass unhindered. In general, however, the measuring process can only be described through the use of statistics.

Because of this a linear superposition state, such as (1.19a), must be interpreted as follows. Before any measurement all the particles are in identical states represented by the vector (1.19a), and all particles have the same quantum number  $m' = 1/2$  defined with respect to  $y$  as the quantization axis. The quantum number  $m$ , defined with respect to the  $z$  axis, is completely undefined in the superposition (1.19a) in the sense that *any* particle in the beam has an equal probability of passing through a  $z$ -oriented filter or being blocked off. [Roughly speaking, it can be said that the particles in the superposition state (1.19a) do not “know” their  $m$  value.] If the beam is sent through a filter oriented parallel to the  $z$  axis the interaction with the apparatus changes the state of the beam and forces the particles into one of the eigenstates.

Consider now a mixture of

$$\begin{aligned} N_1 &= N/2 \text{ particles in the state } | + 1/2 \rangle \\ N_2 &= N/2 \text{ particles in the state } | - 1/2 \rangle \end{aligned} \quad (1.19b)$$

with both subbeams prepared independently. From (1.14) it can be seen that the resulting beam is unpolarized. If this beam is passed through a Stern–Gerlach filter oriented along the  $z$  axis the transmitted beam will have half of the incident intensity. In this particular experiment the mixture (1.19b) and the pure state (1.19a) give the same result; however, it is for a different reason. Whereas in the case of the state  $| 1/2, y \rangle$  all particles in the beam are in one and the same state, there is less information about the mixture (1.19b) since it is only known that any particle has an equal probability of being in the state  $| + 1/2 \rangle$  or  $| - 1/2 \rangle$ . In this sense the state of the mixture is *incompletely determined*. When passing through the filter the particles with  $m = -1/2$  will be blocked off and hence only that half of the beam corresponding to the  $| + 1/2 \rangle$ -component beam will be transmitted.

The above example illustrates that statistics must be used in order to describe the *initial* state of the mixture; the state of the particles is not known with certainty; that is, we cannot assign a single-state vector to the mixed beam.

In conclusion, it can be seen that in the description of spin-1/2 particles statistics enters in two ways. First of all, statistical methods must be used because of the uncontrollable perturbation of states by any measuring apparatus. Secondly, when

dealing with mixtures, it is only known that the particles can be in any one of several spin states. A statistical description must be applied because of the lack of information available on the system. It was primarily for the purpose of describing this latter case that the density matrix formalism was developed.

A more systematic treatment of the problems discussed above will be presented in Chap. 2.

### 1.1.5 The Spin-Density Matrix and Its Basic Properties

#### 1.1.5.1 Basic Definitions

Any question concerning the behavior of pure or mixed states can be answered by specifying the states, present in the mixture, and their statistical weights  $W_i$ . The actual calculations, however, are often very cumbersome. We will therefore now introduce an alternative method of characterizing pure and mixed states.

Consider a beam of  $N_a$  particles prepared in the state  $|\chi_a\rangle$  and a second beam of  $N_b$  particles which have been prepared in the state  $|\chi_b\rangle$  independently of the first one. In order to describe the joint beam we introduce an operator  $\rho$  by the expression.

$$\rho = W_a |\chi_a\rangle\langle\chi_a| + W_b |\chi_b\rangle\langle\chi_b| \quad (1.20)$$

with  $W_a = N_a/N$ ,  $W_b = N_b/N$ , and  $N = N_a + N_b$ .

The operator  $\rho$  is called *density operator* or *statistical operator*. It describes the preparations which have been performed and, therefore, contains all the information obtained on the total beam. In this sense a mixture is completely specified by its density operator. In the special case of a pure state  $|\chi\rangle$  the density operator is given by

$$\rho = |\chi\rangle\langle\chi| \quad (1.21a)$$

It will be seen later that it is usually more convenient to write  $\rho$  in matrix form. To this end we choose a set of basis states, commonly  $|+1/2\rangle$  and  $|-1/2\rangle$  and expand  $|\chi_a\rangle$  and  $|\chi_b\rangle$  in terms of this set according to (1.2):

$$\begin{aligned} |\chi_a\rangle &= a_1^{(a)} \left| +\frac{1}{2} \right\rangle + a_2^{(a)} \left| -\frac{1}{2} \right\rangle \\ |\chi_b\rangle &= a_1^{(b)} \left| +\frac{1}{2} \right\rangle + a_2^{(b)} \left| -\frac{1}{2} \right\rangle \end{aligned} \quad (1.22)$$

In the representation (1.1) we write

$$|\chi_a\rangle = \begin{pmatrix} a_1^{(a)} \\ a_2^{(a)} \end{pmatrix}, \quad |\chi_b\rangle = \begin{pmatrix} a_1^{(b)} \\ a_2^{(b)} \end{pmatrix} \quad (1.23a)$$

and for the adjoint states

$$\langle \chi_a | = \left( a_1^{(a)*}, a_2^{(a)*} \right), \quad \langle \chi_b | = \left( a_1^{(b)*}, a_2^{(b)*} \right) \quad (1.23b)$$

Applying the rules of matrix multiplication we obtain for the “outer product,”  $|\chi_a\rangle\langle\chi_a|$ :

$$\begin{aligned} |\chi_a\rangle\langle\chi_a| &= \begin{pmatrix} a_1^{(a)} \\ a_2^{(a)} \end{pmatrix} \left( a_1^{(a)*}, a_2^{(a)*} \right) \\ &= \begin{pmatrix} |a_1^{(a)}|^2 & a_1^{(a)} a_2^{(a)*} \\ a_1^{(a)*} a_2^{(a)} & |a_2^{(a)}|^2 \end{pmatrix} \end{aligned} \quad (1.24)$$

and similarly for the product  $|\chi_b\rangle\langle\chi_b|$ . Substitution of these expressions into (1.20) yields the *density matrix*.

$$\rho = \begin{pmatrix} W_a |a_1^{(a)}|^2 + W_b |a_1^{(b)}|^2 & W_a a_1^{(a)} a_2^{(a)*} + W_b a_1^{(b)} a_2^{(b)*} \\ W_a a_1^{(a)*} a_2^{(a)} + W_b a_1^{(b)*} a_2^{(b)} & W_a |a_1^{(a)}|^2 + W_b |a_2^{(b)}|^2 \end{pmatrix} \quad (1.25)$$

Since the basis states  $|\pm 1/2\rangle$  have been used in deriving (1.25) this is said to be *the density matrix in the  $\{|\pm 1/2\rangle\}$  representation*.

In order to make subsequent formulas more compact we define  $|+ 1/2\rangle = |\chi_1\rangle$  and  $| - 1/2\rangle = |\chi_2\rangle$ . In this notation the general element of the density matrix corresponding to the  $i$ th row and  $j$ th column is given by the expression

$$\langle \chi_i | \rho | \chi_j \rangle = W_a a_1^{(a)} a_j^{(a)*} + W_b a_i^{(b)} a_j^{(b)*} \quad (1.26)$$

with  $i, j = 1, 2$ .

Clearly the density matrix has a different form in different representations, whereas the operator (1.20) is independent of the choice of the basis states. It will always be assumed that the basis states are orthonormal, that is

$$\langle \chi_i | \chi_j \rangle = \delta_{ij} \quad (1.27)$$

where  $\delta_{ij}$  denotes the Kronecker symbol and for  $i = j$  condition (1.4) is satisfied.

In the normalization (1.4) the trace of the density matrix is given by

$$\text{tr } \rho = W_a + W_b = 1 \quad (1.28)$$

which is independent of the choice of the representation.

As an example, consider the case of a mixture consisting of  $N_1$  particles which have been prepared in the state  $|\chi_1\rangle = |+ 1/2\rangle$  and  $N_2$  particles prepared

independently in the state  $|\chi_2\rangle = | - 1/2\rangle$ . The total beam is then represented by the density operator

$$\rho = W_1 \left| +\frac{1}{2} \right\rangle \left\langle +\frac{1}{2} \right| + W_2 \left| -\frac{1}{2} \right\rangle \left\langle -\frac{1}{2} \right| \quad (1.29a)$$

( $W_i = N_i/N$ ) and the density matrix in the  $\{|\pm 1/2\rangle\}$  representation is diagonal:

$$\langle \chi_i | \rho | \chi_j \rangle = W_i \delta_{ij} \quad (1.29b)$$

### 1.1.5.2 Significance of the Density Matrix

The diagonal elements of the density matrix

$$\langle \chi_i | \rho | \chi_i \rangle = W_a \left| a_i^{(a)} \right|^2 + W_b \left| a_i^{(b)} \right|^2 \quad (i = 1, 2) \quad (1.30)$$

have a direct physical meaning. Since the probability of finding a particle of the mixture in the state  $|\chi_a\rangle$  is  $W_a$  and since the probability that  $|\chi_a\rangle$  is in the state  $|\chi_i\rangle$  is  $\left| a_i^{(a)} \right|^2$ , the product  $W_a \left| a_i^{(a)} \right|^{2a}$  is the probability that a particle originally prepared in the state  $|\chi_a\rangle$  will be found in the state  $|\chi_i\rangle$  after a measurement has been made. *The diagonal element (1.30) therefore gives the total probability of finding a particle in the corresponding basis state  $|\chi_i\rangle$ .*

Thus, if a beam described by a density operator  $\rho$  is sent through a Stern-Gerlach filter oriented parallel (antiparallel) to the  $z$  axis then the diagonal element  $\langle \chi_1 | \rho | \chi_1 \rangle = \left\langle +\frac{1}{2} | \rho | +\frac{1}{2} \right\rangle \left( \left\langle -\frac{1}{2} | \rho | -\frac{1}{2} \right\rangle \right)$  of  $\rho$  in the  $\{|\pm \frac{1}{2}\rangle\}$  representation gives the probability that a particle will pass through the filter.

This result may be generalized to arbitrary states  $|\chi\rangle$ . Consider the matrix element  $\langle \chi | \rho | \chi \rangle$  obtained by “sandwiching” the operator (1.20) between the state  $|\chi\rangle$  and its adjoint  $\langle \chi |$ :

$$\begin{aligned} \langle \chi | \rho | \chi \rangle &= W_a \langle \chi | \chi_a \rangle \langle \chi_a | \chi \rangle + W_b \langle \chi | \chi_b \rangle \langle \chi_b | \chi \rangle \\ &= W_a |a^{(a)}|^2 + W_b |a^{(b)}|^2 \end{aligned} \quad (1.31)$$

where  $a^{(a)} = \langle \chi_a | \chi \rangle$  and  $a^{(b)} = \langle \chi_b | \chi \rangle$ . Comparing (1.30) and (1.31) it can be seen that the *matrix element  $\langle \chi | \rho | \chi \rangle$  is the total probability of finding a particle in the pure state  $|\chi\rangle$  within a mixture which is represented by  $\rho$ .* That is, if a beam represented by  $\rho$  passes through a filter which only fully admits a beam in the state  $|\chi\rangle$  then (1.31) gives the probability that any given particle of the beam will pass through the filter.

For example, suppose that a beam represented by the density matrix (1.29) is sent through a filter oriented in the  $y$  direction. The probability that a particle of the beam will pass through is then given by the matrix element  $\langle +1/2, y | \rho | +1/2, y \rangle$ .

Expressing  $| + 1/2, y \rangle$  in the  $\{| \pm 1/2 \rangle\}$  representation [(1.13c)] and using (1.29) give

$$\begin{aligned} \left\langle +\frac{1}{2}, y | \rho | +\frac{1}{2}, y \right\rangle &= \frac{1}{2}(1, -i) \begin{pmatrix} W_1 & 0 \\ 0 & W_2 \end{pmatrix} \begin{pmatrix} 1 \\ i \end{pmatrix} \\ &= \frac{1}{2}(W_1 + W_2) \end{aligned}$$

The important point is that all the information on the spin state of any given beam can be obtained (in principle at least) by sending the beam through various Stern–Gerlach filters with different orientations. Consequently, once  $\rho$  is known, we can calculate the result of any such experiment by means of (1.31). In this sense,  $\rho$  contains all significant information on the spin state of a given beam.

### 1.1.5.3 The Number of Independent Parameters

We will now consider how many parameters are required in order to completely represent a given density matrix. A complex  $2 \times 2$  matrix such as (1.25) has four complex elements  $\langle \chi_i | \rho | \chi_j \rangle$  corresponding to eight real parameters. The density matrix is *Hermitian*; that is,  $\rho$  satisfies

$$\langle \chi_i | \rho | \chi_j \rangle = \langle \chi_j | \rho | \chi_i \rangle^* \quad (1.32)$$

This can be seen immediately from (1.25) or (1.26). Consequently, the diagonal elements are real, and the real and imaginary parts of the off-diagonal elements are related by the expressions

$$\begin{aligned} \text{Re} \left\langle +\frac{1}{2} | \rho | -\frac{1}{2} \right\rangle &= \text{Re} \left\langle -\frac{1}{2} | \rho | +\frac{1}{2} \right\rangle \\ \text{Im} \left\langle +\frac{1}{2} | \rho | -\frac{1}{2} \right\rangle &= -\text{Im} \left\langle -\frac{1}{2} | \rho | +\frac{1}{2} \right\rangle \end{aligned}$$

These relations reduce the number of independent real parameters to four. The normalization condition (1.28) fixes one further parameter so that the density matrix is completely characterized in terms of three real parameters. It follows from this that *three independent measurements must be performed in order to completely specify the density matrix for any given beam of spin-1/2 particles*.

It will be instructive to consider this result from another point of view. In (1.20) a density operator is defined from a knowledge of how a given beam has been prepared. This definition can be generalized for the case of any number of constituent beams. In order to write down the density operator or the corresponding density matrix from (1.20) and (1.25), it follows that all the pure states  $|\chi_a\rangle$ ,  $|\chi_b\rangle$ , ... present in the mixture must be specified together with their statistical weights  $W_a$ ,  $W_b$ , ... Only three real parameters, however, are required to completely characterize the density matrix of a beam of any complexity, as has been shown.

This is not as surprising as it may seem at first, since one and the same density matrix can represent many different mixtures prepared in entirely different ways. For example, consider a mixture represented by the density operator

$$\rho = \frac{1}{2} \left| +\frac{1}{2} \right\rangle \left\langle +\frac{1}{2} \left| +\frac{1}{2} \right\rangle \left\langle -\frac{1}{2} \right| \right. \left. \left| -\frac{1}{2} \right\rangle \right\langle -\frac{1}{2} \right|$$

and a mixture specified by the operator

$$\rho = \frac{1}{6} \left| +\frac{1}{2} \right\rangle \left\langle +\frac{1}{2} \left| +\frac{1}{6} \right\rangle \left\langle -\frac{1}{2} \right| \right. \left. \left| +\frac{1}{3} \right\rangle \left\langle +\frac{1}{2}, x \right| \right. \left. \left| +\frac{1}{3} \right\rangle \left\langle -\frac{1}{2}, x \right| \right. \left. \left| -\frac{1}{2}, x \right\rangle \right\langle -\frac{1}{2}, x \right|$$

By constructing the corresponding density matrices in the  $\{|\pm 1/2\rangle\}$  representation and applying (1.13a), (1.13b) it can be shown that both beams are represented by the same density matrix:

$$\rho = \frac{1}{2} \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}$$

It follows from (1.31) that the two beams will behave identically in all experiments with respect to their polarization properties. Conversely, a knowledge of the density matrix elements alone is insufficient to determine the method by which the beams have been prepared. In fact such information is insignificant. The only significant information is contained in the three independent parameters specifying the density matrix since these are sufficient to calculate the behavior of the corresponding beam in any polarization experiment. *For this reason we will henceforth consider two beams to be identical if they are described by the same density matrix.*

The definition (1.20) is usually of little importance, and instead of defining the density *operator* by specifying the constituent subbeams and their statistical weights we will apply a more operational point of view and define the density *matrix* by the results of three independent measurements. In the following section we will show how this can be achieved in a simple way by using the polarization vector.

### 1.1.5.4 Parametrization of the Density Matrix

If (1.20) is multiplied by the Pauli matrix  $\sigma_i$  the trace can be calculated as

$$\begin{aligned} \text{tr } \rho \sigma_i &= W_a \text{tr} (|\chi_a\rangle \langle \chi_a| \sigma_i) + W_b \text{tr} (|\chi_b\rangle \langle \chi_b| \sigma_i) \\ &= W_a \langle \chi_a | \sigma_i | \chi_a \rangle + W_b \langle \chi_b | \sigma_i | \chi_b \rangle \end{aligned} \quad (1.33)$$

This result can be obtained by using the explicit matrix representations (1.7) and (1.24) or, more directly, by applying the relation

$$\text{tr} (|\chi\rangle \langle \chi| \sigma_i) = \langle \chi | \sigma_i | \chi \rangle \quad (1.34)$$

Substituting (1.16a) into (1.33) gives the important result

- $\text{tr } \rho \sigma_i = P_i \quad (1.35)$

where  $P_i$  is the  $i$ th component of the polarization vector of the total beam.

Using this result the elements of  $\rho$  can be expressed in terms of the components  $P_i$ . By direct matrix manipulations it may be shown that in the  $\{|\pm 1/2\rangle\}$  representation  $\rho$  is given by

- $\rho = \frac{1}{2} \begin{pmatrix} 1 + P_z & P_x - iP_y \\ P_x + iP_y & 1 - P_z \end{pmatrix} \quad (1.36)$

A more elegant method of deriving this result will be given in Sect. 1.1.6.

The three components  $P_x$ ,  $P_y$ ,  $P_z$  represent a minimum set of data which are required to specify the density matrix of any given beam and *we will henceforth regard the density matrix as defined by (1.36)*.

As an illustration of the use of (1.36) suppose a beam of particles, characterized by the matrix (1.36), passes a filter oriented in the  $z$  direction. The probability that a particle is admitted by the filter is given, according to (1.31), by the expression

$$\left\langle +\frac{1}{2} |\rho| + \frac{1}{2} \right\rangle = \frac{1}{2}(1 + P_z)$$

Similarly, applying (1.13a), (1.13c) and (1.36) the probabilities that a particle will pass through a filter oriented in the  $x$  and  $y$  directions are found to be

$$\begin{aligned} \left\langle +\frac{1}{2}, x |\rho| + \frac{1}{2}, x \right\rangle &= \frac{1}{2}(1 + P_x) \\ \left\langle +\frac{1}{2}, y |\rho| + \frac{1}{2}, y \right\rangle &= \frac{1}{2}(1 + P_y) \end{aligned}$$

Finally, we will give another useful representation of  $\rho$  obtained by transforming to a coordinate system  $x'$ ,  $y'$ ,  $z'$ , where  $z'$  is parallel to  $\mathbf{P}$  and  $x'$  and  $y'$  are chosen arbitrarily but orthogonal to each other and to  $z'$ . In this case,  $P_{x'} = P_{y'} = 0$ ,  $P_{z'} = |P|$ . As a result, in the representation with  $z'$  as the quantization axis,  $\rho$  is given by

$$\rho = \frac{1}{2} \begin{pmatrix} 1 + |\mathbf{P}| & 0 \\ 0 & 1 - |\mathbf{P}| \end{pmatrix} \quad (1.37a)$$

or by

$$\rho = \frac{1}{2}(1 - |\mathbf{P}|) \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix} + |\mathbf{P}| \begin{pmatrix} 1 & 0 \\ 0 & 0 \end{pmatrix} \quad (1.37b)$$

If the beam under consideration is completely polarized,  $|\mathbf{P}| = 1$ , and

$$\rho = \begin{pmatrix} 1 & 0 \\ 0 & 0 \end{pmatrix} \quad (1.38)$$

and the beam is in the pure state  $| + 1/2, z' \rangle$ . If the beam is unpolarized  $|\mathbf{P}| = 0$ , and the corresponding density matrix is given by

$$\rho = \frac{1}{2} \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix} \quad (1.39)$$

### 1.1.5.5 Identification of Pure States

In Sect. 1.1.2 it has been shown that a given beam is in a pure state if and only if its polarization vector has the maximum possible value of  $|\mathbf{P}| = 1$ . This result will now be put into a different form which is more useful for treating more complex systems.

Using (1.36) it can be shown that the trace of  $\rho^2$  is given by

$$\begin{aligned} \text{tr}(\rho)^2 &= (1/2)(1 + P_x^2 + P_y^2 + P_z^2) \\ &= (1/2)(1 + |\mathbf{P}|^2) \end{aligned}$$

It follows from this that

$$\text{tr}(\rho)^2 = 1 \quad (1.40)$$

is a necessary and sufficient condition that the beam under consideration is in a pure state. [Note, the fact that the trace is equal to unity in (1.40) is a consequence of the normalization (1.28).]

In the case of a pure state the condition (1.40) gives an additional restriction on the density matrix elements. Thus *a pure state is characterized by two independent parameters only in accordance with (1.10)*.

### 1.1.6 The Algebra of the Pauli Matrices

The discussion in Sect. 1.1.5 have shown that the result of any experiment performed with a given beam can be calculated from a knowledge of the corresponding density matrix. So far the required mathematical operations have to be carried out using a particular representation and applying the rules of matrix algebra. In general, this is a laborious and time-consuming procedure. In this section a more elegant method of performing the relevant calculations will be described.

The discussion will be based on the following fundamental relation between the Pauli matrices ( $i, j = x, y, z$ ):

$$\sigma_i \sigma_j = \delta_{ij} \mathbf{1} + i \sum_k \epsilon_{ijk} \sigma_k \quad (1.41)$$

where  $\delta_{ij}$  is the Kronecker symbol,  $\mathbf{1}$  denotes the two-dimensional unit matrix, and

$$\epsilon_{ijk} = \begin{cases} 1 & \text{if } i, j, k \text{ is an even permutation of } XYZ \\ -1 & \text{if } i, j, k \text{ is an odd permutation of } XYZ \\ 0 & \text{if two of the indices are the same} \end{cases} \quad (1.42)$$

For example, for  $i = j$  (1.41) becomes

$$\sigma_i^2 = 1 \quad (1.43a)$$

and for  $i = x, j = y$ :

$$\sigma_x \sigma_y = i \sigma_z, \quad \sigma_y \sigma_x = -i \sigma_z \quad (1.43b)$$

From (1.40) and (1.43) it follows that for  $i \neq j$

$$\sigma_i \sigma_j + \sigma_j \sigma_i = 0 \quad (1.43c)$$

Equation 1.41 specifies completely the algebra of the Pauli matrices. Proofs of (1.41) can be found in any textbook on quantum mechanics.

The important property of (1.41) is that it reduces quadratic combinations of Pauli matrices to linear ones. This allows the calculation of traces of products of matrices  $\sigma_i$  by a stepwise reduction of the number of matrices occurring in the given trace. We give some examples. First, from (1.7) it can be seen that

$$\text{tr } \sigma_i = 0 \quad (1.44)$$

By taking the trace of (1.41) and using (1.44) it follows that

$$\text{tr } \sigma_i \sigma_j = 2 \delta_{ij} \quad (1.45a)$$

A product of three Pauli matrices may first be reduced to a quadratic combination by means of (1.41):

$$\sigma_i \sigma_j \sigma_m = \delta_{ij} \sigma_m + i \sum_k \epsilon_{ijk} \sigma_k \sigma_m$$

Taking the trace of this expression and applying (1.44) and (1.45a) give

$$\text{tr } \sigma_i \sigma_j \sigma_m = 2i \sum_k \epsilon_{ijk} \delta_{km} = 2i \epsilon_{ijm} \quad (1.45b)$$

A further important property of the Pauli matrices is that any two-dimensional Hermitian matrix can be expressed as a linear combination of the unit matrix  $\mathbf{1}$  and the matrices  $\sigma_i$ . For example, consider the density matrix. We make the “ansatz”

$$\rho = a\mathbf{1} + \sum_i b_i \sigma_i \quad (1.46)$$

In (1.46) the four coefficients  $a$ ,  $b_x$ ,  $b_y$ ,  $b_z$  are unknowns which must be determined. Such an ansatz is possible because the hermiticity condition reduces the number of independent parameters determining  $\rho$  to four and there are four parameters in (1.46). One of the parameters can immediately be determined from the normalization condition (1.28), which gives, with the help of (1.44),

$$a = 1/2 \quad (1.47a)$$

Multiplying (1.46) by  $\sigma_j$ , taking the trace of the obtained expression, and using (1.44) and (1.45) give

$$\text{tr } \rho \sigma_j = 2 \sum_i b_i \delta_{ij} = 2b_j$$

The trace of  $\rho$  and  $\sigma_j$  gives the corresponding component of the polarization vector and from this it follows that

$$b_j = (1/2)P_j \quad (1.47b)$$

Inserting the results (1.47) into the ansatz (1.46) results in the expression

$$\bullet \quad \rho = \frac{1}{2} \left( \mathbf{1} + \sum_i P_i \sigma_i \right) \quad (1.48)$$

If the Pauli matrices are expressed in the form (1.7) then  $P$  can be obtained in the form (1.36). In the case of a pure state  $|\chi\rangle$  characterized by

$$\rho^{(x)} = |\chi\rangle\langle\chi|$$

and denoting the polarization vector of the state  $|\chi\rangle$  by  $P^{(x)}$ , we write

$$|\chi\rangle\langle\chi| = \frac{1}{2} \left( \mathbf{1} + \sum_i P_i^{(x)} \sigma_i \right) \quad (1.49)$$

This expression allows a simple determination of the probability  $|\chi|\rho|\chi\rangle$ . Equation 1.34 implies

$$\langle\chi|\rho|\chi\rangle = \text{tr}|\chi\rangle\langle\chi|\rho$$

Hence, using this result on the right-hand side of (1.49) gives

$$\begin{aligned}
\langle \chi | \rho | \chi \rangle &= \frac{1}{4} \operatorname{tr} \left[ \left( 1 + \sum_i P_i^{(x)} \sigma_i \right) \left( 1 + \sum_j P_j \sigma_i \right) \right] \\
&= \frac{1}{4} \operatorname{tr} \left( 1 + \sum_i P_i^{(x)} \sigma_i + \sum_j P_j \sigma_j + \sum_{ij} P_i^{(x)} P_j \sigma_i \sigma_j \right) \\
&= \frac{1}{2} (1 + \mathbf{P}^{(x)} \cdot \mathbf{P})
\end{aligned} \tag{1.50}$$

This result can be interpreted in the following way. A beam of particles may be characterized by a density matrix  $\rho$ . This beam may be passed through a Stern–Gerlach filter in a fixed orientation which only completely transmits a beam in the pure state  $|\chi\rangle$  (that is, the filter is oriented parallel to  $\mathbf{P}^{(x)}$ ).

The probability that a particle of the given beam will pass through the filter is then determined by the scalar product  $\mathbf{P}^{(x)} \cdot \mathbf{P}$  of the two polarization vectors. The probability of transmission is a maximum if  $\mathbf{P}$  points in the direction of the magnetic field and is a minimum if  $\mathbf{P}$  is antiparallel to the filter direction. In particular, if the beam is unpolarized, then for *any* filter

$$\langle \chi | \rho | \chi \rangle = 1/2 \tag{1.51}$$

The derivation of (1.50) may serve as a first example of how calculations can be simplified by using (1.48) and the algebraic properties of the Pauli matrices.

### 1.1.7 Summary

The results obtained in the previous two sections allow a redefinition of the basic concepts used so far. We consider as the initial information on a given beam the values of the three components  $P_x$ ,  $P_y$ ,  $P_z$  of the polarization vector.  $\mathbf{P}$  can be determined, for example, by suitably chosen scattering experiments (for a detailed discussion of such experiments we refer particularly to [Kessler 1976](#)). When the polarization vector is known the density matrix can be obtained by means of (1.36) or (1.48). These expressions contain all information on the beam in condensed form. Their usefulness, particularly (1.48), in actual calculations will become evident in [Sect. 2.5](#).

If  $|\mathbf{P}| = 1$  the beam is said to be in a pure spin state, or, alternatively, all particles are in identical states. This joint state of all particles in the given beam is represented by assigning a single state vector to the whole beam. In this case two parameters are sufficient for a complete description of the spin state, for example, the polar angles  $\theta$  and  $\delta$  of  $\mathbf{P}$ , from which the corresponding state vector can be constructed by means of (1.10).

If  $|\mathbf{P}| < 1$  the beam is said to be in a mixed state. Such states are characterized by three parameters, for example, the magnitude and the polar angles of  $\mathbf{P}$ .

## 1.2 Polarization States and Density Matrix of Photons

### 1.2.1 *The Classical Concept of Wave Polarization*

In this section, a description of photon polarization will be given. We will follow the arguments of Sect. 1.1 in order to become more familiar with the abstract concepts introduced there. We will begin with a brief account of the description of light polarization in classical optics.

A monochromatic electromagnetic wave is characterized by three quantities: its angular frequency  $\omega$ , its wave vector  $\mathbf{k} = (2\pi/\Lambda)\mathbf{n}$  (where  $\mathbf{n}$  is a unit vector in the direction of motion and  $\Lambda$  is the wavelength), and its state of polarization, which is defined by the vibrations of the electric field vector  $\mathbf{E}$ . The field vector  $\mathbf{E}$  of a monochromatic wave can be written in the form

$$\mathbf{E} = A\mathbf{e}e^{i(\mathbf{k}\cdot\mathbf{r}-\omega t)} \quad (1.52)$$

where  $A$  is the amplitude and  $\mathbf{e}$  is the polarization vector. Because of the transverse nature of electromagnetic waves,  $\mathbf{e}$  is perpendicular to  $\mathbf{n}$ . In this section we will use a coordinate system  $x$ ,  $y$ ,  $z$  with the  $z$  axis parallel to  $\mathbf{n}$ , and restrict ourselves to a discussion of the polarization properties of light only. If  $\mathbf{E}$  vibrates along the  $x$  axis then the light is said to be linearly polarized along the  $x$  axis. The polarization vector is parallel to  $x$  and denoted by  $\mathbf{e}_x$ . If the electric vector oscillates along the  $y$  axis then the polarization is characterized by assigning a polarization vector  $\mathbf{e}_y$  to the beam pointing in the  $y'$  direction. A general polarization vector  $\mathbf{e}$  can always be expanded in terms of two orthogonal vectors, for example,  $\mathbf{e}_x$  and  $\mathbf{e}_y$ :

$$\mathbf{e} = a_1\mathbf{e}_x + a_2e^{i\delta}\mathbf{e}_y \quad (1.53)$$

where  $a_1$  and  $a_2$  are real coefficients. We will normalize (1.53) such that  $\mathbf{e}$  is always a unit vector in the sense that the scalar product of  $\mathbf{e}$  and its complex conjugate,  $\mathbf{e}^*$ , is equal to 1:  $\mathbf{e} \cdot \mathbf{e}^* = 1$ . The normalization condition is therefore

$$a_1^2 + a_2^2 = 1 \quad (1.54)$$

Equation 1.53 corresponds to a linear superposition of two waves of equal frequency and the same wave vector with amplitudes  $A_1$  and  $A_2$ , polarized along the  $x$  and  $y$  directions, respectively, with a definite phase difference  $\delta$ :

$$\begin{aligned}\mathbf{E} &= A_1 \mathbf{e}_x e^{i(\mathbf{k} \cdot \mathbf{r} - \omega t)} + A_2 \mathbf{e}_y e^{i(\mathbf{k} \cdot \mathbf{r} - \omega t + \delta)} \\ &= A(a_1 \mathbf{e}_x + a_2 e^{i\delta} \mathbf{e}_y) e^{i(\mathbf{k} \cdot \mathbf{r} - \omega t)}\end{aligned}$$

where  $a_1$  and  $a_2$  are the relative amplitudes of the waves normalized to unity:  $a_1 = A_1/A$  ( $i = 1, 2$ ) with  $A = (A_1 + A_2)^{1/2}$ .

We can define a parameter  $\beta$  such that

$$a_1 = \cos \beta, \quad a_2 = \sin \beta \quad (1.55a)$$

[(1.54) is then automatically satisfied] and write the general polarization vector (1.53) in the form

$$\bullet \quad \mathbf{e} = \cos \beta \mathbf{e}_x + e^{i\delta} \sin \beta \mathbf{e}_y \quad (1.55b)$$

In order to become familiar with the use of this expression we will consider some specific cases.

1. Consider a superposition of two waves oscillating in phase, with relative amplitudes  $a_1$  and  $a_2$  and polarized along the  $x$  and  $y$  axes, respectively. From the relative amplitudes the parameter  $\beta$  can be determined, and inserting  $\delta = 0$  into (1.55) the polarization vector of the resulting wave is found to be

$$\mathbf{e} = \cos \beta \mathbf{e}_x + \sin \beta \mathbf{e}_y \quad (1.56)$$

In this case it is possible to give a simple interpretation of  $\beta$ :  $\mathbf{e}$  is a real vector in the  $x - y$  plane and (1.56) represents its decomposition in terms of the two orthogonal basis vectors  $\mathbf{e}_x$  and  $\mathbf{e}_y$ ; hence,  $\beta$  is the angle between  $\mathbf{e}$  and the  $x$  axis (Fig. 1.4).

2. A superposition of two waves with equal amplitudes  $a_1 = a_2$  and a phase difference  $\delta = \pm 90^\circ$  gives a wave with polarization vector

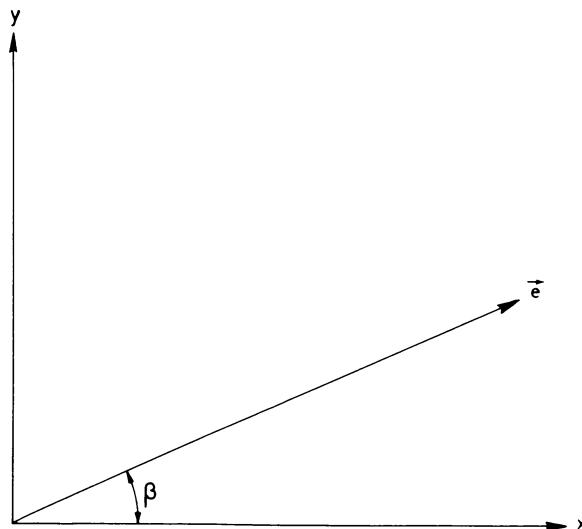
$$\mathbf{e} \sim \mathbf{e}_x \pm i \mathbf{e}_y$$

corresponding to left- and right-handed circular polarization. (For a further discussion of circular polarization see Sect. 1.2.3.)

3. If  $a_1 \neq a_2$  and  $\delta \neq 0$  we have the general case of elliptical polarization. In the following we will refer to a light wave as *completely polarized if its polarization properties can be specified in terms of a single polarization vector  $\mathbf{e}$*  [as in the case of the plane wave (1.1), for example]. It will be useful to reinterpret this definition in terms of some idealized experiments.

Following a treatment similar to that given in Sect. 1.1 the polarization properties of light can be discussed with the help of experiments with various optical polarization filters. We will assume that the filters used are always ideal in the

**Fig. 1.4** Polarization vector of linearly polarized light



sense that the filter is completely transparent to light of a particular polarization and completely absorbs light of the opposite polarization. Hence light passing through the filter will emerge in a definite state of polarization. For example, a beam of light may pass a Nicol prism with its axis of transmission parallel to the  $x$  axis. The transmitted light is then linearly polarized along the  $x$  direction. Similarly, a beam of light passing a Nicol prism oriented parallel to an axis  $\mathbf{n}$  will emerge linearly polarized along this direction. If  $\beta$  is the angle between  $\mathbf{n}$  and the  $x$  axis the corresponding polarization vector is given by (1.56). Conversely, if linearly polarized light with polarization vector  $\mathbf{e}$  is passed through a Nicol prism it is always possible to find such an orientation of the prism which allows the whole beam to be transmitted. This occurs when the axis of transmission is parallel to  $\mathbf{e}$ . A circularly polarized wave will only be completely accepted by a circular polarization filter (for example, a suitably oriented series combination of a quarter wave plate and a Nicol prism).

By applying the converse of these arguments it can be seen that a light beam is completely polarized if such a filter can be found which completely admits the beam.

As is well known from optics light is usually not completely polarized. An ordinary light source consists of a large number of excited atoms each of which emits a pulse of light in a time of order  $\sim 10^{-8}$  s independently of all other atoms. Because constantly new pulses will be contributing to the beam the overall polarization will change very rapidly and there will be no definite polarization vector which is characteristic of the total beam. In the following sections we will consider the problem of describing beams of this kind.

### 1.2.2 Pure and Mixed Polarization States of Photons

When the theory of relativistic quantum mechanics is applied to the electromagnetic field it follows that in interaction with matter the wave behaves as if it were composed of photons. We will start our discussion with the following definition:

- A beam of photons is said to be in a *pure polarization state* if the beam is completely polarized in the sense explained in Sect. 1.2.1.

In terms of our idealized experiments this definition may be reinterpreted as follows: if it is possible to find such a filter which completely admits a beam of photons then the beam is said to be in a pure polarization state. Alternatively we may say that all photons of the beam can be considered to be in one and the same polarization state. This joint state of *all* the photons can be described in terms of a *single* state vector which we will denote by  $|e\rangle$ , by which is meant the polarization state of any photon in the beam which classically has polarization vector  $\mathbf{e}$ . For example, the state vectors  $|e_x\rangle$  and  $|e_y\rangle$  denote the polarization state of photons which are completely transmitted by a Nicol prism oriented in the  $x$  and  $y$  directions, respectively.

The states  $|e_x\rangle$  and  $|e_y\rangle$  can be taken as basis states and any state  $|e\rangle$  can be written as a linear superposition:

$$|e\rangle = a_1|e_x\rangle + a_2|e_y\rangle \quad (1.57)$$

or

$$|e\rangle = \cos \beta |e_x\rangle + e^{i\delta} \sin \beta |e_y\rangle \quad (1.58)$$

These equations are exactly analogous to (1.53) and (1.55), respectively.

These considerations are similar to the discussions in Sect. 1.1. All the experiments and results for spin-1/2 particles and Stern–Gerlach filters which have been described previously can be repeated with photons and polarization filters. In particular, it should be noted that  $a_1^2$  and  $a_2^2$  are the probabilities that a photon in the polarization state (1.57) will pass through a Nicol prism oriented parallel to the  $x$  or  $y$  axis, respectively.

As shown by (1.57) and (1.58) any superposition of two (or more) states which have a definite phase  $\delta$  necessarily results in a pure state. Thus, in order to describe light which is not completely polarized, it is necessary to consider superposition states which do not have a definite phase relation, that is, we have to introduce the concept of a mixture. In general, *a beam of photons is said to be in a mixed state or mixture if it is not possible to describe the beam in terms of a single state vector*.

It is useful to visualize the concept of a mixture in terms of some idealized experiments. Consider two light sources emitting *independently* of each other, where by “independently” is meant that there is no definite phase relationship between the two sources (that is, the relative phase changes much more rapidly than the observation time in an unpredictable manner). Both sources are provided with a polarization filter so that the first source emits a beam of intensity  $I_1$  of definite polarization  $|e_1\rangle$  and the second one a beam of intensity  $I_2$  and polarization  $|e_2\rangle$ .

If the two beams are combined and the polarization properties of the total beam investigated by sending it through various filters, it will be found that, irrespective of the nature of the filter, the transmitted intensity is always less than the incident one. Thus, by definition, the total beam is in a mixed polarization state.

It is not possible to completely characterize a mixture by a single-state vector  $|e\rangle$ . In particular, the mixture cannot be represented as a linear superposition of the states  $|e_1\rangle$  and  $|e_2\rangle$ . The reason for this is that, as has been discussed in Sects. 1.1.1–1.1.4, there is no definite phase  $\delta$  between the constituent beams with which a definite state vector  $|e\rangle$  can be constructed.

### 1.2.3 The Quantum Mechanical Concept of Photon Spin

In classical optics the polarization of light is explained in terms of the vibrations of the electric field vector. We will now investigate how polarization states can be interpreted in terms of the characteristic properties of photons.

To this end we will consider the possible spin states of photons. There are certain limitations to the concept of the photon spin. The total angular momentum  $\mathbf{J}$  of any particle is the resultant of its spin  $\mathbf{S}$  and its orbital angular momentum  $\mathbf{L}$ . Since the rest mass of a photon is zero, the usual definition of spin as the total angular momentum of a particle at rest is inapplicable for a photon. Strictly, only the total angular momentum  $\mathbf{J}$  of the photon has any physical meaning. However, it is convenient to define a spin and an orbital angular momentum in a formal sense. The photon spin is given the value 1 corresponding to the fact that the wave function is a vector [as shown, for example, by (1.52)]. The value of the orbital angular momentum is related to the multipoles which occur in the wave function (see, for example, [Landau and Lifschitz 1965](#)).

In general, if a spin-1 particle has a well-defined momentum  $\mathbf{p}$  the components of its spin along its direction of motion can take three values:  $+1, -1, 0$ . However, because of the transverse nature of electromagnetic waves the value 0 must be excluded for photons. The component of the photon spin along the direction of propagation  $\mathbf{n}$ , which we will denote by the symbol  $\lambda$ , can therefore only have the values  $\lambda = +1$  (“spin up”) and  $\lambda = -1$  (“spin down”).

It is important to note that the two photon states with spin up and spin down with respect to  $\mathbf{n}$  as quantization axis have direct physical meaning. Since the component of the orbital angular momentum vanishes in the direction of propagation  $\mathbf{n}$  we have  $\mathbf{J} \cdot \mathbf{n} = (\mathbf{L} + \mathbf{S}) \cdot \mathbf{n} = \mathbf{S} \cdot \mathbf{n} = \lambda$ ; consequently,

- $\lambda$  is the component of the total angular momentum of the photon in the direction of propagation  $\mathbf{n}$ .

The component of the spin in the direction of motion is generally called the helicity and we will refer to photon states with definite values  $\lambda = \pm 1$  as *helicity states*.

Classically, when a circularly polarized light beam is directed at a target the electrons in the target are set into circular motion in response to the rotating electric field of the wave. This suggests that there is a relationship between circularly polarized light and photons in definite states of angular momentum.

In fact it has been shown in quantum electrodynamics that photons with definite helicity are related to left-handed and right-handed circular polarization states. Unfortunately, this notation is not unambiguous and we will adopt the following convention. We will denote the polarization vector and state of photons with helicity  $\lambda = 1$  by  $\mathbf{e}_{+1}$  and  $|+1\rangle$ , respectively, and refer to light of positive helicity as *right-handed circularly polarized*.

Similarly, if  $\lambda = -1$  we will denote the polarization vector and state of such light by  $\mathbf{e}_{-1}$  and  $| -1\rangle$ , respectively, and refer to the light as *left-handed circularly polarized*.

Note that in the terminology of classical optics the opposite convention is usually adopted: Light of positive (negative) helicity is called left-handed (right-handed) circularly polarized. We will always use the helicity state notation in order to avoid this ambiguity. With this convention the vectors  $\mathbf{e}_{+1}$  and  $\mathbf{e}_{-1}$  and the states  $|\pm 1\rangle$  are then determined apart from a phase factor which has little significance and we write

$$\mathbf{e}_{\pm 1} = \mp \frac{1}{2^{1/2}} (\mathbf{e}_x \pm i \mathbf{e}_y) \quad (1.59)$$

for the polarization vector and for the corresponding states:

$$|\pm 1\rangle = \mp \frac{1}{2^{1/2}} (|e_x\rangle \pm i |e_y\rangle) \quad (1.60)$$

(see, for example, Messiah 1965).

In particular for problems where questions of angular momentum must be taken explicitly into account, it is convenient to use the helicity states as basis states instead of  $|e_x\rangle$  and  $|e_y\rangle$ . We will therefore write the general polarization state  $|e\rangle$  in the form

$$|e\rangle = a_1 |+1\rangle + a_2 |-1\rangle \quad (1.61)$$

There is a close formal analogy between photons and spin-1/2 particles. Because there are only two possible values of the helicity  $\lambda = \pm 1$  (corresponding to states with spin up and spin down with respect to  $\mathbf{n}$  as the quantization axis) these states can be represented by two-dimensional column vectors *as long as  $\mathbf{n}$  is used as the axis of quantization (z axis)*. The basis states can then be written in a similar way to (1.1)):

$$|+1\rangle = \begin{pmatrix} 1 \\ 0 \end{pmatrix}, \quad |-1\rangle = \begin{pmatrix} 0 \\ 1 \end{pmatrix} \quad (1.62)$$

In this representation the general pure state (1.61) is described by the row vector

$$|e\rangle = \begin{pmatrix} a_1 \\ a_2 \end{pmatrix} \quad (1.63a)$$

and its adjoint by the column vector

$$|e\rangle = (a_1^*, a_2^*) \quad (1.63b)$$

For example, the state of light beams which are completely linearly polarized along the  $x$  and  $y$  axes, respectively, is obtained by inverting (1.60):

$$|e_x\rangle = -\frac{1}{2^{1/2}}(|+1\rangle - |-1\rangle) \quad (1.64a)$$

$$|e_y\rangle = -\frac{i}{2^{1/2}}(|+1\rangle + |-1\rangle) \quad (1.64b)$$

The interpretation of these linear superposition states is analogous to that given in Sect. 1.1.4.

As another example, consider a beam of photons prepared in the pure state  $|e_x\rangle$ . It can be seen from (1.64a) that these photons have no definite helicity. However, in any experiment performed on the beam, in which the angular momentum is actually measured, any photon in the beam will be forced into one of the angular momentum eigenstates,  $|+1\rangle$  or  $|-1\rangle$ , with equal probability. In any such experiment any photon of the beam will therefore transfer a definite amount of angular momentum, either  $\lambda = +1$  or  $\lambda = -1$ . Since the corresponding probabilities are equal, the net angular momentum, transferred by the total beam, is zero.

### 1.2.4 The Polarization Density Matrix

A compact expression of the polarization properties of photons is contained in the corresponding density matrix. In Sect. 1.2.5 we will give an operational definition of the photon density matrix. But in this section we will follow the arguments of Sect. 1.1.5.

Consider a beam of photons which is a mixture of two beams which have been prepared independently in the states  $|e_a\rangle$  and  $|e_b\rangle$ , with intensities  $I_a$  and  $I_b$ , respectively. The density operator characterizing the total beam is defined by the expression

$$\rho' = W_a|e_a\rangle\langle e_a| + W_b|e_b\rangle\langle e_b| \quad (1.65)$$

with  $W_a = I_a/I$  and  $W_b = I_b/I$  and  $I = I_a + I_b$ . In order to obtain the density matrix it is necessary to choose a particular representation. We will use the helicity states as basis and expand the two states  $|e_a\rangle$  and  $|e_b\rangle$  according to (1.61) as

$$\begin{aligned} |e_a\rangle &= a_1^{(a)}|+1\rangle + a_2^{(a)}|-1\rangle \\ |e_b\rangle &= a_1^{(b)}|+1\rangle + a_2^{(b)}|-1\rangle \end{aligned}$$

Using the explicit representation (1.62) and applying the rule (1.24) the density matrix in the helicity representation is found to be

$$\rho' = \begin{pmatrix} W_a |a_1^{(a)}|^2 + W_b |a_1^{(b)}|^2 & W_a a_1^{(a)} a_2^{(a)*} + W_b a_1^{(b)} a_2^{(b)*} \\ W_a a_1^{(a)*} a_2^{(a)} + W_b |a_1^{(b)*} a_2^{(b)}| & W_a |a_2^{(a)}|^2 + W_b |a_2^{(b)}|^2 \end{pmatrix} \quad (1.66)$$

From the explicit representation (1.66) it follows that  $\rho'$  is normalized according to

$$\text{tr } \rho' = W_a + W_b = 1 \quad (1.67)$$

It is often more convenient to normalize  $\rho$  in such a way that its trace is equal to the total intensity of the corresponding photon beam. This can be achieved by substituting the intensities  $I_a$  and  $I_b$  for  $W_a$  and  $W_b$  in the definition (1.65) and (1.66). The density operator in this normalization is then given by

$$\rho = I_a |e_a\rangle \langle e_a| + I_b |e_b\rangle \langle e_b| \quad (1.68)$$

The trace of the density matrix is then

$$\text{tr } \rho = I_a + I_b = I \quad (1.69)$$

The density matrix  $\rho$  (and  $\rho'$ ) has the following properties (the proofs are like those in Sect. 1.1.5):

1. The diagonal elements  $\langle +1 | \rho' | +1 \rangle$  and  $\langle -1 | \rho' | -1 \rangle$  of the matrix (1.66) give the probability of finding a photon in the beam in the corresponding helicity state. In the normalization (1.69) the diagonal elements  $\langle +1 | \rho | +1 \rangle$  and  $\langle -1 | \rho | -1 \rangle$  give the corresponding intensities.
2. If the beam under consideration is sent through a filter which fully admits only photons in the pure state  $|e\rangle$  then the element

$$\langle e | \rho' | e \rangle = W_a |a^{(a)}|^2 + w_b |a^{(b)}|^2 \quad (1.70)$$

gives the probability that a photon of the beam will be transmitted through the filter where we used the notation

$$a^{(a)} = \langle e | e_a \rangle$$

$$a^{(b)} = \langle e | e_b \rangle$$

The element  $\langle e | \rho | e \rangle$  obtained from the operator (1.68) gives the transmitted intensity:

$$\langle e | \rho | e \rangle = I_a |a^{(a)}|^2 + I_b |a^{(b)}|^2 \quad (1.71)$$

Since any information on the polarization properties of a given beam can be obtained in principle by allowing the beam to pass through various polarization filters, the result of any such experiment can be calculated by using formulas (1.70) or (1.71). From this it can be concluded that all information on the polarization state of a given beam is contained in its density matrix.

3. The hermiticity condition (1.32) reduces the number of independent parameters to four. One of these is usually the total beam intensity  $I$ . If  $I$  is not of interest it can be dropped by normalizing as in (1.67) where  $\rho'$  then is specified by three real parameters similar to the density matrix of spin-1/2 particles.

It follows that four independent measurements are required in order to specify the matrix  $\rho$  completely for any given beam (one of these is the determination of the intensity  $I$ ). If  $I$  is dropped the matrix (1.66), which requires a set of three independent measurements, is obtained. The result of any further experiment can then be calculated by applying (1.70) or (1.71).

4. In Chap. 2 we will prove that, in general, a necessary and sufficient condition that a given photon density matrix describes a pure state is given by

$$\text{tr}(\rho^2) = (\text{tr} \rho)^2 = I^2 \quad (1.72)$$

In the normalization (1.67) this reduces to (1.40):

$$\text{tr}(\rho^2) = 1$$

In general, the photon density matrix satisfies

$$\text{tr}(\rho^2) \leq I^2 \quad (1.73a)$$

### 1.2.5 Stokes Parameter Description

#### 1.2.5.1 Parametrization of $\rho$ in Terms of the Stokes Parameters

We will henceforth adopt the normalization (1.69). In the preceding section it has been seen that four independent measurements must be performed in order to completely determine the polarization state of any given beam. The most convenient set of measurements is that one which gives the following information:

1. The total intensity  $I$  of the beam;
2. The degree of linear polarization with respect to the  $x$  and  $y$  axes, defined as

$$\eta_3 = \frac{I(0) - I(90^\circ)}{I} \quad (1.74a)$$

where  $I(\beta)$  denotes the intensity transmitted by a Nicol prism oriented at an angle  $\beta$  with respect to the  $x$  axis;

3. The degree of linear polarization with respect to two orthogonal axes oriented at  $45^\circ$  to the  $x$  axes

$$\eta_1 = \frac{I(45^\circ) - I(135^\circ)}{I} \quad (1.74b)$$

4. The degree of circular polarization defined as

$$\eta_2 = \frac{I_{+1} - I_{-1}}{I} \quad (1.74c)$$

where  $I_{+1}$  (and  $I_{-1}$ ) are the intensities of light transmitted by polarization filters which fully transmit only photons with positive (negative) helicity.

The parameters 1–4 are called *Stokes parameters*. A detailed description of these can be found in [Born and Wolf \(1970\)](#). (See also [McMaster 1954](#); [Farago 1971](#).)

We will now relate the Stokes parameters to the elements of the density matrix. Denoting the elements of  $\rho$  by  $\rho_{\lambda'\lambda} \equiv \langle \lambda' | \rho | \lambda \rangle$  we write

$$\rho = \begin{pmatrix} \rho_{+1,+1} & \rho_{+1,-1} \\ \rho_{-1,+1} & \rho_{-1,-1} \end{pmatrix} \quad (1.75)$$

where  $\rho_{+1,-1} = \rho_{-1,+1}^*$  because of the hermicity condition (1.32). Applying (1.69) the total intensity is given by

$$I = \rho_{11} + \rho_{-1,-1} \quad (1.76a)$$

In order to obtain  $\eta_3$  we have to calculate the intensities  $I(0)$  and  $I(90^\circ)$ . From relation (1.71) these are given by

$$I(0) = \langle e_x | \rho | e_x \rangle$$

$$I(90^\circ) = \langle e_y | \rho | e_y \rangle$$

In the helicity representation the state vectors  $|e_x\rangle$  and  $|e_y\rangle$  are expressed by (1.64); hence

$$\begin{aligned} I(0) &= (1/2)(-1, +1) \begin{pmatrix} \rho_{11} & \rho_{1,-1} \\ \rho_{-1,1} & \rho_{-1,-1} \end{pmatrix} \begin{pmatrix} -1 \\ +1 \end{pmatrix} \\ &= (1/2)(\rho_{11} - \rho_{1,-1} - \rho_{-1,1} + \rho_{-1,-1}) \end{aligned}$$

Similarly, we obtain

$$\begin{aligned} I(90^\circ) &= (1/2)(-i, -i) \begin{pmatrix} \rho_{11} & \rho_{1,-1} \\ \rho_{-1,1} & \rho_{-1,-1} \end{pmatrix} \begin{pmatrix} i \\ i \end{pmatrix} \\ &= (1/2)(\rho_{11} + \rho_{1,-1} + \rho_{-1,1} + \rho_{-1,-1}) \end{aligned}$$

It therefore follows that

$$I\eta_3 = -(\rho_{1,-1} + \rho_{-1,1}) \quad (1.76b)$$

In the same way we calculate the parameter  $I\eta_1$ , defined by (1.74c). In this case the axes of transmission of the Nicols are set at angles  $45^\circ$  and  $135^\circ$  to the  $x$  axes, respectively. The intensities transmitted by these prisms are then given by

$$I(45^\circ) = \langle e_1 | \rho | e_1 \rangle$$

$$I(135^\circ) = \langle e_2 | \rho | e_2 \rangle$$

where  $|e_1\rangle$  denotes a photon state which is fully transmitted by the first prism; that is,

$$|e_1\rangle = (1/2^{1/2})(|e_x\rangle + |e_y\rangle)$$

where (1.56) has been used with  $\beta = 45^\circ$ . Similarly,  $|e_2\rangle$  is a photon state which is fully transmitted by the second prism and can be expressed in terms of  $|e_x\rangle$  and  $|e_y\rangle$  by inserting  $\beta = 135^\circ$  in (1.56):

$$|e_2\rangle = (1/2^{1/2})(-|e_x\rangle + |e_y\rangle)$$

Transforming  $|e_x\rangle$  and  $|e_y\rangle$  to the helicity basis gives

$$I\eta_1 = -i(\rho_{1,-1} - \rho_{-1,1}) \quad (1.76c)$$

Similarly,

$$I\eta_2 = \rho_{11} - \rho_{-1,-1} \quad (1.76d)$$

By inverting these equations the elements  $\rho_{\lambda'\lambda}$  can be expressed in terms of the Stokes parameters:

- $\rho = \frac{I}{2} \begin{pmatrix} 1 + \eta_2 & -\eta_3 + i\eta_1 \\ -\eta_3 - i\eta_1 & 1 - \eta_2 \end{pmatrix} \quad (1.77)$

We will use this form of the density matrix throughout this book.

### 1.2.5.2 Examples

It follows from (1.58) that any pure polarization state can be parametrized in the form

$$|e\rangle = \cos \beta |e_x\rangle + e^{i\delta} \sin \beta |e_y\rangle \quad (1.78)$$

The corresponding density operator is given by  $\rho = \mathbf{I}|e\rangle\langle e|$ . We will calculate the Stokes parameters characterizing a beam in the state (1.78). We have

$$I(0) = \langle e_x | \rho | e_x \rangle = I |\langle e_x | e \rangle|^2 = I \cos^2 \beta$$

$$I(90^\circ) = \langle e_y | \rho | e_y \rangle = I |\langle e_y | e \rangle|^2 = I \sin^2 \beta$$

from which follows

$$\eta_3 = \cos 2\beta \quad (1.79a)$$

Similarly we find

$$\eta_1 = \sin 2\beta \cos \delta \quad (1.79b)$$

$$\eta_2 = \sin 2\beta \sin \delta \quad (1.79c)$$

For example, the pure state  $|e_x\rangle$ , characterizing a beam of light with polarization vector pointing in the  $x$  direction, is obtained by inserting  $\delta = 0$ ,  $\beta = 0$  in (1.78). From (1.79) we obtain the Stokes parameters  $\eta_3 = 1$ ,  $\eta_1 = \eta_2 = 0$ . Inserting these values into the density matrix (1.77) gives

$$\rho = \frac{I}{2} \begin{pmatrix} 1 & -1 \\ -1 & 1 \end{pmatrix} \quad (1.80a)$$

A beam which is linearly polarized in the  $y$  direction can be specified by the parameters  $\beta = 90^\circ$ ,  $\delta = 0$  so that

$$\eta_3 = -1, \quad \eta_1 = \eta_2 = 0$$

and

$$\rho = \frac{I}{2} \begin{pmatrix} 1 & 1 \\ 1 & 1 \end{pmatrix} \quad (1.80b)$$

Similarly, as shown in Sect. 1.2.1 a beam linearly polarized in a direction with angle  $\beta$  with respect to the  $x$  axis is described by inserting  $\delta = 0$  in (1.78) and (1.79). The Stokes parameters are therefore given by  $\eta_3 = \cos 2\beta$ ,  $\eta_1 = \sin 2\beta$ ,  $\eta_2 = 0$ , and the corresponding density matrix is

$$\rho = \frac{I}{2} \begin{pmatrix} 1 & -\cos 2\beta + i \sin 2\beta \\ -\cos 2\beta - i \sin 2\beta & 1 \end{pmatrix} \quad (1.80c)$$

Left- and right-handed polarized light are represented by the density matrices

$$\rho = I \begin{pmatrix} 1 & 0 \\ 0 & 0 \end{pmatrix} \quad (1.81a)$$

and

$$\rho = I \begin{pmatrix} 0 & 0 \\ 0 & 1 \end{pmatrix} \quad (1.81b)$$

respectively.

Once, the Stokes parameters, and hence the density matrix, have been determined, it is straightforward to derive a useful expression for the intensity,  $I_e$ , of light transmitted by a filter which only admits photons in the state  $|e\rangle$ : The required element is  $\langle e|\rho|e\rangle$ , which is

- $I_e = (I/2)(1 + \eta_3 \cos 2\beta + \eta_1 \sin 2\beta \cos \delta + \eta_2 \sin 2\beta \sin \delta) \quad (1.82)$

Note that the parameters  $\beta$  and  $\delta$  describe the transmitted beam, whereas the incident beam is specified in terms of the Stokes parameters in (1.82).

### 1.2.5.3 Degree of Polarization

We will now introduce a further notation which will be useful in later discussions. From condition (1.73a) and (1.77) it follows that the Stokes parameters are restricted by the condition

$$\eta_1^2 + \eta_2^2 + \eta_3^2 \leq 1 \quad (1.83)$$

The equality sign holds only if the photons in the beam under discussion are in a pure polarization state. Alternatively, the beam is completely polarized (in the sense explained in Sect. 1.2.1) if and only if the relation

$$\eta_1^2 + \eta_2^2 + \eta_3^2 = 1 \quad (1.84a)$$

holds. These conditions may be conveniently expressed by introducing the quantity

$$P = (\eta_1^2 + \eta_2^2 + \eta_3^2)^{1/2} \quad (1.85)$$

It follows from (1.83) that  $P$  is restricted by

$$P \leq 1 \quad (1.86a)$$

Equations 1.83 and 1.85 can then be summarized as follows:

- A given beam of photons is in a pure polarization state if and only if  $P = 1$ . If  $P < 1$  the beam is in a mixed state.

If a beam is such that  $P > 0$  we will refer to the beam as *polarized* (*completely polarized* if  $P = 1$ ); if  $P = 0$  we will refer to the beam as *unpolarized*. In the latter case all Stokes parameters vanish and the corresponding density matrix is given by

$$\rho = \frac{I}{2} \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix} \quad (1.87)$$

Since the Stokes parameters vanish in *any* representation when  $P = 0$ , (1.87) is independent of the choice of the basis states. Any mixture of independently prepared states  $|e_1\rangle$  and  $|e_2\rangle$  of opposite polarization (for example,  $|+1\rangle$  and  $| -1\rangle$  or  $|e_x\rangle$  and  $|e_y\rangle$ ) and equal intensities  $I_1 = I_2 = I/2$  is represented by the density matrix (1.87). All these mixtures behave identically in their polarization properties and can be used as models for unpolarized light.

#### 1.2.5.4 “Operational” Definition of $\rho$

At this point we will invert some of the results given above, as follows. In order to determine the polarization properties of a given light beam it is necessary to perform four independent measurements by, for convenience, determining the Stokes parameters. These four parameters then serve as data which enable the density matrix to be *defined* by (1.77). The result of any further experiment performed on the beam can then be calculated with the help of (1.71) or (1.82).

A beam of photons is in a pure polarization state if and only if  $P = 1$  (completely polarized beam). In this case the polarization state of the beam can be represented by a single state vector  $|e\rangle$ . In this case the Stokes parameters are not independent; because of condition (1.84a) three of the parameters suffice for a complete characterization of the beam [two parameters in the case of the normalization (1.67)].

Finally, a beam of photons is in a mixed state if  $P < 1$ . In the special case  $P = 0$  the beam is unpolarized and represented by the density matrix (1.87).

# Chapter 2

## General Density Matrix Theory

### 2.1 Pure and Mixed Quantum Mechanical States

In this chapter the concepts introduced in Chap. 1 will be generalized to systems with more than two degrees of freedom. The examples discussed in the preceding sections will provide the physical background for the general treatment in this chapter. We will begin with a further discussion of pure and mixed states.

In classical mechanics the dynamical state of a system, for example, of structureless particles, is completely determined once the values of all positions and momenta of the particles are known. The state of the system at any subsequent time can then be predicted with certainty. But often only averages of the positions and momenta of the particles are given. Because of this incomplete information the methods of statistical mechanics must be applied. We are concerned here with quantum mechanical systems for which the maximum possible information is not available. However, the phrase “maximum possible information” has in quantum mechanics a more restricted meaning than in classical physics since not all physical observables can be measured simultaneously with precision. Our first task, therefore, is to discuss the meaning of the phrase “maximum information” in quantum mechanics.

As is well known, a precise simultaneous measurement of two physical variables is only possible if the two operators corresponding to the two variables commute. Thus, if two operators  $Q_1$ ,  $Q_2$  commute it is possible to find states in which  $Q_1$  and  $Q_2$  have definite eigenvalues  $q_1$ ,  $q_2$ . Similarly, if a third operator commutes with both  $Q_1$  and  $Q_2$  then states can be found in which  $Q_1$ ,  $Q_2$ ,  $Q_3$  have simultaneously definite eigenvalues  $q_1$ ,  $q_2$ ,  $q_3$ , and so on. The eigenvalues  $q_1$ ,  $q_2$ ,  $q_3$ , ... can thus be used to give an increasingly precise classification of the system. The largest set of mutually commuting independent observables  $Q_1$ ,  $Q_2$ , ... that can be found will give the most complete characterization possible. (An important example is the classification of states in terms of constants of the motion.) The measurement of another variable, corresponding to an operator which does not commute with the set  $Q_1$ ,  $Q_2$ , ... necessarily introduces uncertainty into at least one of those already

measured. It is therefore not possible to give a more complete specification of the system.

Thus, in general, the maximum information which can be obtained on a system (in the quantum mechanical sense) consists of the eigenvalues  $q_1, q_2, \dots$  of a complete commuting set of observables which have been measured (“complete experiment”). Once a complete experiment has been performed one can be sure that the state of the system is precisely the corresponding eigenstate of the set  $Q_1, Q_2, \dots$  associated with the measured eigenvalues  $q_1, q_2, \dots$ . The system is then completely specified by assigning the state vector  $|q_1, q_2, \dots\rangle$  to it. If the measurement of the observables  $Q_1, Q_2, \dots$  on the state  $|q_1, q_2, \dots\rangle$  is immediately repeated, one can be sure to find the same values  $q_1, q_2, \dots$  again.

- The existence of such a set of experiments (for which the results can be predicted with certainty) gives a necessary and sufficient characterization for a state of “maximum knowledge” (Fano 1957). *States of maximum knowledge are called pure states.*

Pure states represent the ultimate limit of precise observation as permitted by the uncertainty principle and are the quantum mechanical analog of such classical states where all positions and momenta of all particles are known.

As shown in quantum mechanics, the question when a system of commuting operators is complete can only be answered by experiment.

A complete experiment can be designed to act as a *filter* which can be used to “prepare” a system in a pure state. For example, for a beam of free electrons a complete set of commuting operators is provided by the momentum operator and the  $z$  component  $S_z$  of the spin operator. By sending a beam of electrons through a series combination of two (ideal) filters the first one selecting particles with sharp momentum  $\mathbf{P}$ , the second one selecting particles with sharp eigenvalue  $m$  of  $S_z$ , a beam can be prepared in the state  $|\mathbf{P}, m\rangle$ . That is, the particles in the beam transmitted by both filters will have the same values of  $\mathbf{P}$  and  $m$ . This can be tested by sending the emerging beam through a second set of filters identical to the first pair, and it will be found that the beam will be transmitted completely. We can repeat this experiment again and again; we will always find the same values  $\mathbf{P}$  and  $m$  and we can predict this result with certainty.

If only the spin properties of the beam are of interest the dependence of the state on all other variables than spin can be suppressed (for example, by considering beams where all particles have the same momentum) and the state vector can simply be denoted by  $|m\rangle$  as we did in Chap. 1.

The choice of a complete, commuting set of operators is not unique. For example, instead of expanding a pure spin state in terms of the eigenstates  $|p, m\rangle$  of the momentum operator and  $\hat{S}_z$  the eigenstates  $|p, m'\rangle$  of the momentum operator and  $\hat{S}_{z'}$ , can be used where  $z$  and  $z'$  are not the same. Let us consider two sets of observables  $Q_1, Q_2, \dots$  with eigenstates  $|\psi\rangle = |q_1, q_2, \dots\rangle$ , and  $Q'_1, Q'_2, \dots$  with eigenstates  $|\phi\rangle = |q'_1, q'_2, \dots\rangle$ , where at least one of the operators  $Q'_i$  does not commute with the first set. If a given system is represented by the state vector  $|\psi\rangle$

it can always be written as a linear superposition of all eigenstates of the operators  $Q'_1, Q'_2, \dots$ :

$$|\psi\rangle = \sum_n a_n |\phi_n\rangle \quad (2.1)$$

where the index  $n$  distinguishes the different eigenstates. Equation 2.1 is the mathematical expression for the *principle of superposition*.

The particular states  $|\phi_n\rangle$  that have been used in the expansion (2.1) are termed “basis states” and the state  $|\psi\rangle$  is said to be written in the  $\{|\phi_n\rangle\}$  representation. We will always assume that the basis states are orthonormal:

$$\langle \phi_n | \phi_m \rangle = \delta_{nm} \quad (2.2a)$$

and complete:

$$\sum_n |\phi_n\rangle \langle \phi_n| = 1 \quad (2.2b)$$

A direct consequence of the property (2.2a) is that the expansion coefficients  $a_n$  are given by

$$a_n = \langle \phi_n | \psi \rangle \quad (2.3)$$

We will normalize according to

$$\langle \psi | \psi \rangle = \sum_n |a_n|^2 = 1 \quad (2.4)$$

where (2.2a) has been used together with the expansion

$$\langle \psi | = \sum_n a_n^* \langle \phi_n | \quad (2.5)$$

for the adjoint state  $\langle \psi |$ .

We recall that the absolute squares  $|a_n|^2$  give the probabilities that a measurement will find the system in the  $n$ th eigenstate.

From (2.1) it follows that a pure state can be characterized in two ways. Either it can be specified by giving all eigenvalues  $q_1, q_2, \dots$  of a complete operator set, or it can be specified by the amplitudes  $a_n$  which give  $|\psi\rangle$  in terms of the eigenstates  $|\phi_n\rangle$  of another set of observables. The second set is usually more convenient.

In practice, a complete preparation of a system is seldom achieved, and in most cases the dynamical variables measured during the preparation do not constitute a complete set. As a result the state of the system is not pure and it cannot be represented by a single-state vector. It can be described by stating that the system has certain probabilities  $W_1, W_2, \dots$  of being in the pure states  $|\phi_1\rangle, |\phi_2\rangle, \dots$ , respectively. In the case of incomplete preparations, it is therefore

necessary to use a statistical description in the same sense as in classical statistical mechanics.

- Systems which cannot be characterized by a single-state vector are called *statistical mixtures*.

Examples have already been given in Chap. 1.

Consider an ensemble of particles in the pure state  $|\psi\rangle$ . If this state is not one of the eigenstates of an observable  $Q$  then measurements of the corresponding physical quantity will produce a variety of results, each of which is an eigenvalue of  $Q$ . If similar measurements were made on a very large number of particles, all of which were in the same state  $|\psi\rangle$ , then, in general, all the possible eigenvalues of  $Q$  would be obtained. The average of the obtained results is given by the expectation value  $\langle Q \rangle$  of the observable  $Q$ , which is defined by the matrix element:

$$\langle Q \rangle = \langle \psi | Q | \psi \rangle \quad (2.6)$$

in the normalization (2.4).

In order to obtain  $\langle Q \rangle$  for a mixture of states  $|\psi_1\rangle$ ,  $|\psi_2\rangle$ , ... the expectation values  $\langle Q_n \rangle = \langle \psi_n | Q | \psi_n \rangle$  of each of the pure state components must be calculated and then averaged by summing over all pure states multiplied by its corresponding statistical weight  $W_n$ :

- $$\langle Q \rangle = \sum_n W_n \langle \psi_n | Q | \psi_n \rangle \quad (2.7)$$

It should be noted that statistics enter into (2.7) in two ways: (1) in the quantum mechanical expectation value  $\langle Q_n \rangle$  and (2) in the ensemble average over these values with the weights  $W_n$ . While the first type of averaging is connected with the perturbation of the system during a measurement and is therefore inherent in the nature of quantization, the second averaging is introduced because of the lack of information as to which of several pure states the system may be in. This latter averaging closely resembles that of classical statistical mechanics and it can be conveniently performed by using the density matrix techniques which will be discussed in the following section.

## 2.2 The Density Matrix and Its Basic Properties

Consider a mixture of independently prepared states  $|\psi_n\rangle$  ( $n = 1, 2, \dots$ ) with statistical weights  $W_n$ . These states need not necessarily be orthonormal to each other. The density operator describing the mixture is then defined as

$$\rho = \sum_n W_n |\psi_n\rangle \langle \psi_n| \quad (2.8)$$

where the sum extends over all states present in the mixture,  $\rho$  is also referred to as *statistical operator*.

In order to express the operator (2.8) in matrix form a convenient set of basis states must first be chosen, say,  $|\phi_1\rangle, |\phi_2\rangle, \dots$ , which fulfill the condition (2.2). Using the superposition principle

$$|\psi_n\rangle = \sum_{m'} a_{m'}^{(n)} |\phi_{m'}\rangle \quad (2.9a)$$

and

$$|\psi_n\rangle = \sum_m a_m^{(n)*} \langle \phi_m | \quad (2.9b)$$

then (2.8) becomes

$$\rho = \sum_{mm'm} W_n a_{m'}^{(n)} a_m^{(n)*} |\phi_{m'}\rangle \langle \phi_m| \quad (2.10)$$

Taking matrix elements of (2.10) between states  $|\phi_j\rangle$  and  $\langle \phi_i|$  and applying the orthonormality conditions (2.2a) we obtain

$$\langle \phi_i | \rho | \phi_j \rangle = \sum_n W_n a_i^{(n)} a_j^{(n)*} \quad (2.11)$$

The set of all elements (2.11), where  $i$  and  $j$  run over all basis states over which the sum in (2.9) extends, gives an explicit matrix representation of the operator (2.8), the *density matrix*. Since the basis states  $|\phi_n\rangle$  have been used we will say that the set of (2.11) gives the elements of the density matrix in the  $\{|\phi_n\rangle\}$  representation.

We will now derive and generalize some important properties of the density matrix which were first encountered in Chap. 1. First of all, from (2.11) it is evident that  $\rho$  is *Hermitian*; that is, the matrix (2.11) satisfies the condition

$$\bullet \quad \langle \phi_i | \rho | \phi_j \rangle = \langle \phi_j | \rho | \phi_i \rangle^* \quad (2.12)$$

Secondly, since the probability of finding the system in the state  $|\psi_n\rangle$  is  $W_n$  and since the probability that  $|\psi_n\rangle$  can be found in the state  $|\phi_m\rangle$  is  $|a_m^{(n)}|^2$ , the probability of finding the system in the state  $|\phi_m\rangle$  is given by the diagonal element

$$\rho_{mm} = \sum_n W_n |a_m^{(n)}|^2 \quad (2.13)$$

This relation gives a physical interpretation of the diagonal elements of  $\rho$ . The physical importance of the off-diagonal elements will be considered in Sect. 2.3. Because probabilities are positive numbers it follows from (2.13) that

$$\bullet \quad \rho_{mm} \geq 0 \quad (2.14a)$$

Using the same arguments as in Chap. 1 it can be shown that the probability  $W(\psi)$  of finding the system in the state  $|\psi\rangle$  after a measurement is given by the matrix element:

- $W(\psi) = \langle \psi | \rho | \psi \rangle$  (2.15)

in the normalization (2.4). This becomes evident if (2.8) is substituted for  $\rho$  in (2.15):

$$W(\psi) = \sum_n W_n |\langle \psi_n | \psi \rangle|^2$$

and the coefficients  $|\langle \psi_n | \psi \rangle|^2$  are interpreted according to (2.3).

The trace of  $\rho$  is a constant independent of the representation. From the normalization (2.4) and the condition

$$\sum_n W_n = 1 \quad (2.16a)$$

it follows that

$$\text{tr } \rho = \sum_i \rho_{ii} = \sum_a W_a \sum_n |a_i^{(n)}|^2 = 1 \quad (2.17)$$

The expectation value of any operator  $Q$  is given by the trace of the product of  $\rho$  and  $Q$ :

- $$\begin{aligned} \langle Q \rangle &= \sum_{mm'} \sum_n W_n a_{m'}^n a_m^{(n)*} \langle \phi_m | Q | \phi_{m'} \rangle \\ &= \sum_{mm'} \langle \phi_{m'} | \rho | \phi_m \rangle \langle \phi_m | Q | \phi_{m'} \rangle \\ &= \text{tr} (\rho Q) \end{aligned} \quad (2.18)$$

where we first inserted (2.9) into (2.7) and then applied (2.11).

More generally, if we drop the normalization (2.16a) (as we did in Sect. 1.2.4), then  $\langle Q \rangle$  is given by

$$\langle Q \rangle = \frac{\text{tr} (\rho Q)}{\text{tr } \rho} \quad (2.19a)$$

The relation (2.18) is an important result. We recall from quantum mechanics that all information on the behavior of a given system can be expressed in terms of expectation values of suitably chosen operators. Thus the basic problem is to calculate the expectation values. Since the expectation value of any operator can be obtained by use of (2.18) *the density matrix contains all physically significant information on the system.*

So far the density matrix has been defined by (2.11). In general, however, it is more convenient to consider  $\rho$  to be defined by the expression (2.18) in the following way. As many operators  $Q_1, Q_2, \dots$  as there are independent parameters in  $\rho$  are chosen and their expectation values  $\langle Q_1 \rangle, \langle Q_2 \rangle, \dots$  are given as initial information on the system. The corresponding density matrix can then be determined by solving the set of equations

$$\text{tr} (\rho Q_i) = \langle Q_i \rangle$$

Once  $\rho$  is determined in this way any further expectation value can be obtained by applying (2.18). For example, as discussed in Sect. 1.1, the density matrix of spin-1/2 particles can be obtained from a knowledge of the three expectation values  $\langle \sigma_i \rangle$ , that is, the components of the polarization vector.

This method has two advantages. First of all the definition of a mixture given by (2.8) is not unique for the reasons described in Sect. 1.1.5. Secondly, the initial information on a system is often expressed in terms of expectation values of a set of operators rather than by specifying the pure states present in the mixture. This approach has been particularly advocated by Fano (1957) and we will return to it in Chap. 4.

We will now consider the number of independent parameters which are needed to specify a given density matrix. This will depend on the number of orthogonal states over which the sum in (2.9) extends. In general, this number is infinite, but it is often finite when only one particular property of the system (the spin, for instance) is of interest and the dependence on all other variables can be suppressed. In the following discussion we will consider the case in which the number of basis states in the expansion (2.9) is equal to  $N$ .  $\rho$  is then an  $N$ -dimensional square matrix with  $N^2$  complex elements corresponding to  $2N^2$  real parameters. The hermiticity condition (2.12) restricts the number of independent real parameters to  $N^2$ , and since the trace of  $\rho$  is fixed by the normalization condition it follows that an  $N$ -dimensional density matrix is completely specified in terms of  $N^2 - 1$  real parameters [ $N^2$  parameters if we drop the normalization (2.17) as, for example, in (1.69)]. This number may be reduced by symmetry requirements and further reduced if the system under consideration is known to be in a pure state. We will give an explicit example of this in Sect. 3.5.

If a given system is in a pure state, represented by the state vector  $|\psi\rangle$ , the corresponding density operator is given by

$$\rho = |\psi\rangle\langle\psi| \quad (2.20)$$

The density matrix can be constructed in a representation in which  $|\psi\rangle$  is one of the basis states. For example, a set of orthonormal states  $|\psi_1\rangle = |\psi\rangle, |\psi_2\rangle, \dots$  could be chosen and then, clearly, all the elements of  $\rho$  would be zero in this representation except for the element in the first row and column. It is evident from this that

$$\text{tr} (\rho^2) = (\text{tr} \rho)^2 \quad (2.21)$$

Consider now the inverse problem of determining whether a given density matrix describes a pure state or not. In principle the problem can always be solved by transforming the given matrix to diagonal form. If this is done and it is found that all elements of  $\rho$  vanish except one, say, the  $i$ th diagonal element, then the system is in a pure state represented by the  $i$ th basis vector. However, the diagonalization is often tedious and it will therefore be useful to derive a condition which is easier to apply.

First of all, we will prove that the relation

$$\text{tr} (\rho^2) \leq (\text{tr} \rho)^2 \quad (2.22)$$

is valid in general. Consider an arbitrary density matrix which has been transformed into diagonal form with diagonal elements  $W_n$ . Then

$$\text{tr} (\rho^2) = \sum_n W_n^2 \quad (2.23a)$$

and

$$(\text{tr} \rho)^2 = \left( \sum_n W_n \right)^2 \quad (2.23b)$$

Because the probabilities  $W_n$  are positive numbers it immediately follows that (2.22) is valid for the diagonal representation. Because the numerical values of traces remain unchanged under a transformation of the basis states it follows that (2.22) is valid in *any* representation, and not only in a diagonal one.

Suppose now that the equality sign holds in (2.22). In the diagonal representation this yields the condition

$$\sum_n W_n^2 = \left( \sum_n W_n \right)^2$$

from (2.23). This condition can only be satisfied if all  $W_n$  vanish except one, say,  $W_i$ . Consequently,  $\rho$  contains only one nonvanishing diagonal element in the diagonal representation and the system is in a pure state represented by the  $i$ th basis vector.

In conclusion, we have proved that (2.21) is a sufficient and necessary condition that a given density matrix describes a pure state. Some consequences to this result have been discussed in Chap. 1 and further examples will be given in Chap. 3.

Finally, let us consider the case of a *random distribution* of a complete set of states  $|\phi_n\rangle$ . As an example, consider an ensemble of atoms with spin  $S$  and third component  $M$  characterized by state vectors  $|n, S, M, \rangle$ , where  $n$  collectively denotes all other variables necessary to specify the states completely. Consider the case where all atoms have the same values of  $n$  and  $S$  but where the ensemble is a mixture with respect to  $M$  such that all different spin states can be found with the same probability  $W_m = 1/(2S + 1)$ , represented by the density operator

$$\begin{aligned}\rho &= \frac{1}{2S+1} \sum_M |nSM\rangle \langle nSM| \\ &= \frac{1}{2S+1} \mathbf{1}\end{aligned}\quad (2.24)$$

where  $\mathbf{1}$  is the  $(2S+1)$ -dimensional unit matrix in spin space. Here, we have applied the completeness relation (2.2b) to the spin states. Evidently, the corresponding density matrix is diagonal with equal elements  $1/(2S+1)$  in *any* representation. Generalizing the definition given in Sect. 1.2.5 [see (1.87)] we will call an atomic system *unpolarized* if it can be represented by the operator (2.24).

## 2.3 Coherence Versus Incoherence

### 2.3.1 Elementary Theory of Quantum Beats

We will begin this section with a discussion of quantum beats. The treatment given here is oversimplified in several respects. In particular the polarization of the initial photons will be completely neglected. A general theory will be presented in Chap. 5. The discussion given in this section is intended partly as an introduction to the important concept of “coherent superposition” and partly as an introduction to the topics in Chaps. 3 and 5.

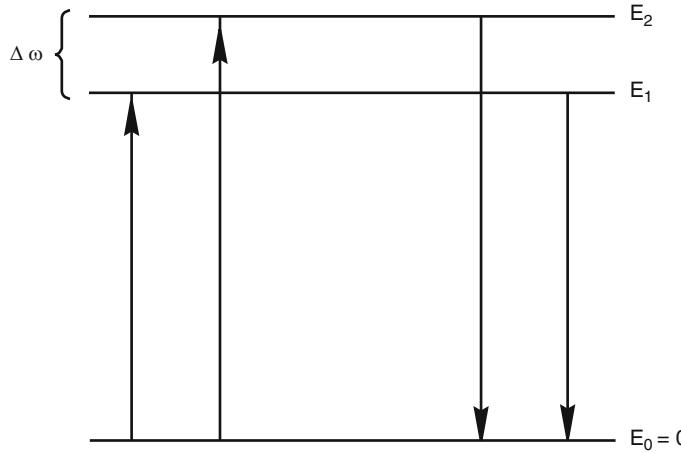
Consider an ensemble of atoms all of which are in their ground state  $|0\rangle$  of well-defined energy  $E_0$  (which we will put equal to zero). The atoms may be excited to higher-lying states by photon absorption. If the excitation is caused by very short pulses of light such that the duration of the pulse  $\Delta t$  is much smaller than the mean lifetime of the excited atoms then the excitation can be considered to have occurred “instantaneously,” say, at time  $t = 0$ . A light pulse of duration  $\Delta t$  has a bandwidth  $\Delta\omega \sim 1/\Delta t$  and the photons have no well-defined energy. We will assume that the energy spread  $\hbar\Delta\omega$  is greater than the energy difference  $E_1 - E_2$  of two atomic levels  $|\phi_1\rangle$  and  $|\phi_2\rangle$  (see Fig. 2.1). The energy of the excited atoms will then be undefined and we represent the state of the excited atoms by a linear superposition of both states

$$|\psi(0)\rangle = a_1|\phi(0)_1\rangle + a_2|\phi(0)_2\rangle \quad (2.25)$$

immediately after the absorption (for a more detailed discussion of the underlying principles see Chap. 3).

Any state  $|\phi(0)_i\rangle$  of definite energy evolves in time according to the law

$$|\phi(t)_i\rangle = \exp[-(i/\hbar)E_I t]|\phi(0)_i\rangle$$



**Fig. 2.1** Illustration of two levels decaying to the same ground state

If the decay of the excited atoms is described phenomenologically by the factor  $\exp[-(1/2\gamma_i t)]$  then the time development of the state (2.25) is given by

$$|\psi(t)\rangle = a_1 \exp[-(i/\hbar)E_1 t - \gamma_1/2)t]|\phi(0)_1\rangle + a_2 \exp[-(i/\hbar)E_2 t - (\gamma_2/2)t]|\phi(0)_2\rangle \quad (2.26)$$

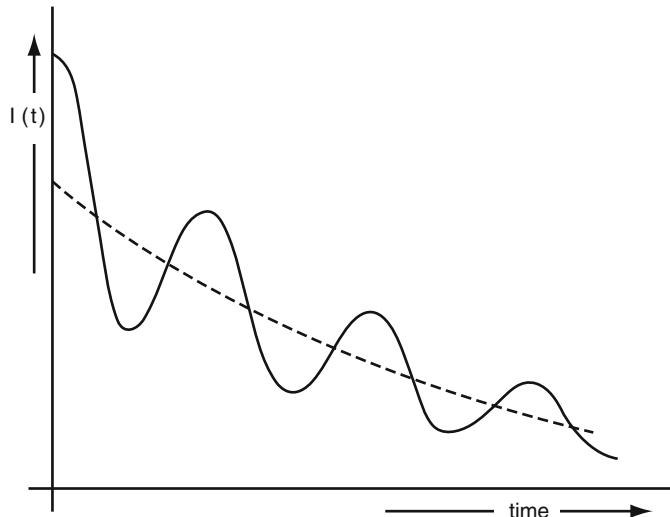
where  $\gamma_1$  and  $\gamma_2$  are the decay constants of the states  $|\phi_1\rangle$  and  $|\phi_2\rangle$ , respectively. An expression for the intensity of the light emitted at time  $t$  can be derived from elementary radiation theory and is given by the expression

$$I(t) \sim |\langle 0|\mathbf{e}\mathbf{r}|\psi(t)\rangle|^2 = |a_1 \langle 0|\mathbf{e}\mathbf{r}|\phi(t)_1\rangle + a_2 \langle 0|\mathbf{e}\mathbf{r}|\phi(t)_2\rangle|^2 \quad (2.27)$$

where  $\mathbf{e}$  is the polarization vector of the emitted photons and  $\mathbf{r}$  the dipole operator. Denoting  $\langle 0|\mathbf{e}\mathbf{r}|\phi_i(0)\rangle$  by  $A_i$  and  $(1/2)(\gamma_1 + \gamma_2)$  by  $\gamma$  and using (2.26) gives

$$I(t) \sim |a_1 A_1|^2 \exp(-\gamma t) + |a_2 A_2|^2 \exp(-\gamma t) + a_1 a_2^* A_1 A_2^* \exp[-(i/\hbar)(E_1 - E_2)t - \gamma t] + a_1^* a_2 A_1^* A_2 \exp[+(i/\hbar)(E_1 - E_2)t - \gamma t] \quad (2.28)$$

Equation 2.28 shows that  $I(t)$  varies periodically with a frequency  $(1/\hbar)(E_1 - E_2)$  (Fig. 2.2). This phenomenon is known as *quantum beats* and can be understood as an *interference effect* in the sense of (2.27): In order to obtain  $I(t)$  the amplitudes must



**Fig. 2.2** Illustration of “quantum beats”

be added before the modulus is taken. Equation 2.28 illustrates that it is possible to measure small energy differences by determining the beat frequency. This method is now widely used in atomic spectroscopy (see, for example, the articles in Hanle and Kleinpopp 1978, 1979).

### 2.3.2 The Concept of Coherent Superposition

It is instructive to generalize (2.28) as follows. The density operator of the excited atoms immediately after the excitation is given by  $|\psi(0)\rangle\langle\psi(0)|$ . Using the states  $|\phi_1\rangle$  and  $|\phi_2\rangle$  of definite energy as basis the elements of the excited state density matrix in the energy representation are found to be  $\langle\phi_i|\rho(0)|\phi_j\rangle = \rho_{ij} = a_i a_j^*(i, j = 1, 2)$ . It is therefore plausible to make the following generalization of (2.28) (a formal proof will be given in Chap. 5). Suppose that at time  $t = 0$  an excited atomic state is not pure but represented by a  $2 \times 2$  density matrix  $\rho(0)$  with basis vectors  $|\phi_1\rangle$  and  $|\phi_2\rangle$ . In this case (2.28) still holds if the elements  $\rho_{ij}$  of this density matrix are substituted for the corresponding quantities  $a_i a_j^*$ . It follows that the quantum beats are associated with the time evolution of the off-diagonal elements of the excited state density matrix  $\rho(0)$ . No interference terms will occur in (2.28) if the density matrix  $\rho(0)$  is diagonal in the energy representation.

This connection between interference and off-diagonal elements of the relevant density matrix is a general one, as will be shown by our subsequent discussions.

We will therefore give the following definition. If a given system may be characterized by a density matrix written in a representation with basis vectors  $|\phi_n\rangle$ , then

- The system is a *coherent superposition* of *basis* states  $|\phi_n\rangle$  if its density matrix is not diagonal in the  $\{|\phi_n\rangle\}$  representation. If, in addition, the system is in a pure state it is said to be *completely coherent*. If  $\rho$  is diagonal the system is said to be an *incoherent superposition* of the *basis* states (provided there is more than one nonvanishing element) (Cohen-Tannoudji 1962).

In this sense the time modulation of  $I(t)$  is a manifestation of the coherent excitation of states with different energy as expressed by (2.25).

The distinction between “complete coherence” and “coherence” is often of little significance, and in the literature the term “coherence” is usually applied to both situations. We will follow this custom in cases where we are not interested in whether the system under consideration is in a pure state or not. The concept of coherent superposition depends on the choice of representation for the density matrix. For example, the mixture of independently prepared states (2.8) is an incoherent superposition of states  $|\psi_n\rangle$ , but in general it is also a coherent superposition of basis states as shown by (2.10) and (2.11).

The above definition can also be considered from the following point of view. A pure state state can always be written as a linear (completely coherent) superposition of basis states. The magnitudes and phases of the coefficients in this expansion are well defined (apart from the overall phase); that is, there exists a definite phase relationship between the basis states. The other extreme is a mixture of independently prepared basis states  $|\phi_n\rangle$  represented by the density operator

$$\rho = \sum_n W_n |\phi_n\rangle\langle\phi_n|$$

without any definite phase relation.  $\rho$  is diagonal in the  $\{|\phi_n\rangle\}$  representation and, by definition, the states  $|\phi_n\rangle$  overlap incoherently. A mixture of states  $|\psi_1\rangle$ ,  $|\psi_2\rangle$ , ... represented by a density matrix which is not diagonal in the  $\{|\phi_n\rangle\}$  representation [see, for example, (2.10) and (2.11)] lies between the two extreme cases of “complete coherence” and “incoherence” with respect to  $|\phi_n\rangle$ .

Let us now give the following, more general, definition:

- A system is said to be an *incoherent superposition* of states  $|\psi_1\rangle$ ,  $|\psi_2\rangle$ , ... if it can be represented by the density operator

$$\rho = \sum_n W_n |\psi_n\rangle\langle\psi_n|$$

When the set  $|\psi_n\rangle$  is orthonormal these states can be used as basis states and this definition is then equivalent to the one given previously.

As an example consider an atomic system being in a coherent superposition of its ground state (angular momentum  $J = 0$ ) and an excited state with  $J = 1$ .

The elements of the density matrix describing the system will be denoted by

$$\langle J' M' | \rho | J M \rangle = \rho(J' J)_{M' M} \quad (2.29)$$

In an explicit matrix form  $\rho$  is given by

$$\rho = \begin{pmatrix} \rho(0, 0)_{00} & \rho(01)_{01} & \rho(01)_{00} & \rho(01)_{0-1} \\ \hline \rho(10)_{10} & \rho(11)_{11} & \rho(11)_{10} & \rho(11)_{1-1} \\ \rho(10)_{00} & \rho(11)_{01} & \rho(11)_{00} & \rho(11)_{0-1} \\ \rho(10)_{-10} & \rho(11)_{-11} & \rho(11)_{-10} & \rho(11)_{-1-1} \end{pmatrix} \quad (2.30)$$

The matrix (2.30) is divided into four submatrices. The upper one consists of one element, the probability  $\rho(00)_{00}$  of finding the system in its ground state. The elements of the square submatrix characterize the excited state. Its diagonal elements are the probabilities of finding an atom in the corresponding substate with quantum number  $M$ . Its off-diagonal elements describe the coherence between different substates. The remaining elements in the first row and first column of the matrix (2.30) characterize the interference between the ground and the excited states. Density matrices of the form (2.30) occur, for example, in optical pumping theory corresponding to transitions  $J = 0 \leftrightarrow J = 1$ .

## 2.4 Time Evolution of Statistical Mixtures

### 2.4.1 The Time Evolution Operator

The time development of quantum mechanical states is described by the Schrödinger equation:

$$i\hbar \frac{\partial |\psi(t)\rangle}{\partial t} = H |\psi(t)\rangle \quad (2.31)$$

and the equation for the adjoint state is

$$-i\hbar \frac{\partial \langle \psi(t)|}{\partial t} = \langle \psi(t)| H \quad (2.32a)$$

The Hamiltonian may depend explicitly on the time, for example, if  $H$  contains an interaction term  $V(t)$  caused by an external time-varying field. However, we will assume at present that  $H$  is time independent.

In this section we will consider how the information contained in (2.31) can be expressed in another useful way. We will denote an eigenstate of  $H$  with energy

$E_n$  by  $|\mu_n\rangle$ :

$$H|\mu_n\rangle = E_n|\mu_n\rangle \quad (2.33)$$

If a system is represented at time  $t = 0$  by an eigenstate  $|\mu_n\rangle$  then at a time  $t$  the system will be found in the state

$$|\mu_n(t)\rangle = e^{-(i/\hbar)E_n t}|\mu_n\rangle \quad (2.34)$$

which is clearly a solution of (2.31). Thus the time development of eigenstates of the total Hamiltonian is simply obtained by multiplying  $|\mu_n\rangle$  by the exponential factor  $e^{-(i/\hbar)E_n t}$ .

Equation 2.34 can be generalized in the following way. Any solution of (2.31) can be expanded in terms of the set of eigenstates  $|\mu_n\rangle$ :

$$|\psi(t)\rangle = \sum_n C_n |\mu_n(t)\rangle = \sum_n C_n e^{-(i/\hbar)E_n t} |\mu_n\rangle \quad (2.35)$$

where the coefficients  $C_n$  are time independent. This can be shown by inserting (2.35) into the Schrödinger equation and applying (2.33). In particular, at time  $t = 0$

$$|\psi(0)\rangle = \sum_n C_n |\mu_n\rangle \quad (2.36a)$$

In this case (that is, where the eigenstates of a time-independent total Hamiltonian have been used as basis set) the coefficients  $C_n$  can be determined by specifying the initial conditions. Equation 2.35 illustrates how any state  $|\psi(t)\rangle$  evolves in time. If the eigenstates and eigenvalues of  $H$  are known, then the dynamical evolution of any state vector can be predicted. Equation 2.35 can be written in a more abstract form. First of all, since

$$e^{-(i/\hbar)E_n t} |\mu_n\rangle = e^{-(i/\hbar)H t} |\mu_n\rangle \quad (2.37)$$

where the exponential operator function is defined by

$$e^{-(i/\hbar)H t} = 1 - \frac{i}{\hbar} H t - \frac{1}{2\hbar^2} H^2 t^2 - \dots \quad (2.38)$$

them by operating on  $|\mu_n\rangle$  with the operator given by (2.38) and applying (2.33) to any term, (2.37) is obtained. Substitution of the expression (2.37) into (2.35) yields

$$|\psi(t)\rangle = e^{-(i/\hbar)H t} \sum_n C_n |\mu_n\rangle = e^{-(i/\hbar)H t} |\psi(0)\rangle \quad (2.39)$$

$|\psi(t)\rangle$  in the form (2.39) may also be obtained in a more direct manner by formally integrating (2.31).

The operator  $e^{-(i/\hbar)H t}$  contains all the information on the time evolution of any state  $|\psi(t)\rangle$  and hence also on the dynamics of the system. If the state  $|\psi(0)\rangle$  of a system at time  $t = 0$  is known then the state representing the system at a later time

$t$  is obtained by operating on  $|\psi(0)\rangle$  with  $e^{-(i/\hbar)Ht}$ . If  $|\psi(0)\rangle$  is an eigenstate  $|\mu_n\rangle$  of the total Hamiltonian then (2.39) reduces to (2.34). In general, however, (2.39) only represents a formal solution of the Schrödinger equation. Since, in order to use this equation to obtain the time development of a state, it is necessary to know the effect of the exponential operator on  $|\psi(0)\rangle$ , which requires, for example, a knowledge of all eigenstates and eigenvalues of  $H$ . Nevertheless, the form (2.39) will prove to be very useful.

We will now consider the case where *the Hamiltonian depends explicitly on the time*. In this case the Schrödinger equation

$$i\hbar \frac{\partial |\psi(t)\rangle}{\partial t} = H(t)|\psi(t)\rangle \quad (2.40)$$

does not have the simple solutions (2.35) and (2.39). However, (2.39) may be generalized by introducing an operator  $U(t)$ , the *time evolution operator*, which transforms a state  $|\psi(0)\rangle$  into a state  $|\psi(t)\rangle$ :

- $|\psi(t)\rangle = U(t)|\psi(0)\rangle \quad (2.41)$

and for the adjoint states

- $\langle\psi(t)| = \langle\psi(0)|U(t)^\dagger \quad (2.42a)$

Substitution of (2.41) into the Schrödinger (2.40) gives

$$i\hbar \frac{\partial |U(t)|\psi(0)\rangle}{\partial t} = H(t)U(t)|\psi(0)\rangle \quad (2.43a)$$

Since (2.43a) holds for any state  $|\psi(0)\rangle$  this condition can be written as an operator equation:

$$i\hbar \frac{\partial U(t)}{\partial t} = H(t)U(t) \quad (2.44)$$

In order to ensure that the system is in the state  $|\psi(0)\rangle$  at time  $t = 0$  it is necessary to impose the initial condition

$$U(0) = \mathbf{1} \quad (2.45)$$

For the adjoint operator we have

$$-i\hbar \frac{\partial U(t)^\dagger}{\partial t} = U(t)^\dagger H(t) \quad (2.46)$$

Operating on (2.43a) on the left by  $U^\dagger$  and on (2.46) on the right by  $U$  and then subtracting both equations gives

$$i\hbar \left( U^\dagger \frac{\partial U}{\partial t} + \frac{\partial U^\dagger}{\partial t} U \right) = i\hbar \frac{\partial (U^\dagger U)}{\partial t} = 0$$

It follows that  $U^\dagger U$  must be a constant operator and since it satisfies the initial condition (2.45):

$$U(0)^\dagger U(0) = 1 \quad (2.47)$$

it must also be a unitary operator. From these conditions follows that  $U^\dagger U$  must be the identity operator.

Equation 2.41 can be interpreted by noting that

$$|\langle \phi | \psi(t) \rangle|^2 = |\langle \Phi | U(t) | \psi(0) \rangle|^2$$

is the probability of finding a system at time  $t$  in the state  $|\phi\rangle$  if it was represented at  $t = 0$  by  $|\psi(0)\rangle$ .

We can summarize the contents of this section as follows. The time evolution of a state  $|\psi(t)\rangle$  can be determined either by solving the Schrödinger (2.40) or, equivalently, by determining  $U(t)$  by solving (2.43a). If  $H$  is time independent we obtain by formally integrating (2.43a):

$$U(t) = e^{-(i/\hbar)Ht} \quad (2.48)$$

where the initial condition is given by (2.45). In this case (2.41) reduces to (2.39). For the adjoint operator we have

$$U(t)^\dagger = e^{+(i/\hbar)Ht} \quad (2.49a)$$

In general, however,  $H$  will have an explicit time dependence and the solution of (2.43a) will be more complicated than (2.44). We will consider this problem in Sect. 2.4.3.

## 2.4.2 The Liouville Equation

Suppose that at time  $t = 0$  a certain mixture is represented by the density operator

$$\rho(0) = \sum_n W_n |\psi(0)_n\rangle \langle \psi(0)_n|$$

The states  $|\psi(0)_n\rangle$  vary in time according to (2.41) and, consequently, the density operator becomes a function of time:

$$\begin{aligned}\rho(t) &= \sum_n W_n |\psi(t)_n\rangle\langle\psi(t)_n| \\ &= \sum_n W_n U(t) |\psi(0)_n\rangle\langle\psi(0)_n| U(t)^\dagger\end{aligned}$$

which gives

- $\rho(t) = U(t)\rho(0)U(t)^\dagger \quad (2.50)$

If  $H$  is time independent then

- $\rho(t) = e^{-(i/\hbar)Ht} \rho(0) e^{(i/\hbar)Ht} \quad (2.51a)$

Differentiating (2.50) with respect to  $t$  and applying (2.43a) and (2.46) yields

$$\begin{aligned}i\hbar \frac{\partial \rho(t)}{\partial t} &= i\hbar \frac{\partial U(t)}{\partial t} \rho(0) U(t)^\dagger + i\hbar U(t) \rho(0) \frac{\partial U^\dagger}{\partial t} \\ &= H(t) U(t) \rho(0) U(t)^\dagger - U(t) \rho(0) U(t)^\dagger H(t)\end{aligned}$$

Inserting (2.50) we obtain

- $i\hbar \frac{\partial \rho(t)}{\partial t} = [H(t), \rho(t)] \quad (2.52)$

with the commutator

$$[H(t), \rho(t)] = H(t)\rho(t) - \rho(t)H(t)$$

Thus the time development of a density operator can be determined either from (2.50) or, equivalently, from (2.52). The differential (2.52) is often called the *Liouville equation* because it assumes the same form as the equation of motion for the phase space probability distribution in classical mechanics (see, for example, Tolman 1954).

Equations 2.18 and 2.52 are basic equations of the theory. It is the simultaneous solution of these equations which leads to equations of motion for the observables. We will give an explicit example in Sect. 2.5.

Let us now assume that we can write

$$H(t) = H_0 + V(t) \quad (2.53)$$

where  $H_0$  is assumed to be time independent and  $V(t)$  describes a time-varying external field which induces transitions between the eigenstates  $|\mu_n^{(0)}\rangle$  of  $H_0$ . Using these eigenstates as a basis we write

$$|\Psi(t)_n\rangle = \sum_n C(t)_n |\mu_n^{(0)}\rangle = \sum_n C(t)_n e^{-(i/\hbar)E_n^{(0)}t} |\mu_n^{(0)}\rangle \quad (2.54)$$

since the time evolution of the eigenstates of  $H_0$  is given by (2.34) where the eigenvalues  $E_n^{(0)}$  of  $H_0$  have been substituted for the corresponding  $E_n$ . The time dependence treated by the external force  $V(t)$  is entirely contained in the coefficients  $C(t)_n$  which are time independent if  $V(t) = 0$ , as discussed in the preceding section.

We will now derive an expression for the time evolution of the density matrix elements in the  $\{|\mu_n^{(0)}\rangle\}$  representation. The matrix elements of  $H = H_0 + V(t)$  are given by the expression

$$\langle \mu_{m'}^{(0)} | H(t) | \mu_m^{(0)} \rangle = E_m^{(0)} \delta_{m'm} + \langle \mu_{m'}^{(0)} | V(t) | \mu_m^{(0)} \rangle \quad (2.55)$$

If the Liouville equation is multiplied by  $|\mu_{m'}^{(0)}\rangle$  on the left hand and by  $|\mu_m^{(0)}\rangle$  on the right then writing  $\rho(t)_{m'm} = \langle \mu_{m'}^{(0)} | \rho(t) | \mu_m^{(0)} \rangle$  we find

$$\begin{aligned} i\hbar \frac{\partial \rho(t)_{m'm}}{\partial t} &= \sum_n \left[ E_{m'}^{(0)} \delta_{m'm} \rho(t)_{nm} + \langle \mu_{m'}^{(0)} | V(t) | \mu_n^{(0)} \rangle^* \rho(t)_{nm} \right. \\ &\quad \left. - \rho(t)_{m'n} E_m^{(0)} \delta_{nm} - \rho(t)_{m'n} \langle \mu_n^{(0)} | V(t) | \mu_m^{(0)} \rangle \right] \\ &= \left( E_{m'}^{(0)} - E_m^{(0)} \right) \rho(t)_{m'm} \\ &\quad + \sum_n \left[ \langle \mu_{m'}^{(0)} | V(t) | \mu_n^{(0)} \rangle \rho(t)_{nm} - \rho(t)_{m'm} \langle \mu_n^{(0)} | V(t) | \mu_m^{(0)} \rangle \right] \quad (2.56) \end{aligned}$$

This can be written in the equivalent form

$$i\hbar \frac{\partial \rho(t)_{m'm}}{\partial t} = \left( E_{m'}^{(0)} - E_m^{(0)} \right) \rho(t)_{m'm} + \langle \mu_{m'}^{(0)} | [V(t), \rho(t)] | \mu_m^{(0)} \rangle \quad (2.57)$$

which is the required result.

### 2.4.3 The Interaction Picture

The main topic of this section will be the (approximate) determination of the time evolution operator. With the help of the obtained expressions we will also discuss the solution of the Liouville equation.

In general, an exact solution of (2.43a) is not possible. Often however, the interaction  $V(t)$  in (2.53) is a small perturbation and (2.44) can be solved by applying the methods of time-dependent perturbation theory.

To begin with some preliminary remarks, we first of all note that a large part of the time dependence of the state vectors  $|\psi(t)\rangle$  is created by  $H_0$ . This is actually quite evident from (2.54), which contains the rapidly varying factors  $e^{-(i/\hbar)E_n^{(0)}t}$ . This dependence can be explicitly removed by writing (2.54) in the form

$$|\psi(t)\rangle = e^{-(i/\hbar)H_0t} \sum_n C(t)_n |\mu_n^{(0)}\rangle = e^{-(i/\hbar)H_0t} |\psi(t)_I\rangle \quad (2.58)$$

where  $e^{-(i/\hbar)H_0t}$  is defined as in (2.38) and where

$$|\psi(t)_I\rangle = \sum_n C_n(t) |\mu_n^{(0)}\rangle \quad (2.59)$$

Substituting (2.58) into the Schrödinger (2.40) and assuming that (2.53) holds gives

$$\begin{aligned} i\hbar \frac{\partial |\psi(t)\rangle}{\partial t} &= i\hbar \left( -\frac{i}{\hbar} \right) H_0 e^{-(i/\hbar)H_0t} |\psi(t)_I\rangle + i\hbar (e^{-(i/\hbar)H_0t}) \frac{\partial |\psi(t)_I\rangle}{\partial t} \\ &= [H_0 + V(t)] e^{-(i/\hbar)H_0t} |\psi(t)_I\rangle \end{aligned}$$

The terms containing  $H_0$  cancel each other and we obtain the equation of motion for the state vector  $|\psi(t)_I\rangle$ :

$$i\hbar \frac{\partial |\psi(t)_I\rangle}{\partial t} = V(t)_I |\psi(t)_I\rangle \quad (2.60)$$

where we defined

$$V(t)_I = e^{(i/\hbar)H_0t} V(t) e^{-(i/\hbar)H_0t} \quad (2.61)$$

Equation 2.60 shows that  $\partial|\psi(t)_I\rangle/\partial t = 0$  if  $V(t) = 0$ , that is, *the time dependence of  $|\psi(t)_I\rangle$  is created entirely by the external potential term  $V(t)$* . If  $V(t)$  is a small perturbation  $|\psi(t)_I\rangle$  will vary slowly with time. For this reason (2.60) can be solved approximately within the framework of time-dependent perturbation theory and is more amenable to practical calculation than (2.40).

The discussions in Sects 2.4.1 and 2.4.2 relied on the fact that the state vectors  $|\psi(t)\rangle$  contained all the time dependence caused by  $H_0$  and  $V(t)$ , and all the information on the time development of the system. This particular description of time evolution is called the *Schrödinger picture*. As discussed above it is often convenient to remove the rapidly varying factors due to  $H_0$  from the states. As shown by (2.58) this can be achieved by applying the operator

$$U(t)_0^\dagger = e^{+(i/\hbar)H_0 t} \quad (2.62)$$

to all Schrödinger picture states  $|\psi(t)\rangle$  to give

- $|\psi(t)_I\rangle = e^{(i/\hbar)H_0 t} |\psi(t)\rangle \quad (2.63)$

Simultaneously, all operators  $Q(t)$  can be transformed as in (2.61) and new operators  $Q(t)_I$  can be defined as

- $Q(t)_I = e^{(i/\hbar)H_0 t} Q(t) e^{-(i/\hbar)H_0 t} \quad (2.64a)$

The inverse of these transformations are given by

- $|\psi(t)\rangle = e^{-(i/\hbar)H_0 t} |\psi(t)_I\rangle \quad (2.65a)$

- $Q(t) = e^{-(i/\hbar)H_0 t} Q(t)_I e^{(i/\hbar)H_0 t} \quad (2.65b)$

Clearly,  $U(t)_0$  is unitary. The time dependence of the states  $|\psi(t)_I\rangle$  is now generated by the term  $V(t)$  and the time dependence of the operator  $Q(t)_I$  is now due to their inherent time dependence and, in addition, to the  $H_0$  terms. The description of time evolution in terms of the states  $|\psi(t)_I\rangle$  and operators  $Q(t)_I$  is called the *interaction picture*.

Since  $U(0)_0 = 1$ , the Schrödinger and interaction pictures are the same for  $t = 0$ :

$$|\psi(0)\rangle = |\psi(0)_I\rangle \quad (2.66a)$$

After these introductory remarks we return to the problem of determining the time evolution operator. This will be done using the interaction picture. The time evolution of a Schrödinger picture state  $|\psi(t)\rangle$  is described by (2.41). An analogous expression can be established for their interaction picture counterparts  $|\psi(t)_I\rangle$ . Substituting (2.41) into (2.63) gives

$$|\psi(t)_I\rangle = e^{(i/\hbar)H_0 t} U(t) |\psi(0)\rangle$$

Applying relation (2.66a)

$$|\psi(t)_I\rangle = U(t)_I |\psi(0)_I\rangle \quad (2.67)$$

where

- $U(t) = (e^{-(i/\hbar)H_0 t}) U(t) \quad (2.68)$

and the inverse relation is

$$U(t) = (e^{-(i/\hbar)H_0 t})U(t)_I \quad (2.69)$$

The operator  $U(t)_I$  determines the time development of the states in the interaction picture.

In order to determine  $U(t)_I$  (2.69) is inserted into (2.43a). The terms involving  $H_0$  cancel and we obtain

$$i\hbar \frac{\partial U(t)_I}{\partial t} = V(t)_I U(t)_I \quad (2.70)$$

Where  $V(t)_I$  is the solution of this equation subject to the initial condition:

$$U(0)_I = \mathbf{1} \quad (2.71)$$

Equation 2.70 shows that the time dependence of  $U(t)_I$  is entirely due to  $V(t)$ . For this reason time-dependent perturbation theory can be more conveniently applied to (2.70) than to its counterpart (2.43a) in the Schrödinger picture.

In order to solve (2.70) we first formally integrate the equation to obtain

$$U(t)_I = \mathbf{1} - \frac{i}{\hbar} \int_0^t V(\tau)_I U(\tau)_I d\tau \quad (2.72)$$

where the initial condition (2.71) has been used. Equation 2.72 is not yet a solution of (2.70) but is merely a transformation of (2.70) into an integral equation which contains the unknown  $U(\tau)_I$  within the integral. Equation 2.72 can be solved by iteration. If  $V(t) = 0$  then  $U(t)_I = \mathbf{1}$ , and if  $V(t)$  is sufficiently small  $U(t)_I$  will only differ slightly from  $\mathbf{1}$ . The operator  $U(\tau)_I$  can therefore be replaced by the identity operator in the integral which gives the time evolution operator in the first-order perturbation theory:

$$\bullet \quad U(t)_I = \mathbf{1} - \frac{i}{\hbar} \int_0^t V(\tau)_I d\tau \quad (2.73)$$

Inserting this relation into (2.72) gives the evolution operator in second-order perturbation theory and higher-order terms can be determined by further iteration.

From (2.72) and (2.73) the corresponding expressions for the Schrödinger picture operator  $U(t)$  can be derived with the help of (2.69).

We now proceed to the equation of motion for the density operator. Applying the unitary transformation (2.62) to the density operator (2.50) in the Schrödinger picture gives

$$\rho(t)_I = \sum_n W_n |\psi(t)_{n,I}\rangle \langle \psi(t)_{n,I}| \quad (2.74)$$

where the density operator in the interaction picture is defined as

$$\rho(t)_I = (e^{(i/\hbar)H_0 t})\rho(t)(e^{-(i/\hbar)H_0 t}) \quad (2.75)$$

Substitution of (2.50) into (2.75) then yields the equation of motion:

- $\rho(t)_I = U(t)_I \rho(0)_I U(t)_I^\dagger \quad (2.76)$

with

$$\rho(0) = \rho(0)_I \quad (2.77)$$

Similarly, substituting

$$\rho(t) = (e^{-(i/\hbar)H_0 t})\rho(t)_I e^{+(i/\hbar)H_0 t} \quad (2.78)$$

into (2.52) gives the *Liouville equation in the interaction picture*:

- $i\hbar \frac{\partial \rho(t)_I}{\partial t} = [V(t)_I, \rho(t)_I] \quad (2.79)$

In order to obtain an approximate solution of (2.79) we first transform it into an integral equation. Formal integration gives

- $\rho(t)_I = \rho(0)_I - \frac{i}{\hbar} \int_0^t [V(\tau)_I, \rho(\tau)_I] d\tau \quad (2.80)$

This integral equation can be solved iteratively in a similar way to (2.72). Suppose, for example, that  $V(t) = 0$  for all times  $t \leq 0$ . The given mixture is then represented in the interaction picture by the time-independent density operator  $\rho(t)_I = \rho(0)_I$ . If at all times  $t > 0$  a perturbation  $V(t)$  is applied, then if  $V(t)$  is small for times  $t > 0$ ,  $\rho(t)_I$  will not change substantially from its initial value  $\rho(0)_I$ .

Thus  $\rho(\tau)_I$  can be replaced in the integral by its initial value  $\rho(0)_I$  and the solution of (2.80) in first-order perturbation theory is obtained as

$$\rho(t)_I = \rho(0)_I - \frac{i}{\hbar} \int_0^t [V(\tau)_I, \rho(0)_I] d\tau \quad (2.81)$$

$\rho(\tau)_I$  can be iterated in this equation as before to give higher-order terms.

The relations derived in this section will be illustrated by our discussions in the following chapters. A more detailed discussion of the various “pictures” used to describe time evolution may be found in any textbook on quantum mechanics.

## 2.5 Spin Precession in a Magnetic Field

As an example of the use of the formalism presented in the preceding sections we will now consider the precession of spin-1/2 particles in a static magnetic field. The components of the magnetic moment of a spin-1/2 particle are given by

$$\mu_i = \frac{1}{2} \gamma \hbar \sigma_i \quad (2.82)$$

( $i = x, y, z$ ), where  $\gamma$  is the gyromagnetic ratio and  $\sigma_i$  denote the Pauli matrices. The interaction between particles possessing the magnetic moment  $\mu_i$  and an external magnetic field  $\mathbf{H}$  is described by the Hamiltonian:

$$H = -\mu \cdot \mathbf{H} = -\frac{1}{2} \gamma \hbar \sum_j \sigma_j H_j \quad (j = x, y, z) \quad (2.83)$$

The polarization vector will change with the time and the density matrix  $\rho$  of the particles will become time dependent. The rate of change of the polarization vector  $\mathbf{P}$  is determined by (2.18), (2.52), and (2.83):

$$\begin{aligned} i \hbar \frac{\partial \langle \sigma_i \rangle}{\partial t} &= i \hbar \frac{\partial}{\partial t} (\text{tr} \rho \cdot \sigma_i) \\ &= i \hbar \text{tr} \left( \frac{\partial \rho}{\partial t} \sigma_i \right) \\ &= \text{tr} \{ [H, \rho(t)] \sigma_i \} \\ &= \text{tr} \{ [\sigma_i, H] \rho(t) \} \\ &= -\frac{1}{2} \gamma \hbar \sum_j H_j \text{tr} \{ [\sigma_i, \sigma_j] \rho(t) \} \end{aligned} \quad (2.84a)$$

where we used that the trace is invariant under cyclic permutations of the operators.

Substitution of expression (1.48) for  $\rho$  into (2.84a) yields

$$i \hbar \frac{\partial \langle \sigma_i \rangle}{\partial t} = -\frac{1}{4} \gamma \hbar \sum_j H_j \left( \text{tr} [\sigma_i, \sigma_j] + \sum_k P_k \text{tr} ([\sigma_i, \sigma_j] \sigma_k) \right) \quad (2.85)$$

Application of (1.45a) gives

$$\text{tr} [\sigma_i, \sigma_j] = 0$$

and of (1.45b)

$$\text{tr} ([\sigma_i, \sigma_j] \sigma_k) = 4i \epsilon_{ijk}$$

because of the antisymmetry of the tensor  $\epsilon_{ijk}$  [see (1.42)]. Inserting these results into (2.85) gives

$$\frac{d\langle\sigma_i\rangle}{dt} = -\gamma \sum_{jk} H_j P_k \epsilon_{ijk} \quad (2.86)$$

For example, for the component  $P_x$  from (1.42) and (2.86),

$$\frac{dP_x}{dt} = -\gamma(H_y P_z - H_z P_y) = +\gamma(\mathbf{P} \times \mathbf{H})_x \quad (2.87a)$$

where the subscript denotes the  $x$  component of the vector product of  $\mathbf{P}$  and the field  $\mathbf{H}$ . In vector notation (2.86) can be written as

$$\frac{d\mathbf{P}}{dt} = \gamma(\mathbf{P} + \mathbf{H}) \quad (2.88)$$

Note that (2.88) is just the classical equation for the precession of the vector  $\mathbf{P}$  around the direction of the field.

The derivation of (2.88) is a good example of the use of the basic (2.18) and (2.52) in deriving the equations of motion. It also illustrates the considerable ease with which this calculation can be performed through the use of the compact expression (1.48) for the density matrix and the subsequent use of the algebraic properties of the Pauli matrices expressed by (1.41). Equation 2.88 can also be derived without using density matrix techniques but the calculation is then considerably more tedious.

## 2.6 Systems in Thermal Equilibrium

A very important application of the density matrix is the one to a dynamical system which is in thermal equilibrium with the surrounding medium. It is shown in quantum statistical mechanics that the state of a system at temperature  $T$  can be represented by the density operator

$$\rho = \exp(-\beta H)/Z \quad (2.89)$$

where  $\beta = 1/kT$  and  $k$  is the Boltzmann constant. The partition function

$$Z = \text{tr } \exp(-\beta H) \quad (2.90)$$

ensures that the normalization condition

$$\text{tr } \rho = 1 \quad (2.91)$$

is satisfied. Equation 2.89 holds for a canonical ensemble, that is, a system with a constant volume, a constant number of particles, and a given mean value  $\langle H \rangle$  of the Hamiltonian.

The density operator (2.89) plays the same role in quantum statistics as the canonical distribution function in classical statistical mechanics. This equivalence can be shown by considering the energy representation,  $H|n\rangle = E_n|n\rangle$  in which the density matrix elements are given by

$$\langle n'|\rho|n\rangle = [\exp(-\beta E_n)/Z]\delta_{n'n} \quad (2.92)$$

The diagonal elements  $\langle n|\rho|n\rangle$  give the probability of finding the system in the state with energy  $E_n$ , respectively. Hence a system in thermal equilibrium is represented by an incoherent sum of energy eigenstates  $n$  with statistical weights proportional to the Boltzmann factor  $\exp(-\beta E_n)$ .

The expectation values  $\langle Q \rangle$  of an operator  $Q$  acting on the system is given by

$$Q = (1/Z) \operatorname{tr} [Q \exp(-\beta H)] \quad (2.93)$$

which follows from (2.18).

Equations 2.89 and 2.92 will be applied in Chap. 8. Here we will illustrate these equations with a simple example. Consider a system of spin-1/2 particles subjected to a static magnetic field  $H_z$  in the  $z$  direction. The Hamiltonian is given by (2.83):

$$H = -\boldsymbol{\mu} \cdot \mathbf{H} = -\gamma\hbar H_z \sigma_z/2$$

The macroscopic magnetization  $\mathbf{M}$  of the system is defined as

$$M_i = N\gamma\hbar\langle\sigma_i\rangle/2 \quad (2.94)$$

where  $N$  is the number of particles per unit volume. Under thermal equilibrium the density matrix is diagonal and the magnetic substates will be populated according to the Boltzmann distribution (2.92). Hence  $M_x = M_y = 0$  and

$$M_z = N\gamma\hbar \operatorname{tr} [\exp(-\beta H)\sigma_z]/2Z \quad (2.95)$$

Suppose that the temperature is sufficiently high to justify setting  $\exp(-\beta H) \approx 1 - \beta H = 1 + \beta\gamma\hbar H_z \sigma_z/2$  and using  $\operatorname{tr} \sigma_z = 0$  and  $\operatorname{tr} \sigma_z^2 = 2$  we obtain

$$M_z = N\beta\gamma^2\hbar^2 H_z/2Z$$

From (2.90)

$$Z = \sum_m \langle m | \exp(-\beta H) | m \rangle \approx 2 \quad (2.96)$$

in the high-temperature limit, and finally

$$M_z = N\beta\gamma^2\hbar^2 H_z/4 \quad (2.97)$$

which is the Curie law for the magnetization of spin-1/2 particles.

# Chapter 3

## Coupled Systems

### 3.1 The Nonseparability of Quantum Systems after an Interaction

In Chap. 2 the basic equations of motion, (2.50) and the Liouville equation (2.52), were derived and applied to the description of interactions between a quantum system and an external *classical* field. In this chapter we will consider the problem of describing the state of a quantum system which is interacting with other (detected or undetected) *quantum* systems. This is an important topic and is of central importance to the following discussions in this book. The quantum mechanical theorems which will be introduced provide the basis for the understanding of phenomena such as quantum beats, angular correlations, and spin-depolarization effects. In Sects. 3.1 and 3.2 we will describe the general theory which is required and in Sects. 3.3, and 3.4, and 3.5 we will give specific examples which illustrate the meaning and application of the theorems.

To begin with consider the following situation. Two separated, noninteracting systems of particles are brought together and allowed to interact with each other. We will consider the problem of analyzing the final state of the system when the constituent systems are again separated and have ceased to interact. An example of the kind of process for which this would be relevant would be the scattering of two particle beams, for example, electrons and atoms. We will denote the two subsystems by the symbols  $\Phi$  and  $\varphi$ , respectively. A complete set of orthogonal state vectors  $|\phi_i\rangle$  can be chosen to describe the  $\Phi$  system, so that any state of the system can be written as a linear superposition of the basis states  $|\Phi_i\rangle$ . Similarly, a set of basis states  $|\varphi_j\rangle$  can be chosen to describe the  $\varphi$  system. The indices  $i$  and  $j$  refer to the set of quantum numbers which are necessary to completely specify each system. If before the interaction the two separated systems were in *pure* states represented by the vectors  $|\Phi_\alpha\rangle$  and  $|\varphi_\beta\rangle$ , respectively (these need not necessarily be members of the chosen basis sets), then the state of the combined systems prior

to the interaction is represented by a well-defined state vector  $|\psi_{\text{in}}\rangle = |\Phi_\alpha\rangle|\varphi_\beta\rangle$  in the composite space (see Appendix A.1).

During the interaction the time development of the state vector  $|\psi_{\text{in}}\rangle$  is determined by the relevant time evolution operator which is a *linear* operator in the *composite* space. Since linear operators transform a *single* state vector into another *single* state vector, the initial pure state  $|\psi_{\text{in}}\rangle$  must evolve such that the final state of the *combined system* can also be represented by a single state vector which will be denoted by  $|\psi(\alpha\beta)_{\text{out}}\rangle$ :

$$|\psi_{\text{in}}\rangle = |\Phi_\alpha\rangle|\varphi_\beta\rangle \rightarrow |\psi(\alpha\beta)_{\text{out}}\rangle \quad (3.1a)$$

where the arrow symbolizes the effect of the time evolution operator. The state  $|\psi(\alpha\beta)_{\text{out}}\rangle$  depends on the variables of both subsystems. This can be seen explicitly by expanding  $|\psi(\alpha\beta)_{\text{out}}\rangle$  in terms of basis states  $|\Phi_i\rangle|\varphi_j\rangle = |\phi_i\varphi_j\rangle$  of the uncoupled systems:

$$|\psi(\alpha\beta)_{\text{out}}\rangle = \sum_{ij} \alpha(ij, \alpha\beta) |\Phi_i\rangle|\varphi_j\rangle \quad (3.1b)$$

where the sum may include integrals over continuous variables.

The coefficient  $a(ij, \alpha\beta)$  is the probability amplitude for a transition  $|\Phi_\alpha\rangle|\varphi_\beta\rangle \rightarrow |\Phi_i\rangle|\varphi_j\rangle$  so that the absolute square  $|a(ij, \alpha\beta)|^2$  gives the probability of finding a particle of the  $\Phi$  system in the state  $|\Phi_i\rangle$  and simultaneously a particle of the  $\varphi$  system in the state  $|\varphi_j\rangle$  after the interaction. Only those combinations  $|\Phi_i\rangle|\varphi_j\rangle$  which are allowed by the conservation laws will contribute to the expansion (3.1b). In other words, a particular final state  $|\Phi_i\rangle$  is correlated to one (or several) final states  $|\varphi_j\rangle$  in such a way that all the relevant conservation laws are fulfilled.

In general, the sum in (3.1b) contains more than one term. The essential point is that the amplitudes depend on the variables of *both* subsystems. Consequently, it is not possible to write (3.1b) in the form  $|\psi_{\text{out}}\rangle = |\Phi\rangle|\varphi\rangle$ , where  $|\Phi\rangle$  is a state vector depending *solely* on the variables of the  $\Phi$  system and  $|\varphi\rangle$  is a state vector depending *solely* on the variables of the  $\varphi$  system. In fact, such a separation of this kind would destroy the correlations which necessarily exist between the two component systems.

In order to clarify this point consider the case in which the two systems have not interacted at all. In this case the probability of finding the  $\Phi$  system in a state  $|\phi_i\rangle$  and the  $\varphi$  system in a state  $|\varphi_j\rangle$  are independent of each other and the amplitudes can be factorized as  $a(ij, \alpha\beta) = a(i, \alpha)a(j, \beta)$  (see Appendix A.1). Substituting this into (3.1b) then yields

$$|\psi(\alpha\beta)_{\text{out}}\rangle = \left( \sum_i a(i, \alpha) |\phi_i\rangle \right) \left( \sum_j a(j, \beta) |\varphi_j\rangle \right) \quad (3.2a)$$

$$= |\Phi\rangle|\varphi\rangle \quad (3.2b)$$

where  $|\Phi\rangle$  and  $|\varphi\rangle$  are defined by the first and second factors in (3.2a), respectively. In this case  $|\Phi\rangle$  depends only on the variables of the  $\Phi$  system, and  $|\varphi\rangle$  depends only on the variables of the  $\varphi$  system. In general, however, once the two systems have interacted in the past, the probability amplitudes are correlated and cannot be factorized. These results can be summarized as follows:

- If two systems have interacted in the past it is, in general, not possible to assign a single state vector to either of the two subsystems.

This is the essence of what is sometimes called the *principle of nonseparability* (d'Espagnat 1976). We have shown that this principle is a direct consequence of the general rules of quantum mechanics. It should be noted that this principle has important conceptional implications and is the source of many discussions on the interpretation of quantum mechanics culminating, perhaps, in the famous Einstein–Rosen–Podolsky argument (see, for example, d'Espagnat 1976; Jammer 1974). An important consequence of this principle is the following. Suppose that only one of the systems, the  $\varphi$  system, is observed after the interaction. Although both systems were initially in pure states the interaction produces correlations between the two systems and, hence, at a later time  $\varphi$  will be found in a mixed state. Thus *the nonobservation of the  $\Phi$  system results in a loss of coherence in the  $\varphi$  system*. This important result of the principle of nonseparability will be illustrated by various examples in Sects. 3.3 and 3.4, where coherence only between degenerate states will be discussed. The more general case of coherently excited states with different energies, which have been excited coherently, requires a more detailed discussion of the time evolution of the system and will be considered in Chap. 5.

## 3.2 Interaction with an Unobserved System. The Reduced Density Matrix

Consider two (or more) interacting quantal systems. In many cases only one of the component systems is of interest and the others are left undetected. We will denote the states of the system of interest by  $|\varphi_j\rangle$ , the states of the undetected systems collectively by  $|\Phi_i\rangle$ , and the elements of the density matrix  $\rho(t)$  describing the total system at time  $t$ , by  $|\Phi_{i'}\varphi_{j'}|\rho(t)|\Phi_i\varphi_j\rangle$ . It was shown in the preceding section that, because of the interaction, the  $\varphi$  system is in a mixed state. It is therefore necessary to consider how the relevant density matrix  $\rho(\varphi, t)$  which characterizes the system of interest alone, can be constructed.

Consider an operator  $Q(\varphi)$  which acts only on the variables of the  $\varphi$  system, that is, its matrix elements are given by

$$\langle\Phi_{i'}\varphi_{j'}|Q(\varphi)|\Phi_i\varphi_j\rangle = \langle\varphi_{j'}|Q(\varphi)|\varphi_j\rangle\delta_{i'i} \quad (3.3)$$

where orthogonality of the states  $|\phi_i\rangle$  has been assumed. The expectation value  $\langle Q(\varphi) \rangle$  is found using (2.18) and (3.3):

$$\begin{aligned}
 \langle Q(\varphi, t) \rangle &= \text{tr } \rho(t) Q(\varphi) \\
 &= \sum_{i'j'j} \langle \Phi_{i'} \varphi_{j'} | \rho(t) | \Phi_i \varphi_j \rangle \langle \Phi_i \varphi_j | Q(\varphi) | \Phi_{i'} \varphi_{j'} \rangle \\
 &= \sum_{j'j} \left[ \sum_i \langle \Phi_i \varphi_{j'} | \rho(t) | \Phi_i \varphi_j \rangle \right] \langle \varphi_j | Q(\varphi) | \varphi_{j'} \rangle
 \end{aligned} \tag{3.4}$$

Defining the elements of a matrix  $\rho(\varphi, t)$  by

- $\langle \varphi_{j'} | \rho(\varphi, t) | \varphi_j \rangle = \sum_i \langle \Phi_i \varphi_{j'} | \rho(t) | \Phi_i \varphi_j \rangle$

Equation 3.4 can be written in the form

- $$\begin{aligned}
 \langle Q(\varphi, t) \rangle &= \sum_{j'j} \langle \varphi_{j'} | \rho(\varphi, t) | \varphi_j \rangle \langle \varphi_j | Q(\varphi) | \varphi_{j'} \rangle \\
 &= \text{tr } \rho(\varphi, t) Q(\varphi)
 \end{aligned}
 \tag{3.6}$$

which is of the form of (2.18).

All information on the  $\varphi$  system can be expressed in terms of expectation values  $\langle Q(\varphi, t) \rangle$  of as many operators as necessary. It follows from (3.6) that any of these expectation values can be calculated once  $\rho(\varphi, t)$  is known. *In this sense  $\rho(\varphi, t)$  contains all information on the  $\varphi$  system.*

$\rho(\varphi, t)$  is usually called the *reduced density matrix*. As is shown by (3.5) it is obtained by taking those matrix elements of the total density matrix  $\rho(t)$  which are diagonal in the unobserved variable  $i$ , and summing these elements over all  $i$ . In this way all nonessential indices can be eliminated. In essence, the total density matrix  $\rho(t)$  is calculated and then projected onto the subspace of interest. This is a most useful property of the density matrix and considerable use of it will be made in the rest of this book.

For convenience we will introduce the shorthand notation

$$\text{tr}_\Phi \rho(t) = \sum_i \langle \Phi_i | \rho(t) | \Phi_i \rangle$$

where  $\text{tr}_\Phi$  is the trace over all unobserved variables. Equation 3.5 can then be written in the form

$$\begin{aligned}
 \langle \varphi_{j'} | \rho(\rho, t) | \varphi_j \rangle &= \left\langle \varphi_{j'} \left| \left[ \sum_i \langle \phi_i | \rho(t) | \Phi_i \rangle \right] \right| \varphi_j \right\rangle \\
 &= \langle \varphi_{j'} | \text{tr}_\Phi \rho(t) | \varphi_j \rangle
 \end{aligned}$$

or in operator notation

- $\rho(\varphi, t) = \text{tr}_\Phi \rho(t)$  (3.7)

A quantum mechanical system which is *closed*, or isolated from the rest of the world, has a “Hamiltonian” evolution, that is, there exists a time-independent Hamiltonian  $H$  and a unitary operator  $U(t) = \exp(-iHt/\hbar)$  such that the temporal evolution of the system is given by the unitary transform (2.51a) or, alternatively, by the Liouville equation (2.52). Under such an evolution a pure state is always transformed into another pure state so that mixtures can neither be created nor destroyed.

Consider now the interaction between a quantum system and external “classical” forces. The term *classical* means that the reaction of the system back on the source of the fields can be neglected. Examples are semiclassical radiation theories or the theory of potential scattering where the influence of the target on the projectile particles is approximated by a potential function. The time evolution of the quantum system is described by a unitary operator  $U(t)$  and the system obeys the Liouville equation (or the Schrödinger equation in the case of a pure state). For time-dependent external forces the observables, in particular the Hamiltonian, will depend explicitly upon the time discussed in Sect. 2.4.

When the reaction of a quantum system ( $\varphi$ ) back to the external world ( $\Phi$ ) cannot be neglected one can enlarge the  $\varphi$  system by  $\Phi$  so that the combined system is closed and has a Hamiltonian evolution. Often  $\Phi$  is undetected. In this case we will refer to  $\varphi$  as an *open* quantum mechanical system. The dynamical evolution of such an open system is fundamentally different from that of a closed one. In particular, as discussed in Sect. 3.1, the  $\varphi$  system will be found in a mixed state after an interaction with an unobserved quantum system even if before the interaction the component systems were in pure states. Hence

- The time evolution of an open quantum mechanical system cannot be described by the Liouville equation (or the Schrödinger equation).

In other words, the relevant reduced density matrix  $\rho(\varphi, t)$  is not expressible as the unitary transform of a density matrix  $\rho(\varphi, 0)$  at an earlier instant of time  $t = 0$ . This is an important difference between open systems and systems which are closed, or which can be described semiclassically. (This difference has played an important role, for example, in recent discussions on the validity of “neoclassical” radiation theories. For details we refer particularly to the paper by [Chow et al. \(1975\)](#).)

The starting point for the discussion of the time variations of open systems is the Liouville equation for the corresponding “enlarged” system which includes all interacting systems. Suppose, for example, that a closed system can be divided into two interacting quantum systems  $\varphi$  and  $\Phi$ . The combined system is described by a Hamiltonian  $H$  which consists of three parts:

$$H = H(\varphi)_0 + H(\Phi)_0 + V(\varphi, \Phi)$$

referring to the free motion of the systems and the interaction between  $\varphi$  and  $\Phi$ , respectively. We assume that only  $\varphi$  is experimentally relevant and  $\Phi$  undetected. Because of the interaction term  $V$ , which couples  $\varphi$  and  $\Phi$ , no Hamiltonian exists describing the dynamics of the  $\varphi$  system alone. The time evolution of the reduced density matrix  $\rho(\varphi, t)$  is obtained by taking the partial trace  $\text{tr}_\Phi$  on both sides of (2.50) and using (3.7):

$$\bullet \quad \rho(\varphi, t) = \text{tr}_\Phi U(t)\rho(0)U(t)^\dagger \quad (3.8a)$$

or, from (2.52),

$$\dot{\rho}(\varphi, t) = -\frac{i}{\hbar} \text{tr}_\Phi [H, \rho(t)] \quad (3.8b)$$

where  $\rho(t)$  and  $U(t)$  are operators of the closed systems and  $H$  is time independent.

It should be noted that the variation in time of the combined system is *reversible* inasmuch as the initial state  $\rho(0)$  can be obtained mathematically from  $\rho(t)$  by the inverse transformation  $\exp(iHt/\hbar) \cdot \rho(t) \exp(-iHt/\hbar)$ . Open systems, however, will frequently show an *irreversible* behavior. This is a consequence of the interaction with unobserved systems (for example, a “heat bath”), which is expressed formally by the sum over all unobserved variables in (3.8). The process of taking the trace provides a fundamental quantum mechanical source of irreversibility. We will discuss this in detail in Chap. 8.

The abstract results obtained in this and the preceding section deserve considerable illustration and interpretation. The remainder of this chapter will be devoted to this task where we will concentrate on some simple examples. Equations 3.8 will then be developed and further applied in the following chapters.

In conclusion, in this and the preceding section we have considered situations where we are confronted with coupled quantum mechanical systems only one of which ( $\varphi$ ) is of experimental relevance. It is then economic to look for a description of  $\varphi$  alone. We have shown that, in general, no state vector exists which describes the dynamical behavior of a subsystem coupled with other quantum systems. *Hence an open system must be characterized in terms of its reduced density matrix.* In principle, all physical systems are interrelated since it is never possible to completely isolate a system. The conventional framework of quantum mechanics in terms of state vectors is therefore always an idealization.

We have then considered the time evolution of an open quantum mechanical system under the influence of its surroundings. The theory has to be based upon the Liouville equation which gives a complete microscopic description of closed systems. By constructing the relevant reduced density matrix, that is, by eliminating all unobserved variables, an equation describing the dynamical behavior of an open system can be obtained.

The results obtained in Sects. 3.1 and 3.2 are of fundamental importance in the quantum theory of measurement. We will not discuss here this interesting but highly controversial field of modern physics. The reader is referred, for example, to d’Espagnat (1976) and the references cited therein. As an introduction we recommend Jauch (1973).

### 3.3 Analysis of Light Emitted by Atoms (Nuclei)

#### 3.3.1 The Coherence Properties of the Polarization States

In order to illustrate the theory which has been developed in the preceding sections we will consider the decay of an ensemble of excited atoms (or nuclei) by photon emission. In particular, we will study the coherence which exists between states of different *polarization*.

To begin with consider an ensemble of excited atoms in identical states represented by the state vector  $|\alpha_0 J_0 M_0\rangle$ , where  $J_0$  and  $M_0$  denote the atomic angular momentum and its  $z$  component and  $\alpha_0$  collectively describes all other variables which are necessary for a complete specification of the states. In order to analyze the final combined state of atoms and photons we will use the procedure outlined in Sect. 3.1. The initial state is pure and hence it is possible to assign a single state vector  $|\psi_{\text{out}}\rangle$  to the combined atom-photon system:

$$|\psi_{\text{in}}\rangle = |\alpha_0 J_0 M_0\rangle \rightarrow |\psi_{\text{out}}\rangle$$

where  $|\psi_{\text{out}}\rangle$  can be expanded in terms of a set of basis states  $|\alpha_1 J_1 M_1\rangle$  and  $|\omega_1 \mathbf{n}_1 \lambda_1\rangle$  characterizing the final atoms and photons, respectively.

The number of possible combinations  $|\alpha_1 J_1 M_1\rangle |\omega_1 \mathbf{n}_1 \lambda_1\rangle$  of final states is restricted by the relevant conservation laws (conservation of energy and angular momentum).  $|\psi_{\text{out}}\rangle$  is then obtained by multiplying all the allowed combinations  $|\alpha_1 J_1 M_1\rangle |\omega_1 \mathbf{n}_1 \lambda_1\rangle$  with the corresponding transition amplitudes and summing (integrating) over all discrete (continuous) variables.

The conditions which prevail in a given experiment will select a particular set of states from all the states which contribute to the expansion of  $|\psi_{\text{out}}\rangle$ . For the sake of simplicity we will assume that the photon detector can be tuned to accept only photons with a single frequency, say,  $\omega_1 = \omega'_1$ . In addition, the position of the photon detector determines the direction,  $\mathbf{n}_1 = \mathbf{n}'_1$ . The observation is therefore restricted to photons with sharp frequency  $\omega'_1$  detected in the direction  $\mathbf{n}'_1$ .

Since the observed photons have a fixed energy, the atoms which have emitted these photons have sharp values of  $\alpha_1$  and  $J_1$  (say,  $\alpha'_1$  and  $J'_1$ ) so that energy is conserved:  $E(\alpha'_1 J'_1) = E(\alpha_0 J_0) - h\omega'_1$ . Consequently, the final state vector of interest is given by the expansion

$$|\psi_{\text{out}}\rangle = \sum_{M_1 \lambda_1} a(M_1 \lambda_1, M_0) |\alpha'_1 J'_1 M_1\rangle |\omega'_1 \mathbf{n}'_1 \lambda_1\rangle \quad (3.9)$$

If no polarization measurements are performed on the photons the quantum numbers  $M_1$  and  $\lambda_1$  remain undefined and (3.9) shows that the sum over these undetected variables must be taken. The coefficients  $a(M_1 \lambda_1, M_0)$  are the probability amplitudes for the corresponding transition  $|\alpha_0 J_0 M_0\rangle \rightarrow |\alpha'_1 J'_1 M_1\rangle |\omega'_1 \mathbf{n}'_1 \lambda_1\rangle$ ,

and the absolute square  $|a(M_1\lambda_1, M_0)|^2$  gives the probability of finding an atom in the final state  $|\alpha'_1 J'_1 M_1\rangle$  when a photon in the state  $|\omega'_1 \mathbf{n}'_1 \lambda_1\rangle$  has been detected. Henceforth the dependence of the states on all fixed variables will be suppressed.

It should be noted that the state vector (3.9) describes only a subensemble of atoms and photons, namely, only those photons registered by the detector with sharp  $\omega'_1$  and  $\mathbf{n}'_1$  and only those atoms which have emitted the detected photons.

Let us consider the polarization state of the photons. Equation 3.9 can be written as

$$\begin{aligned} |\psi_{\text{out}}\rangle &= \sum_{M_1} |M'_1\rangle \sum_{\lambda_1} a(M_1\lambda_1, M_0) |\lambda_1\rangle \\ &= \sum_{M_1} |M_1\rangle |e(M_1, M_0)\rangle \end{aligned} \quad (3.10)$$

where the state vector

$$|e(M_1, M_0)\rangle = \sum_{\lambda_1} a(M_1\lambda_1, M_0) |\lambda_1\rangle \quad (3.11)$$

describes the polarization state of the subensemble of photons emitted in a transition between states  $|M_0\rangle \rightarrow |M_1\rangle$  (see Fig. 3.1 for a case of dipole radiation). Equation 3.11 states that these photons are in identical polarization states characterized by the state vector  $|e(M_1 M_0)\rangle$ . Thus if the photon detector registers only those photons which have been emitted by atoms in a transition to a single state  $|M_1\rangle$  then the detected photons are in the pure state  $|e(M_1 M_0)\rangle$ . In principle, this can be achieved by filtering the final atoms through a Stern–Gerlach filter which accepts

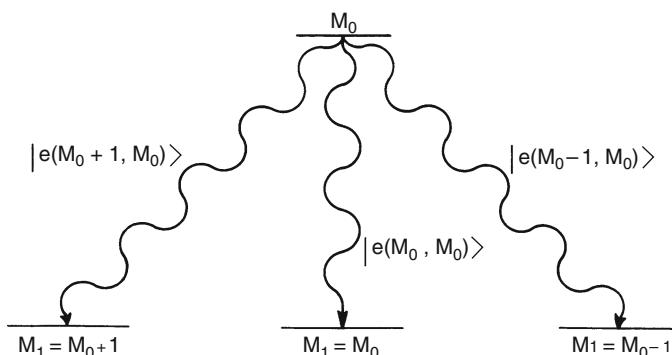


Fig. 3.1 See text for explanations

only atoms with definite magnetic quantum number  $M_1$ . The filtered atoms can then be detected by a counter and the coincidence between this counter and the photon detector observed. The subensemble of photons which are observed in this way is necessarily completely polarized in the sense discussed in Sect. 1.2: The degree of polarization  $P$  has its maximum possible value  $P = 1$ . The actual polarization state is specified by magnitude and relative phase of the two coefficients  $a(M_1\lambda_1, M_0)$  with  $\lambda_1 = +1$  and  $\lambda_1 = -1$  respectively [for example, if  $a(M_1, \lambda_1 = +1, M_0) = -a(M_1\lambda = -1, M_0)$  the photons are linearly polarized in the  $x$  direction as in (1.64a)].

It is important to note that, in general, the detection of completely polarized photons requires that the observation is restricted to a subensemble of photons only. One exception to this is the case where the final atoms have angular momentum  $J_1 = 0$ . Denoting the corresponding state by  $|0\rangle$ , (3.9) can be written in the form

$$|\psi_{\text{out}}\rangle = |0\rangle \left[ \sum_{\lambda_1} a(\lambda_1, M_0) |\lambda_1\rangle \right] \quad (3.12)$$

Since all atoms are in the same final state the corresponding state vector can be separated out to the front of the sum in (3.12). The photon state is then a pure state represented by the bracket in (3.12), and hence in this case *all* photons emitted in the direction  $\mathbf{n}'_1$  are necessarily completely polarized.

### 3.3.2 *Description of the Emitted Photon*

Let us consider the case where emitted photons are detected in direction  $\mathbf{n}'_1$  (frequency  $\omega'_1$ ) with the final atoms unobserved.

The principle of nonseparability requires then that, in general, the state of the detected photons cannot be characterized by a single state vector. Thus the detected radiation is not in a pure polarization state and is necessarily incompletely polarized in the sense that  $P$  is less than 1 (see Sect. 1.2.5). This can be demonstrated by constructing the reduced density matrix  $\rho(\gamma)$  describing the photon-only system. Since the final state of the total system is represented by the state vector  $|\psi_{\text{out}}\rangle$  the corresponding density matrix is simply

$$\begin{aligned} \rho_{\text{out}} &= |\psi_{\text{out}}\rangle \langle \psi_{\text{out}}| \\ &= \sum_{\substack{M'_1 M_1 \\ \lambda'_1 \lambda_1}} a(M'_1 \lambda'_1, M_0) a(M_1, \lambda_1, M_0)^* |M'_1 \lambda'_1\rangle \langle M_1 \lambda_1| \end{aligned}$$

where (3.10) has been used. The elements of the reduced density matrix are then obtained by applying (3.5):

$$\begin{aligned}\langle \lambda'_1 | \rho(\gamma) | \lambda_1 \rangle &= \sum_{M_1} \langle M_1 \lambda'_1 | \rho_{\text{out}} | M_1 \lambda_1 \rangle \\ &= \sum_{M_1} a(M_1 \lambda'_1, M_0) a(M_1 \lambda_1, M_0)^*\end{aligned}\quad (3.13)$$

This matrix corresponds to a density operator given by

$$\begin{aligned}\rho(\gamma) &= \sum_{M_1 \lambda'_1 \lambda_1} a(M_1 \lambda'_1, M_0) a(M_1 \lambda_1, M_0)^* | \lambda'_1 \rangle \langle \lambda_1 | \\ &\quad \sum_{M_1} \left[ \sum_{\lambda'_1} a(M_1 \lambda'_1, M_0) | \lambda'_1 \rangle \right] \left[ \sum_{\lambda_1} a(M_1 \lambda_1, M_0)^* \langle \lambda_1 | \right] \\ &\quad \sum_{M_1} | e(M_1 M_0) \rangle \langle e(M_1 M_0) | \end{aligned}\quad (3.14)$$

Equation 3.14 suggests the following interpretation of the operator  $\rho(\gamma)$ : Photons in different polarization states  $|e(M_1 M_0)\rangle$  can be thought of as being emitted *independently*, so that no definite phase relation exists between photons emitted in transitions to different atomic states. Thus in accordance with the definition given in Sect. 2.3.2, *the photon-only system can be thought of as being an incoherent superposition of states  $|e(M_1 M_0)\rangle$  corresponding to the various transitions*.

Since no definite phase relation exists between photons in the different polarization states these photons can in principle be distinguished (for example, by observing the final atoms in coincidence with the emitted radiation or by using suitably chosen polarization filters). The various polarization states correspond to the different “paths” by which radiation is emitted, as shown diagrammatically by the arrows in Fig. 3.1. The above result is therefore often expressed in the following form: *If it is possible in principle to distinguish between photons taking the different “paths” then the total ensemble of photons can be considered as an incoherent superposition of the corresponding photon states.*

These results can be summarized in the following alternative form, due to [Fano \(1957\)](#):

- Incomplete polarization of light is necessarily associated with an incomplete determination of the final (or initial) atomic state.

It should be noted that this is a direct consequence of the principle of non-separability. The basic result that the photon state is not pure can also be shown by proving that the matrix (3.13) does not satisfy condition (2.21).

The discussion given here is incomplete, since only the decay of excited states with a single quantum number  $M_0$  has been considered. The important case of the excitation of atoms in superposition states with different  $M_0$  and the decay from such superposition states will be considered via a particular example in Sect. 3.4.2.

## 3.4 Some Further Consequences of the Principle of Nonseparability

### 3.4.1 Collisional Spin Depolarization

As a further illustration of the theory presented in Sect. 3.1 we will consider elastic scattering of electrons by spin-1/2 atoms (or of protons or neutrons on nuclei). It will be assumed that initially both the atoms and electrons are completely polarized, for example, in states with definite values of their respective spin components,  $M_0$  and  $m_0$ . All atoms will be assumed to be in their ground state with orbital angular momentum 0, and assumed to be sufficiently heavy to allow their recoil to be neglected. The collision will be described in the rest frame of the atoms. The electrons will be assumed to have been prepared in states with the same momentum  $\mathbf{p}_0$ . The atomic and electronic states can then be denoted by  $|M_0\rangle$  and  $|m_0\rangle$ , respectively. The combined system is represented by the vector  $|\psi_{\text{in}}\rangle = |M_0\rangle|m_0\rangle$  and, since the initial states are pure, the final state of the combined system can be represented by a single-state vector  $|\psi_{\text{out}}\rangle$ . We expand  $|\psi_{\text{out}}\rangle$  in terms of state vectors  $|M_1\rangle$  and  $\langle p_1 m_1 \rangle$  describing the final atomic and electronic states, respectively. For simplicity it will be assumed that the electron detector is tuned to accept only electrons with fixed momentum  $\mathbf{p}_1$  ( $|\mathbf{p}_1| = |\mathbf{p}_0|$ ). The state vector of interest is then given by

$$\begin{aligned} |\psi_{\text{out}}\rangle &= \sum_{M_1 M_1} a(M_1 m_1, M_0 m_0) |M_1\rangle |m_1\rangle \\ &= \sum_{M_1} |M_1\rangle |\chi(M_1)\rangle \end{aligned} \quad (3.15)$$

where  $|m_1\rangle$  implicitly describes the momentum state of the electrons as well as their spins. The two state vectors  $|\chi(M_1)\rangle$  ( $M_1 = \pm 1/2$ ) in (3.15) are given by

$$|\chi(M_1)\rangle = \sum_{m_1} a(M_1 m_1, M_0 m_0) |m_1\rangle \quad (3.16)$$

and describe the state of electrons with fixed momentum  $\mathbf{p}_1$  scattered by atoms which have simultaneously made the transition  $|M_0\rangle \rightarrow |M_1\rangle$ . In order to select a subensemble of the electrons in one of the states  $|\chi(M_1)\rangle$  (say, with  $M_1 = +1/2$ ) it must be ensured that the electron detector registers a scattered electron only when it has interacted with an atom which has undergone the transition  $|M_0\rangle \rightarrow |M_1\rangle$ . (See the discussion in Sect. 3.3.1.) Since these electrons are in a pure state they are necessarily completely polarized as demonstrated in Sect. 1.1. The direction of the new polarization vector with respect to the initial direction depends on the magnitudes and relative phase of the amplitudes  $a(M_1 m_1, M_0, m_0)$ , which in turn depends on the dynamics of the scattering process.

The situation is particularly simple in the case of scattering by a spinless target. If the corresponding atomic state is denoted by  $|0\rangle$  then this state will remain unchanged during the collision and it can be placed in front of the sum in (3.15):

$$|\psi_{\text{out}}\rangle = |0\rangle [\sum_{m_1} a(m_1, m_0) |m_1\rangle] = |0\rangle \chi \quad (3.17)$$

where  $|\chi\rangle$  is defined by the bracket in (3.17). Evidently, as shown by (3.17), the electrons are in a pure polarization state. Consequently, in elastic scattering processes on a spinless target the electrons observed in a fixed direction with fixed energy will be completely polarized if the initial state was pure. No depolarization is possible and only the direction of the polarization vector will change.

In the general case (3.15) the spin state of the detected electrons is not pure but a mixture of the two states  $|\chi(M_1)\rangle$  if the final atoms are not observed. Consequently, the observed electrons are necessarily depolarized:  $|P| < 1$ . This can be shown by using the method described in Sect. 3.3. The reduced density matrix  $\rho(e)$  of the detected electrons is given by

$$\langle m'_1 | \rho(e) | m_1 \rangle = \sum_{M_1} a(M_1 m'_1, M_0 m_0) a(M_1 m_1, M_0 m_0)^* \quad (3.18)$$

With this we may associate the density operator

$$\begin{aligned} \rho(e) &= \sum_{M_1 m'_1 m_1} a(M_1 m'_1, M_0 m_0) a(M_1 m_1, M_0 m_0)^* |m'_1\rangle \langle m_1| \\ &= \sum_{M_1} |\chi(M_1)\rangle \langle \chi(M_1)| \end{aligned} \quad (3.19)$$

It follows that the electronic state can be thought of as being an incoherent superposition of the states  $|\chi(+1/2)\rangle$  and  $|\chi(-1/2)\rangle$ . *The depolarization of the electrons (which were originally in a pure state) is therefore necessarily associated with an incomplete determination of the atomic state after (or before) the collision.* (For a more complete treatment see Sect. 3.5.1.)

### 3.4.2 “Complete Coherence” in Atomic Excitation

As a second example we will consider the excitation of helium atoms from their ground state  $|0\rangle$  to the  ${}^1P$  state by electron impact. Spin-orbit interaction can be neglected in this case, and because the initial and final atoms are spinless the transition amplitudes are spin independent (this will be shown for the general case in Sect. 3.5). It follows that the electronic spin has no influence on the excitation process and can be neglected. Assuming that the initial electrons have definite

momentum  $\mathbf{p}_0$  we separate orbital and spin part of the initial state vector and write  $|\mathbf{p}_0 m_0\rangle = |\mathbf{p}_0\rangle |m_0\rangle$  and, if the spin state is not pure, the initial density matrix  $\rho$ :

$$\rho = |\mathbf{p}_0\rangle \langle \mathbf{p}_0| \rho_{\text{spin}} \quad (3.20)$$

and neglect the spin components.

The relevant initial state vector is then given by  $|\psi_{\text{in}}\rangle = |0\rangle |\mathbf{p}_0\rangle$ . Detecting scattered electrons with momentum  $\mathbf{P}_1$  the final state vector of interest is given by

$$|\Psi\rangle = \left[ \sum_M a(M \mathbf{P}_1, \mathbf{p}_0) |M\rangle \right] |\mathbf{P}_1\rangle = |\psi(\mathbf{P}_1)|\mathbf{P}_1\rangle \quad (3.21)$$

where  $M$  denotes the final atomic state of magnetic quantum number  $M$ . Equation 3.21 shows that it is possible to select an ensemble of atoms which are in *identical states*  $|\psi(\mathbf{P}_1)\rangle$  defined by the brackets in (3.21), by restricting the observation to electrons with fixed momentum  $P_1$ .

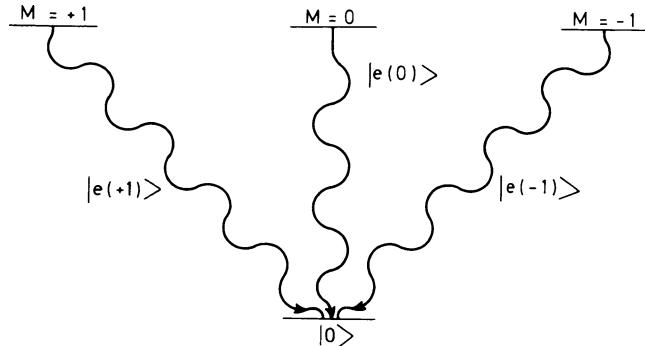
Let us now consider the decay of the excited atoms to the ground state by photon emission with the assumption that excitation and decay can be treated as independent processes. The emitted photons may be observed in a fixed direction  $\mathbf{n}$ . If electrons (with momentum  $\mathbf{p}_1$ ) and photons are detected *in coincidence* then the observation is restricted to radiation emitted by those atoms only which are in one and the same state  $|\psi(\mathbf{p}_1)\rangle$ . The detected photons have therefore been emitted in a transition between the same pure states  $|\psi(\mathbf{p}_1)\rangle \rightarrow |0\rangle$ . As a result, the photons which are detected in the coincidence experiment are necessarily completely polarized.

Unlike the case discussed in Sect. 3.3 the excited atomic state considered here has no well-defined magnetic quantum number. This, however, is not important for our conclusions. The essential point is that the atoms before and after the excitation are in *identical* states. This guarantees that the detected photons are completely polarized. This can also be shown formally for the state given by (3.21) as follows. The radiative decay from a substate  $|M\rangle$  to the ground state  $|0\rangle$  is described in a way similar to (3.12):

$$|M\rangle \rightarrow |0\rangle \sum_{\lambda} a(\lambda, M) |\lambda\rangle \quad (3.22)$$

suppressing the dependence of the photon state on the direction  $\mathbf{n}$ . In order to obtain the state of the photons emitted in the transition  $|\psi(\mathbf{p}_1)\rangle \rightarrow |0\rangle$  (3.22) must be multiplied by the amplitude  $a(M, \mathbf{p}_1, p_0)$  and summed over all  $M$  as in (3.21):

$$\begin{aligned} |\psi_{\text{out}}\rangle &= |0\rangle \sum_{M\lambda} a(M \mathbf{p}_1, \mathbf{p}_0) a(\lambda, M) |\lambda\rangle \\ &= |0\rangle \sum_M |e(M)\rangle \end{aligned} \quad (3.23)$$



**Fig. 3.2** See text for explanations

where

$$|e(M)\rangle = \sum_{\lambda} a(M \mathbf{p}_1, \mathbf{p}_0) a(\lambda, M) |\lambda\rangle \quad (3.24)$$

and  $M = \pm 1, 0$ . In (3.24) the state vectors  $|e(M)\rangle$  denote the polarization state of photons emitted in a transition  $|M\rangle \rightarrow |0\rangle$  (see Fig. 3.2) and the coefficients  $a(M, \mathbf{p}_1, \mathbf{p}_0)$  are the probability amplitudes of finding an atom in the state  $|M\rangle$  when the atomic system is in the state characterized by  $|\psi(\mathbf{p}_1)\rangle$ . Equation 3.23 explicitly shows that the total beam of photons detected in a given direction is in a *pure* polarization state represented by the state vector

$$|e\rangle = \sum_M |e(M)\rangle$$

The main result of this section can be summarized as follows: *The complete coherence between the initial states  $|M\rangle$  implies that the photon state is pure* and can therefore be represented by a completely coherent superposition of the states  $|e(M)\rangle$  corresponding to the different transitions shown in Fig. 3.2. The particular case which we have considered is an example of what is called a *transfer of coherence*. We will consider the problem from a more general point of view in Chaps. 5 and 6.

## 3.5 Excitation of Atoms by Electron Impact I

### 3.5.1 The Reduced Density Matrix of the Atomic System

In this section we will consider the excitation of atoms by electron impact in more detail. The main assumption which will be implicit throughout this section is that

all spin-dependent forces can be neglected during the collision. In particular all explicitly spin-dependent interactions between the projectile and the atoms will be neglected so that changes in the spin variables are entirely caused by *electron exchange* processes. In addition, we neglect the fine (and hyperfine) coupling inside the atom during the collision. This spin uncoupling may be understood physically as follows: In the excited atomic states the orbital angular momentum  $\mathbf{L}$  and spin  $\mathbf{S}$  couple under the influence of the fine-structure interaction, and precess around the total angular momentum  $\mathbf{J}$  of the atom. This precession takes place in a time  $t_{LS} \sim 1/\Delta E_{LS}$ , where  $\Delta E_{LS}$  denotes the fine-structure splitting of the relevant level. If the collision time  $t_c$  is much shorter than the spin-orbit precession time then the spin vector will not have time to precess appreciably during the collision and  $\mathbf{L}$  and  $\mathbf{S}$  can be considered to be uncoupled during the collision. The state of the excited atoms immediately after the collision can then be adequately described in the *LS*-coupling scheme. The assumption that  $t_c \ll t_{LS}$  means that the atoms can be considered as *instantaneously* excited (say, at a time  $t = 0$ ) with respect to the much longer spin-orbit precession time (see also Chap. 5 for a more detailed discussion of this point).

Our main interest here is the description of experiments where the scattered electrons (detected in a direction  $\mathbf{n}_1$ ) and the photons, emitted in the subsequent decay of the excited atomic states, are observed *in coincidence*. As discussed in Sect. 3.4.1, the observation is then restricted to radiation emitted by atoms which have been excited by the detected electrons. Thus a subensemble of atoms is “selected” in the experiment, so to speak, and this selection is the essence of the coincidence method. It is the state of this subensemble only which will be considered throughout this section.

Using the assumptions detailed above, the description of the coincidence experiment can be divided into three parts: First of all the characterization of the atomic subensemble of interest immediately after the excitation, secondly, the time evolution of the excited states under the influence of fine (and hyperfine) coupling, and finally the description of the photons observed at a time  $t$ . In this section we will commence a full treatment of the coincidence experiment with a discussion of the first part of the above program.

The atoms are assumed to be initially in their ground state with orbital angular momentum 0 and quantum numbers  $\gamma_0 = \alpha_0 S_0 M_{s_0}$ , where  $S_0$  and  $M_{s_0}$  denote the atomic spin and its third component, respectively, and  $\alpha_0$  describes all other quantum numbers which are necessary for a complete characterization of the state. The initial state of the electrons may be characterized in terms of momentum  $\mathbf{p}_0$  and spin component  $m_0$ . It will be assumed that all atoms have the same sharp values of  $\alpha_0$  and  $S_0$  and the electrons the same momentum. We will use a coordinate system where the  $z$  axis is parallel to  $\mathbf{p}_0$  and the  $x-z$  plane is the scattering plane (“collision system”) where the scattering plane is spanned by  $\mathbf{p}_0$  and  $\mathbf{p}_1$ .

Usually both the atoms and electrons are unpolarized in their initial states. The atomic density operator is then given by (2.24):

$$\rho_A = \frac{1}{2S_0 + 1} \sum_{M_{s_0}} |\alpha_0 S_0 M_{s_0}\rangle \langle \alpha_0 S_0 M_{s_0}| \quad (3.25a)$$

and the initial electrons are characterized in terms of the density operator:

$$\rho_e = \frac{1}{2} \sum |\mathbf{p}_0 m_0\rangle \langle \mathbf{p}_0 m_0| \quad (3.25b)$$

Electrons and atoms are uncorrelated before the interaction begins, and hence the density matrix  $\rho_{\text{in}}$  of the combined system factorizes and can be represented by the direct product

$$\begin{aligned} \rho_{\text{in}} &= \rho \times \rho_e \\ &= \frac{1}{2(2S_0 + 1)} \sum_{M_{s_0}} |\alpha_0 S_0 M_{s_0} \mathbf{p}_0 m_0\rangle \langle \alpha_0 S_0 M_{s_0} \mathbf{p}_0 m_0| \end{aligned} \quad (3.25c)$$

Suppressing the dependence on the fixed variables  $\alpha_0 S_0 \mathbf{p}_0$  we represent the elements of  $\rho_{\text{in}}$  by

$$\langle M'_{S_0} m'_0 | \rho_{\text{in}} | M_{s_0} m_0 \rangle = \frac{1}{2(2S_0 + 1)} \delta_{M_{s_0} M'_{s_0}} \delta_{m'_0 m_0} \quad (3.26)$$

The matrix (3.26) is a  $2(2S_0 + 1)$ -dimensional diagonal matrix in the composite spin space spanned by the  $2(2S_0 + 1)$  basis states  $|M_{s_0}\rangle \equiv |\alpha_0 S_0 M_{s_0}\rangle$  and  $|m_0\rangle \equiv |\mathbf{p}_0 m_0\rangle$ .

Using the assumption that  $t_c \ll t_{LS}$  the excited atomic states immediately after the collision can be described in the  $LS$ -coupling scheme with quantum numbers  $\gamma_1 = \alpha_1 L M S_1 M_{s_1}$ , where  $M$  is the  $z$  component of the orbital angular momentum  $L$ . It will be assumed that only atoms in states with sharp values of  $\alpha_1 L S_1$  are “selected” (experimentally, this can be achieved by resolving the emitted photons spectroscopically). The removal of this restriction will be considered in Chap. 4. In the coincidence experiments performed so far no spin analysis of the final particles has been carried out, and we will therefore restrict the discussion to *the reduced density matrix characterizing the orbital states of the atomic subensemble of interest*.

For the discussion of scattering experiments it is convenient to change the normalization of the density matrix. For this purpose we will characterize a transition between states

$$\Gamma_0 = \gamma_0 \mathbf{p}_0 m_0 \rightarrow \Gamma_1 = \gamma_1 \mathbf{p}_1 m_1 \quad (3.27)$$

in terms of the corresponding *scattering amplitude*  $f(\Gamma_1, \Gamma_0)$ , which is defined as the matrix element of the transition operator  $T$  (see Appendix E.1 for details):

$$f(\Gamma_1, \Gamma_0) = \langle \Gamma_1 | T | \Gamma_0 \rangle \quad (3.28)$$

$f(\Gamma_1 \Gamma_0)$  will be normalized according to the condition

$$|f(\Gamma_1, \Gamma_0)|^2 = \sigma(\Gamma_1, \Gamma_0) \quad (3.29)$$

where  $\sigma(\Gamma_1, \Gamma_0)$  is the differential cross section for the indicated transition. The equations derived in Sects. 3.1 and 3.2 can be transformed to the new normalization by substituting  $f(\Gamma_1, \Gamma_0)$  for the corresponding transition amplitudes  $a(\Gamma_1, \Gamma_0)$  (the absolute square of which gives the probability for the corresponding transition).

Let us denote the final atomic states by  $|\alpha_1 LMS_1 M_{s_1}\rangle \equiv |MM_{s_1}\rangle$  and the state of the final electrons by  $|p_1 m_1\rangle \equiv |m_1\rangle$ . The density matrix  $\rho_{\text{out}}$  is given by (E.5):

- $\rho_{\text{out}} = T \rho_{\text{in}} T^\dagger$

Taking matrix elements between final states and applying twice the completeness relation for the initial states

$$\sum_{M_{s_0} m_0} |M_{s_0} m_0| = 1$$

we obtain

$$\begin{aligned} & \langle M' M'_{s_1} m'_1 | \rho_{\text{out}} | MM_{s_1} m_1 \rangle \\ &= \sum_{\substack{M'_{s_0} m'_0 \\ M'_{s_0} m_0}} \langle M' M'_{s_1} m'_1 | T | (M'_{s_0} m'_0) \langle M'_{s_0} m'_0 | \rho_{\text{in}} | M_{s_0} m_0 \rangle \langle M_{s_0} m_0 | T^\dagger | MM_{s_1} m_1 \rangle \\ &= \frac{1}{2(2S_0 + 1)} \sum_{M_{s_0} m_0} f(M' M'_{s_1} m'_1, M_{s_0} m_0) f(MM_{s_1} m_1, M_{s_0} m_0^*) \quad (3.30) \end{aligned}$$

where (3.26) has been used.

When no spins are observed the density matrix of interest is the reduced density  $\rho(L)$  describing the orbital states of the atoms only. Using (3.5) the elements of this matrix can be obtained by taking the elements of  $\rho_{\text{out}}$  which are diagonal in all the unobserved variables (that is,  $M_{s_1}$  and  $M_1$ ) and summing over these variables:

$$\begin{aligned} \langle M' | \rho(L) | M \rangle &= \sum_{M_{s_1} m_1} \langle M' M'_{s_1} m_1 | \rho_{\text{out}} | MM_{s_1} m_1 \rangle \\ &= \frac{1}{2(2S_0 + 1)} \sum_{M_{s_1} m_1 M_{s_0} m_0} f(M' M_{s_1} m_1, M_{s_0} m_0) f(MM_{s_1} m_1, M_{s_0} m_0)^* \\ &= \langle f(M') f(M)^* \rangle \quad (3.31) \end{aligned}$$

where the notation  $\langle \dots \rangle$  indicates that the averages over the spins have been performed.

The matrix (3.31) is a  $(2L + 1)$ -dimensional matrix containing all information on the orbital system of the excited atomic subensemble of interest. In the normalization (3.29) the diagonal elements of  $\rho$  are given by

$$\begin{aligned} \langle M | \rho(L) | M \rangle &= \frac{1}{2(2S_0 + 1)} \sum_{\substack{M_{s_1} m_1 \\ M_{s_0} m_0}} |f(MM_{s_1}m_1, M_{s_0}m_0)|^2 \\ &= \sigma(M) \end{aligned} \quad (3.32a)$$

where  $\sigma(M)$  denotes the differential cross section for excitation of the magnetic substate  $M$  averaged over all spins. The trace of  $\rho(L)$  gives the differential cross section  $\sigma$  summed over all  $M$ :

$$\text{tr } \rho(L) = \sum_M \sigma(M) = \sigma \quad (3.33)$$

For example, the explicit expression of  $\rho(L)$  for the case  $L = 1$  is

$$\rho(L) = \begin{pmatrix} \sigma(1) & \langle f(+1)f(0)^* \rangle & \langle f(+1)f(-1)^* \rangle \\ \langle f(+1)f(0)^* \rangle^* & \sigma(0) & \langle f(0)f(-1)^* \rangle \\ \langle f(+1)f(-1)^* \rangle^* & \langle f(0)f(-1)^* \rangle^* & \sigma(-1) \end{pmatrix} \quad (3.34)$$

where the hermiticity condition (2.12) has been used:

$$\langle M' | \rho(L) | M \rangle = \langle M | \rho(L) | M' \rangle^* \quad (3.35)$$

Equations 3.31 and 3.34 show that, in general,  $\rho$  has nonvanishing off-diagonal elements and hence that the excited atomic subensemble of interest is a coherent superposition state of magnetic substates.

By determining the angular distribution and polarization of the emitted photons in coincidence with the scattered electrons the density matrix (3.34) can be completely determined (see Sect. 6.1). This allows more information on the scattering processes to be extracted than from traditional experiments where only the differential cross section  $\sigma$  is measured. In particular the off-diagonal elements of  $\rho$  contain information on the phases of the various scattering amplitudes with different  $M$  and these phases cannot be determined without the use of coincident techniques. In order to see how many measurements must be performed for complete determination of  $\rho$  the number of independent parameters specifying  $\rho$  must be determined, which will be done in the following section.

### 3.5.2 Restrictions due to Symmetry Requirements

In addition to the hermiticity condition (3.35) the number of independent parameters describing  $\rho$  is further restricted by certain symmetry conditions. The scattering

plane ( $x - z$  plane of the collision system) is defined by  $\mathbf{p}_0$  and  $\mathbf{p}_1$  but no direction is defined perpendicular to the scattering plane by geometry of the experiment; that is, the atomic subensemble under discussion cannot distinguish between “up” and “down” with respect to this plane. As a result, the density matrix (3.31) must be *invariant under reflection in the scattering plane*.

This symmetry condition is expressed by the relation

$$f(MM_{s_1}m_1, M_{s_0}m_0) = (-1)^{M+S_1-S_0} f(-M - M_{s_1} - m_1, -M_{s_0} - m_0) \quad (3.36a)$$

for the scattering amplitudes and

$$\langle M'|\rho|M\rangle = (-1)^{M'+M} \langle -M'|\rho| - M \rangle \quad (3.36b)$$

for density matrix. [For a proof see the textbooks on scattering theory, for example, [Rodberg and Thaler \(1967\)](#) (3.36b) gives in particular

$$\sigma(M) = \sigma(-M) \quad (3.37a)$$

In case  $L = 1$  combining (3.36b) with the hermiticity condition (3.35) gives

$$\langle f(0)f(-1)^* \rangle = -\langle f(0)f(-1)^* \rangle = -\langle f(1)f(0)^* \rangle^* \quad (3.37b)$$

Furthermore, the element  $\langle f(+1)f(-1)^* \rangle$  is real:

$$\langle f(+1)f(-1)^* \rangle = \langle f(-1)f(+1)^* \rangle = \langle f(-1)f(+1)^* \rangle^* \quad (3.37c)$$

Thus for  $L = 1$  the density matrix becomes

$$\rho(L) = \begin{pmatrix} \sigma(1) & \langle f(+1)f(0)^* \rangle & \langle f(+1)f(-1)^* \rangle \\ \langle f(+1)f(0)^* \rangle^* & \sigma(0) & -\langle f(+1)f(0)^* \rangle^* \\ \langle f(+1)f(-1)^* \rangle^* & -\langle f(+1)f(0)^* \rangle & \sigma(1) \end{pmatrix} \quad (3.38)$$

which is completely specified in terms of *five* real parameters, for example,  $\sigma(1)$ ,  $\sigma(0)$ ,  $\langle f(+1)f(-1)^* \rangle$ , and the real and imaginary parts of  $\langle f(+1)f(0)^* \rangle$ .

A convenient parametrization of the matrix (3.38) has been given by [Hertel and Stoll \(1978\)](#). In this parametrization the four parameters

$$\begin{aligned} \lambda &= \frac{\sigma(0)}{\sigma}, & \cos \chi &= \frac{\text{Re} \langle f(1)f(0)^* \rangle}{[\sigma(0)\sigma(1)]^{1/2}} \\ \sin \Phi &= \frac{\text{Im} \langle f(1)f(0)^* \rangle}{[\sigma(0)\sigma(1)]^{1/2}}, & \cos \alpha &= \frac{\langle f(1)f(-1)^* \rangle}{\sigma(1)} \end{aligned} \quad (3.39)$$

together with the differential cross section (3.33) constitute a set of five independent real parameters.

The number of independent parameters can be further reduced if *spin conservation* is taken explicitly into account. Since all explicit spin-dependent terms have been neglected in the Hamiltonian describing the collision, total spin  $S$  and its  $z$  component  $M_s$  are conserved during the collision; hence

$$S = S_0 \pm \frac{1}{2} = S_1 \pm \frac{1}{2}, \quad M_s = M_{s_1} + m_1 = M_{s_0} + m_0 \quad (3.40)$$

It is shown in textbooks on scattering theory that the dependence of the scattering amplitudes on the spin components can be factored out as

$$f(MM_{s_1}m_1, M_{s_0}m_0) \sum_{SM_s} \left( S_1 M_{s_1}, \frac{1}{2} m_1 \middle| SM_s \right) \left( S_0 M_{s_0}, \frac{1}{2} m_0 \middle| SM_s \right) f(M)^{(s)} \quad (3.41)$$

where,  $F(M)^{(s)}$  denotes the scattering amplitude for excitation of the magnetic substate  $M$  in the channel with total spin  $S$ . Note that the amplitudes  $f(M)^{(s)}$  are independent of all spin components. The brackets in (3.41) denote the standard Clebsch–Gordan coefficients.

Substituting (3.41) into (3.31) and applying the orthonormality properties of the Clebsch–Gordan coefficients gives

$$\langle M' | \rho(L) | M \rangle = \langle f(M') f(M)^* \rangle \quad (3.42)$$

$$= \frac{1}{2(2S_0 + 1)} \sum_s (2S + 1) f(M')^{(s)} f(M)^{(s)*} \quad (3.43)$$

The symmetry condition (3.36a) reduces to

$$f(M)^{(s)} = (-1)^M f(-M)^{(s)} \quad (3.44a)$$

as can be shown using (3.41) and the symmetry properties of the Clebsch–Gordan coefficients after some algebraic manipulations. From this and (3.42) the following additional symmetry condition is obtained:

$$\begin{aligned} \langle M' | \rho(L) | -M \rangle &= \frac{1}{2(2S_0 + 1)} \sum_s (2S + 1) f(M')^{(s)} f(-M)^{(s)*} \\ &= \frac{(-1)^M}{2(2S_0 + 1)} \sum_s (2S + 1) f(M')^{(s)} f(-M)^{(s)*} \\ &= (-1)^M \langle M' | \rho | M \rangle \end{aligned} \quad (3.44b)$$

In the case of  $L = 1$  this gives

$$\cos \alpha = -1$$

so that the density matrix (3.38) is completely specified by four parameters,  $\sigma$ ,  $\lambda$ ,  $\chi$ ,  $\phi$ .

A smaller number of independent parameters is required if initial and final atoms are spinless ( $S_0 = S_1 = 0$ ). In this case only one spin channel with total spin  $S = 1/2$  is allowed and (3.42) reduces to

$$|M'| \rho(L) |M\rangle = f(M') f(M)^* \quad (3.45)$$

No spin average is necessary in this case and the total spin  $S$  can be suppressed in this notation.

The factorization (3.45) of the density matrix elements into two factors, one depending only on  $M'$ , the other one only on  $M$ , is typical of cases where  $\rho$  describes a pure state. In fact, it has been shown in Sect. 3.4.2 that, if  $S_0 = S_1 = 0$ , then the state of the atomic subensemble under discussion is pure and represented by the state vector

$$|\Psi(\mathbf{P}_1)\rangle = \sum_M f(M) |M\rangle \quad (3.46)$$

written as a completely coherent superposition of magnetic substates. In this case the atoms in the subensemble have been identically excited.

Since the amplitudes  $f(M)$  satisfy the symmetry condition (3.44a) (with  $S = 1/2$ ) and since the overall phase of  $|\Psi(\mathbf{P}_1)\rangle$  is arbitrary the state (3.46) is completely specified in terms of  $(2L + 1)$  parameters.

For pure states the density matrix (3.38) must satisfy condition (2.21). When this is applied to the parameters (3.39) this gives for the case  $L = 1$

$$\cos^2 \chi + \sin^2 \phi = 1 \quad (3.47)$$

and the atomic subensemble under discussion can be completely characterized in terms of the three parameters  $\sigma$ ,  $\gamma$ ,  $\chi$ , where  $\chi$  is now the relative phase between the amplitudes  $f(=1)$  and  $f(0)$ .

In conclusion, we have considered experiments where the scattered electrons are detected in a fixed direction with momentum  $\mathbf{p}_1$  and where no spin analysis of initial and final particles is performed. We have constructed the reduced density matrix  $\langle M' | \rho | M \rangle$  characterizing the orbital states of the atomic subensemble excited by the detected electrons. We have in particular considered the case  $L = 1$  as an example and have shown that in this case  $\rho$  is specified in terms of five independent parameters because of the hermiticity condition and reflection invariance in the scattering plane. Using conservation of total spin this number is reduced to four. If (and only if) the atoms have been excited into *identical* states three parameters are sufficient. In this case the distinction between “coherence” (in the sense that  $\rho$  is nondiagonal) and “complete coherence” is important: In the latter case less parameters and, thus, less experiments are necessary for a complete specification of  $\rho$ .

## 3.6 Nonseparability, Entanglement, and Correlations in Two-Particle Spin-1/2 Systems

### 3.6.1 *Introduction and Basic Definitions*

In the previous chapters of this book we have introduced three fundamental concepts of quantum mechanics:

1. The superposition principle and its interpretation (Sects. 1.1 and in particular 1.1.4).
2. The principle of nonseparability (Sect. 3.1) which is the fundamental basis for most derivations in this book.
3. The concept of the reduced density matrix (Sect. 3.2) which allows to describe parts of interacting systems.

In the present section (which can be read immediately after Sects. 1.1, 3.1, and 3.2) we will examine the quantum states of two spin-1/2 particles. We will explore the extraordinary consequences of the principle of nonseparability. Its interpretation is deeply connected with the foundation and even the philosophy of quantum mechanics, and the study of these relationships has lead to many far-reaching conceptual and experimental developments in recent years.

Spin-1/2 systems provide an excellent model system which will allow us to derive the basic properties of entangled pure or mixed states in a transparent way. In addition, the examples to be discussed will give additional insight into the abstract concepts of the previous chapters. The treatment will be kept on an introductory level.

In order to introduce some of the basic notations it will be useful to start with a special example. Consider low energy elastic collisions between polarized electrons and polarized hydrogen atoms, or light alkali atoms. It will be assumed that energies and scattering angle are kept fixed and we will suppress the dependence of state vectors and amplitudes on these variables, concentrating only on the spin components. States with spin up and spin down with respect to a given quantization axis will be denoted by  $|+\rangle$  and  $|-\rangle$ , respectively.

For simplicity it will be assumed that initially both particle beams are completely polarized with opposite spin directions. Under the premise that both beams have been prepared independently the joint initial spin state is given by

$$|\psi_{in}\rangle = |+\rangle|-\rangle = |+-\rangle. \quad (3.48)$$

Here and in the following the spin component in first position will refer to the first beam (say, the free electrons) and the spin in second position will refer to the second beam (atoms). In low energy electron-hydrogen scattering all explicit spin-dependent forces can be neglected in good approximation, so that the total  $z$ -component of the spins is conserved during the collision.

The collision partners will be observed after the scattering, when they have separated and ceased to interact. Because the initial combined state is described by the single state vector  $|\psi_{in}\rangle$ , the linearity of quantum mechanics guarantees that the *total* final state is also characterized in terms of a single state vector

$$|\psi_{in}\rangle \longrightarrow |\psi\rangle,$$

which can be expressed in terms of a conveniently chosen set of basis states (see Sect. 3.1), for example

$$|\psi\rangle = f|+-\rangle + g|-\rangle, \quad (3.49)$$

where the amplitudes depend on the scattering dynamics. A change in spin is only possible when the initially free electron (with spin up) and the initial valence electron (spin down) change their places during the collision. Conservation of the total spin component is taken into account so that only two terms appear in (3.49). We will normalize according to the condition

$$|f|^2 + |g|^2 = 1. \quad (3.49a)$$

Spin states of the general form (3.49) will be our standard example throughout this section. Our discussion has shown one way of how such states can be prepared experimentally. Besides this special example the theory to be developed will be concerned with two interacting spin-1/2 systems in general, for example two beams of spin-1/2 atoms, or of protons and hydrogen atoms as in the experiment by [Lamehi-Racht and Mittig \(1976\)](#) to be discussed below.

As discussed in Sect. 3.1 it is in general not possible to write  $|\psi\rangle$  in product form

$$|\psi\rangle = |\psi_1\rangle|\psi_2\rangle, \quad (3.50)$$

where  $|\psi_1\rangle$  describes completely the spin properties of the first beam, and  $|\psi_2\rangle$  those of the second one. (See also the formal proof in the following subsection.) This result is fundamental and leads to the following

**Definition.** States, which cannot be factorized similar to (3.50) are called nonseparable or *entangled* (*verschränkt* in German) ([Schrödinger 1935](#)).

As the following examples will show it is necessary that both systems have interacted in order to obtain an entangled state.

Examples of entangled states have already been given in Sects. 3.3 and 3.4. Equation 3.9 represents an entangled state where the various eigenstates of the atom are correlated with those of the photon. Equation 3.15 refers to a more general entanglement between the spin states of atoms and electrons.

The history of entangled states goes back to the year 1935 when Schrödinger introduced the concept of *Verschränkung*, and when [Einstein et al. \(1935\)](#) pointed out some of its surprising consequences. The term *entangled* has come into general use in recent years.

Experimentally, spin states like (3.49) can be investigated by measuring the spin polarizations, individually for one beam only, or in coincidence. In principle, polarization measurements can be performed on both beams of scattered particles, with spin analyzers I and II, respectively. The analyzer I, oriented along the direction of unit vector  $\mathbf{a}$ , splits the beam into two sub-beams, with spin up or spin down, respectively, with respect to  $\mathbf{a}$  as quantization axis (see for example the Stern–Gerlach magnet in Fig. 1.1, although more effective analyzers are today available which work also with free electrons). One of the two beams may be blocked as in Fig. 1.1.

Similarly, for the second beam, analyzer II might be set along the direction of unit vector  $\mathbf{b}$ . Each analyzer is followed by a detector, counting and registering the number of particles in the transmitted beams,  $N(\mathbf{a})_+$  and  $N(\mathbf{a})_-$ , and  $N(\mathbf{b})_+$  and  $N(\mathbf{b})_-$ , respectively. Finally, a coincidence counter records the number of coincidences for various settings of the analyzer–detector assemblies as will be discussed below. More details on the experimental arrangements, and also on many results, can be found in [Kessler \(1985\)](#).

We will assume that the intensity of the two beams is arranged to be sufficiently low, and the detectors operate fast enough for the collision pairs to be individually detected (that is, a particle in the first beam is detected in coincidence with that particle in the second beam with which it has interacted).

It will be convenient to introduce a standard notation for vectors and polar angles for use in this section. A right-handed coordinate system might be chosen arbitrarily (For example, in case of initial state (3.48), we will choose the quantization axis of the initial spin states as  $z$ -axis. The  $x$ - and  $y$ -axes are not defined by the initial conditions, and might be chosen conveniently).

The two unit vectors  $\mathbf{a}$  and  $\mathbf{b}$ , introduced above, can be written in the form

$$\mathbf{a} = \mathbf{e}_x \sin \beta \cos \alpha + \mathbf{e}_y \sin \beta \sin \alpha + \mathbf{e}_z \cos \beta, \quad (3.51a)$$

$$\mathbf{b} = \mathbf{e}_x \sin \beta' \cos \alpha' + \mathbf{e}_y \sin \beta' \sin \alpha' + \mathbf{e}_z \cos \beta', \quad (3.51b)$$

where  $\beta$  and  $\beta'$ , and  $\alpha$  and  $\alpha'$  denote polar and azimuthal angles, respectively. The vectors  $\mathbf{e}_i$  denote unit vectors along the corresponding axes ( $i = x, y, z$ ).

### 3.6.2 Two-Particle Density Matrices and Reduced Density Matrices. Criterion for Entanglement

An explicit matrix representation of the two-particle spin density matrix is obtained by taking the states  $|Mm\rangle$  as basis ( $M = \pm 1/2, m = \pm 1/2$  with respect to a given quantization axis):

$$\rho = \begin{pmatrix} \langle + + | \rho | + + \rangle \langle + + | \rho | + - \rangle \langle + + | \rho | - + \rangle \langle + + | \rho | - - \rangle \\ \langle + - | \rho | + + \rangle \langle + - | \rho | + - \rangle \langle + - | \rho | - + \rangle \langle + - | \rho | - - \rangle \\ \langle - + | \rho | + + \rangle \langle - + | \rho | + - \rangle \langle - + | \rho | - + \rangle \langle - + | \rho | - - \rangle \\ \langle - - | \rho | + + \rangle \langle - - | \rho | + - \rangle \langle - - | \rho | - + \rangle \langle - - | \rho | - - \rangle \end{pmatrix}. \quad (3.52)$$

The Hermiticity condition (1.1.29) reads

$$\langle M'm'|\rho|Mm\rangle = \langle Mm|\rho|M'm'\rangle^*. \quad (3.52a)$$

Consider the state (3.49) as a simple example. Its corresponding density operator is given by the expression

$$\begin{aligned} \rho &= |\psi\rangle\langle\psi| \\ &= |f|^2|+-\rangle\langle+-| + fg^*|+-\rangle\langle-+| \\ &\quad + f^*g|-\rangle\langle+-| + |g|^2|-\rangle\langle-+|. \end{aligned} \quad (3.53)$$

In the explicit matrix representation (3.52) we obtain

$$\rho = \begin{pmatrix} 0 & 0 & 0 & 0 \\ 0 & |f|^2 & fg^* & 0 \\ 0 & f^*g & |g|^2 & 0 \\ 0 & 0 & 0 & 0 \end{pmatrix}. \quad (3.54)$$

The diagonal element

$$\langle + - |\rho| + - \rangle = |f|^2$$

gives the probability that a particle in the first beam is found with spin up (with respect to the given quantization axis), and simultaneously a particle in the second beam with spin down. A similar interpretation holds for

$$\langle - + |\rho| - + \rangle = |g|^2.$$

The off-diagonal elements characterize the coherence or correlation properties as will be discussed below. Equation (3.49), or alternatively (3.53) and (3.54), contain the full information on the spin properties of the combined two-particle system.

Assume now that the spin polarization of one subsystem only is measured (say, that of the first beam), and that the spins of the second subsystem remain unobserved. What is the spin state of the first beam after the measurement?

As discussed in Sect. 3.2 it is in general not possible to ascribe a single state vector to one observed system which has interacted with a second one. Both systems remain entangled. One is forced to generalize the concept of the state vector or wave function to that of the reduced density matrix. Its elements are obtained by applying (3.5).

Denoting the spin components of the observed and unobserved subsystem by  $M$  and  $m$ , respectively, we obtain the elements of the reduced density matrix  $\rho_1$ :

$$\langle M'|\rho_1|M\rangle = \sum_m \langle M'm|\rho|Mm\rangle. \quad (3.55)$$

That is, one takes those elements of the full density matrix  $\rho$ , which are diagonal in the unobserved variable  $m$  and sums over all unobserved variables. For our present case of interest we obtain from (3.54) and (3.55):

$$\begin{aligned}\langle +|\rho_1|+\rangle &= \langle + +|\rho| + +\rangle + \langle + -|\rho| + -\rangle \\ &= |f|^2,\end{aligned}$$

since the first element is zero, and

$$\begin{aligned}\langle -|\rho_1|-\rangle &= \langle - +|\rho| - +\rangle + \langle - -|\rho| - -\rangle \\ &= |g|^2.\end{aligned}$$

The off-diagonal elements of  $\rho_1$  vanish. In explicit matrix notation this yields:

$$\rho_1 = \begin{pmatrix} |f|^2 & 0 \\ 0 & |g|^2 \end{pmatrix}. \quad (3.56a)$$

Similarly, we obtain the reduced spin density matrix  $\rho_2$  of the second beam, when the spins of the first beam are not observed:

$$\rho_2 = \begin{pmatrix} |g|^2 & 0 \\ 0 & |f|^2 \end{pmatrix}. \quad (3.56b)$$

The two density matrices are not independent as will be discussed in Sect. 3.6.4.

The components of the corresponding polarization vectors follows from (1.36) and (3.56):

$$P_z^{(1)} = |f|^2 - |g|^2 = -P_z^{(2)}. \quad (3.57)$$

The  $x$ - and  $y$ -components are zero.

The reduced density matrices (3.56) contain the maximal information that can be obtained on the individual subsystems. Nevertheless, it is impossible to reconstruct the original state  $|\psi\rangle$  of the composite system from a knowledge of the reduced density matrices. In the special case of (3.56) this is evident since  $\rho_1$  and  $\rho_2$  contain no information on the coherence which originally existed between both subsystems.  $\rho_1$  and  $\rho_2$  describe statistical mixtures, whereas the combined system is in the pure state (3.49).

The question whether a given state vector factorizes as in (3.50) is often not easy to decide since  $|\psi_1\rangle$  and  $|\psi_2\rangle$  could both be complicated superpositions of certain basis states. An exception are pure bipartite states like (3.49) where density matrix theory provides us with a simple criterion. The necessary information is contained in the reduced density matrices of the two subsystems. The relevant criterion is provided by (1.40) (or more generally by (2.21)). If  $\rho_1$  or  $\rho_2$  satisfy this

condition then the corresponding subsystem is necessarily in a pure state,  $|\psi_1\rangle$  or  $|\psi_2\rangle$ , respectively. The total state vector factorizes and the system is not entangled. Note, that the traces are independent of the chosen basis.

For spin-1/2 systems one can also apply (1.18): The two subsystems are only then both in a pure state if the corresponding polarization vectors  $\mathbf{P}^{(1)}$  and  $\mathbf{P}^{(2)}$  have both magnitude one.

This condition is violated for the two individually measured polarization vectors (3.57). The two subsystems can consequently not be represented in terms of single state vectors, and the combined state (3.49) is not separable but entangled.

Further conditions have been derived in Appendix J.1. We refer in particular to the condition (J.14) which provides a simple test for separability.

For example, consider the state

$$|\psi\rangle = \frac{1}{2}(|++\rangle + |+-\rangle + |-+\rangle + |--\rangle).$$

Comparing with (J.9) we obtain for the coefficients

$$a = b = c = d = \frac{1}{2},$$

from which follows that condition (J.14) is satisfied. Hence,  $|\psi\rangle$  must be factorizable. It is easy to see that  $|\psi\rangle$  can be written in the form

$$|\psi\rangle = |x(+)\rangle|x(+)\rangle,$$

where  $|x(+)\rangle$  is given by (1.13a) (where we have changed the notation  $|+\frac{1}{2}, x\rangle$  to  $|x(+)\rangle$ ).

On the other hand, for the state (3.49) we obtain  $a = d = 0$  and  $b = c = 1/\sqrt{2}$  so that condition (J.14) is violated.

### 3.6.3 Correlation Parameters and Their Interpretation. Joint Probabilities

In Sect. 1.1 it has been shown that the one-particle density matrix is completely characterized by the three components of the polarization vector. In order to achieve a similar complete description of the two-particle spin density matrix knowledge of the two individual polarization vectors  $\mathbf{P}^{(1)}$  and  $\mathbf{P}^{(2)}$  does clearly not suffice.

The most general  $4 \times 4$  density matrix (3.52) has 16 real independent parameters if the Hermiticity condition (3.52a) is taken into account. One parameter is provided by the normalization condition, and six parameters by the components of the individual polarization vectors  $\mathbf{P}^{(1)}$  and  $\mathbf{P}^{(2)}$ . Hence, nine further real parameters are required.

In order to obtain these we have to generalize the concept of polarization vector. We define a set of nine parameters by the expression

$$P_i^{(1)} \times P_j^{(2)} = \text{tr} \rho (\sigma_i \times \sigma_j) = \langle \sigma_i \times \sigma_j \rangle, \quad (3.58)$$

where  $\sigma_i$  and  $\sigma_j$  denote Pauli matrices ( $i, j = x, y, z$ ), and the cross denotes the direct product (see Appendix A.1). The parameters (3.58) are the components of a second-rank tensor, the polarization or correlation tensor.

The general  $4 \times 4$  density matrix (3.52) can be expanded in terms of the components of the polarization vectors and tensor (see Appendix F.1). This expression proves that any two-particle spin-1/2 system can be uniquely defined in terms of this set of observables. An experimental determination of these parameters gives all information on the system.

Let us discuss the physical significance of the correlation parameters (3.58) and their measurement. Let us first consider two completely uncorrelated density matrices  $\rho_1$  and  $\rho_2$ . The combined density matrix  $\rho$  is then given by (A.11) as direct product

$$\rho = \rho_1 \times \rho_2. \quad (3.59a)$$

By applying (A.2a), (A.2b), and (1.35) we obtain

$$\begin{aligned} P_i^{(1)} \times P_j^{(2)} &= \text{tr} (\rho_1 \times \rho_2) (\sigma_i \times \sigma_j) \\ &= \text{tr} (\rho_1 \sigma_i) \text{tr} (\rho_2 \sigma_j) \\ &= P_i^{(1)} \cdot P_j^{(2)}, \end{aligned} \quad (3.59b)$$

and the direct product reduces in this case to the normal product for all  $i$  and  $j$ .

Let us now consider two beams of spin-1/2 particles, which have interacted in the past, and are characterized by a joint density matrix  $\rho$ . We will derive an explicit expression for the  $z$ - $z$ -component of the tensor (3.58). The spin states of the particles in the first and second beam will be described by  $|M\rangle$  and  $|m\rangle$ , respectively. Using (A.8) and the fact that  $\sigma_z$  is diagonal in the representation (1.7), we obtain

$$\begin{aligned} P_z^{(1)} \times P_z^{(2)} &= \text{tr} \rho (\sigma_z \times \sigma_z) \\ &= \sum_{Mm} \langle Mm | \rho | Mm \rangle \langle M | \sigma_z | M \rangle \langle m | \sigma_z | m \rangle. \end{aligned} \quad (3.60a)$$

The expression can be interpreted in a simple way. The product of the two  $\sigma_z$ -elements can have only two values,  $+1$  or  $-1$ . The result  $+1$  implies that both particles have the same spin component, both spin up or both spin down. The result  $-1$  means that both spins are opposite to each other.  $P_z^{(1)} \times P_z^{(2)}$  is the sum of these values, each one multiplied by the corresponding probability for joint detection, for which we introduce the notation

$$\langle Mm | \rho | Mm \rangle = W(zz)_{Mm}, \quad (3.60b)$$

indicating that both measuring instruments are aligned in  $z$ -direction.

Substitution of the matrix elements of  $\sigma_z$  into (3.60a) and using the notation (3.60b) yields

$$P_z^{(1)} \times P_z^{(2)} = W(zz)_{++} + W(zz)_{--} - W(zz)_{+-} - W(zz)_{-+}. \quad (3.60)$$

Alternatively, we can write

$$P_z^{(1)} \times P_z^{(2)} = \frac{1}{N} (N(zz)_{++} + N(zz)_{--} - N(zz)_{+-} - N(zz)_{-+}). \quad (3.61)$$

Here,  $N(zz)_{++}$  is the number of coincidence events where a particle in the first beam has been registered with spin up by the first detector, and simultaneously its collision partner in the second beam has been found in the same spin state, and similar for the other terms.  $N$  is the total number of measurements, which is always assumed to be large.

Hence, the parameter  $P_z^{(1)} \times P_z^{(2)}$  refers to a coincidence experiment where both spin analyzers are oriented parallel to the  $z$ -axis.

Let us now consider the general case where the first and second beams (after they had interacted with each other) are sent through analyzers aligned along arbitrary directions  $\mathbf{a}$  and  $\mathbf{b}$ , respectively. Let  $\sigma_a = \boldsymbol{\sigma} \cdot \mathbf{a}$  denote the component of the Pauli matrix in direction of the unit vector  $\mathbf{a}$ , and  $\sigma_b = \boldsymbol{\sigma} \cdot \mathbf{b}$  the component along unit vector  $\mathbf{b}$  (where  $\sigma_x, \sigma_y, \sigma_z$  are the components of  $\boldsymbol{\sigma}$ ). The corresponding correlation parameter is defined by the expression

$$P_a^{(1)} \times P_b^{(2)} = \text{tr } \rho (\sigma_a \times \sigma_b) = \langle \sigma_a \times \sigma_b \rangle, \quad (3.62)$$

In order to find a physical interpretation we use the fact that the trace is independent of the chosen basis set for the spins. It is therefore convenient to choose the basis  $|M = \pm \frac{1}{2}\rangle$  and  $|m = \pm \frac{1}{2}\rangle$  for the first and second beam, respectively, which diagonalize  $\sigma_a$  and  $\sigma_b$ , respectively. Then,  $M$  denotes the spin component of the first particle with respect to  $\mathbf{a}$  as quantization axis, and  $m$  the spin of the particles in the second beam with respect to  $\mathbf{b}$  as quantization axis. The matrices  $\sigma_a$  and  $\sigma_b$  assume then both the form of  $\sigma_z$ .

Repeating the steps leading to (3.60) we obtain:

$$P_a^{(1)} \times P_b^{(2)} = W(\mathbf{a}, \mathbf{b})_{++} + W(\mathbf{a}, \mathbf{b})_{--} - W(\mathbf{a}, \mathbf{b})_{+-} - W(\mathbf{a}, \mathbf{b})_{-+}. \quad (3.63)$$

Here,  $W(\mathbf{a}, \mathbf{b})_{Mm}$  denotes the joint probability that a particle in the first beam is found with spin  $M$  with respect to  $\mathbf{a}$ , and simultaneously its collision partner in the second beam with spin component  $m$  with respect to  $\mathbf{b}$  as quantization axis. Explicit calculations of these probabilities are given in Sect. 3.6.6 for a specific case.

The general correlation parameter  $P_a^{(1)} \times P_b^{(2)}$  refers therefore to a coincidence experiment with spin analyzers aligned along  $\mathbf{a}$  and  $\mathbf{b}$ , respectively. Special cases are the components of the correlation tensor (3.58). For example,  $P_x^{(1)} \times P_y^{(2)}$  corresponds to a coincidence experiment with analyzers oriented parallel to the  $x$ - and  $y$ -directions, respectively, and so on.

From the normalization condition of probabilities

$$\sum_{Mm} W(\mathbf{a}, \mathbf{b})_{Mm} = 1, \quad (3.63a)$$

follows the constraint

$$|P_a^{(1)} \times P_b^{(2)}| \leq 1. \quad (3.64)$$

The upper limit of the correlation parameter can only be obtained if the joint probabilities  $W(\mathbf{a}, \mathbf{b})_{+-}$  and  $W(\mathbf{a}, \mathbf{b})_{-+}$  are zero in (3.63) which gives together with the normalization condition of probabilities

$$\begin{aligned} P_a^{(1)} \times P_b^{(2)} &= W(\mathbf{a}, \mathbf{b})_{++} + W(\mathbf{a}, \mathbf{b})_{--} \\ &= 1. \end{aligned} \quad (3.65a)$$

Hence, any time a particle in the first beam is found with spin up or down with respect to **a**, its collision partner in the second beam will be detected in the identical spin state with respect to **b**, and vice versa. We say that results of the measurements are perfectly correlated.

Similarly, the lower limit can only hold if the probabilities  $W(\mathbf{a}, \mathbf{b})_{++}$  and  $W(\mathbf{a}, \mathbf{b})_{--}$  vanish both, which yields

$$\begin{aligned} P_a^{(1)} \times P_b^{(2)} &= -(W(\mathbf{a}, \mathbf{b})_{+-} + W(\mathbf{a}, \mathbf{b})_{-+}) \\ &= -1. \end{aligned} \quad (3.65b)$$

This result implies that the two correlated particles will always be found in opposite spin states with respect to **a** and **b**, respectively, and we have perfect anticorrelation between the measuring results.

Finally, we will say that the two measurements are uncorrelated if the condition

$$P_a^{(1)} \times P_b^{(2)} - P_a^{(1)} \cdot P_b^{(2)} = 0 \quad (3.65c)$$

is satisfied (similarly to (3.59b)).

As an exercise let us calculate the correlation tensor (3.58) for the system characterized by (3.49), or alternatively by the density matrix (3.53). Mathematical details are exposed in Appendix G.1, here we present only the results. For the *zz*-component we obtain:

$$\begin{aligned} P_z^{(1)} \times P_z^{(2)} &= -(|f|^2 + |g|^2) \\ &= -1. \end{aligned} \quad (3.66a)$$

This expression shows that there is strict anticorrelation as expected from the structure of (3.49). We will analyze this result in detail in the following subsection.

In a similar way we calculate the other components of the tensor (3.58) and obtain after some algebra (see Appendix G.1):

$$P_x^{(1)} \times P_x^{(2)} = P_y^{(1)} \times P_y^{(2)} = 2|f||g| \cos \delta, \quad (3.66b)$$

$$P_x^{(1)} \times P_y^{(2)} = -P_y^{(1)} \times P_x^{(2)} = -2|f||g| \sin \delta, \quad (3.66c)$$

where  $\delta$  is the relative phase between the amplitudes

$$f = |f|, \quad g = |g| e^{i\delta}.$$

The other components of the correlation tensor vanish.

The parameters (3.57) together with (3.66) characterize uniquely the state (3.49), and give an *operational* definition of this state.

Finally, we will show that any correlation parameter  $P_a^{(1)} \times P_b^{(2)}$  can be expanded in terms of the nine tensor components (3.58). Since the Pauli matrices transform as vector components we can write

$$\sigma_a = \boldsymbol{\sigma} \cdot \mathbf{a} = \sum_i \sigma_i a_i, \quad (3.67a)$$

and

$$\sigma_b = \boldsymbol{\sigma} \cdot \mathbf{b} = \sum_j \sigma_j b_j, \quad (3.67b)$$

with  $i, j = x, y, z$  in an arbitrarily chosen coordinate system. Substitution of (3.67a) and (3.67b) into the definition (3.62) yields

$$\begin{aligned} P_a^{(1)} \times P_b^{(2)} &= \sum_{ij} a_i b_j \operatorname{tr} \rho (\sigma_i \times \sigma_j) \\ &= \sum_{ij} a_i b_j (P_i^{(1)} \times P_j^{(2)}). \end{aligned} \quad (3.67c)$$

This expression shows explicitly that all information on the correlation properties of two spin-1/2 particles are contained in the nine components of the correlation tensor.

As a simple exercise we consider the state (3.49). Using (3.51), and the components (3.66) of the correlation tensor, we obtain from (3.67c) after some algebra:

$$\begin{aligned} P_a^{(1)} \times P_b^{(2)} &= (a_x b_x + a_y b_y) (P_x^{(1)} \times P_x^{(2)}) \\ &\quad + (a_x b_y - a_y b_x) (P_x^{(1)} \times P_y^{(2)}) + a_z b_z (P_z^{(1)} \times P_z^{(2)}) \\ &= 2|f||g| \sin \beta \sin \beta' \cos(\alpha' - \alpha + \delta) - \cos \beta \cos \beta'. \end{aligned} \quad (3.68)$$

Only the difference  $\alpha' - \alpha$  occurs in (3.68) which expresses the axial symmetry of the state (3.49) around the  $z$ -axis.

In conclusion,  $P_a^{(1)} \times P_b^{(2)}$  refers to a coincidence experiment where the first analyzer is oriented parallel to the unit vector  $\mathbf{a}$  with polar angle  $\beta$  and azimuth  $\alpha$  (see for example Fig. 1.3), and the second analyzer is set along the unit vector  $\mathbf{b}$  with polar angle  $\beta'$  and azimuth angle  $\alpha'$ . Equation 3.63 relates the parameters  $P_a^{(1)} \times P_b^{(2)}$  to the directly measurable coincidence rates.

The results derived in the present subsection will provide the basis for the subsequent discussions.

### 3.6.4 Entanglement Versus Classical Correlations. LOCC-Procedures. Entanglement in Mixtures

The state (3.49) is in general entangled as shown in Sect. 3.6.2. The state vector predicts a strict anticorrelation between the two spin systems, if both spin analyzers are oriented along the  $z$ -axis. Thus, if the first observer finds a particle with spin up at time  $t_1$ , then the second observer will necessarily find a particle with spin down in his beam, even if the second measurement is performed at a later time. If the intensity of the beams is sufficiently low one can be practically sure that the two measurements are performed on the same collision pair.

Let us discuss these measurements in more detail. Assume that each detector has been provided with a printer, and that the results (*spin up* or *spin down*) have been printed out. If we consider the outputs of both printers separately we see a probability distribution for finding particles in states  $|+\rangle$  or  $|-\rangle$ . However, if the two outputs are compared, we detect a strict correlation: the two printers will always register particles with opposite spins. If we have seen the printed list of the first detector we can predict with absolute certainty the measurement result for the second beam, and vice versa. The probability of finding a particle of the first beam in state  $|+\rangle$  is  $|f|^2$  according to (3.56a). With the same probability  $|f|^2$  its collision partner in the second beam will be found in state  $|-\rangle$ , according to (3.56b). Similarly, the opposite results will be found with probability  $|g|^2$ . This strong correlation of the probabilities is expressed in the structure of the reduced density matrices (3.56). A separate study of the two matrices gives the individual probabilities, if we compare both matrices we detect the correlations.

At first one might think that there is nothing particularly remarkable in these observations. The results seem to appear just as an obvious consequence of spin conservation. Such correlations between distant measurements, caused by conservation laws, are common in classical physics.

However, in quantum mechanics, the situation is not so simple, and much more interestingly. Because the state  $|\psi\rangle$  in (3.49) cannot be factorized into a product of two state vectors associated to each beam, we cannot ascribe any well defined spin state to each particle before a measurement has been performed. The states

are indeterminate rather than unknown. That is, prior to a measurement, it is highly unlikely that a particle of the combined system (3.49) is exactly in state  $|+\rangle$ , or  $|-\rangle$ , or in any other definite spin state.<sup>1</sup> Only the joint system is described by a well defined state vector  $|\psi\rangle$ .

For a single particle, being in a superposition of states  $|+\rangle$  and  $|-\rangle$  for example, the situation has been analyzed in Sect. 1.1.4. But there is a new feature in two-particle systems, and this concerns the respective correlations. By passing an analyzer oriented along  $z$ , a particle of, say, the first beam is projected with a certain probability into an eigenstate of the analyzer,  $|+\rangle$  or  $|-\rangle$ . This is not surprising. However, after the measurement on particle one has been performed, its former collision partner in the second beam, which had not a well-defined spin component before this measurement, is projected with 100% certainty into the opposite spin state of particle one, even before it passes its analyzer. The striking feature of these results is that this change in the state of particle two happens instantaneously at the moment of the first measurement, independently of how far the particles are separated. A measurement on one particle determines immediately the state of the other one, and vice versa. This is a remarkable property of entangled states which requires further discussion, which will be provided in Sects. 3.6.5 and 3.6.6.

It should be noted that the perfect anticorrelation holds only if both analyzers are set parallel to the  $z$ -axis. For all other directions the degree of correlation is reduced. The state (3.49) is entangled, but not maximally entangled, as will be discussed in the following subsection.

It is instructive to compare the pure state (3.49) with a mixture, prepared in a special way. Suppose that two spatially separated observers (commonly called *Alice* and *Bob*) have both a source of spin-1/2 particles and spin filters at their disposal. For example, Alice prepares electrons and Bob hydrogen atoms. Any time Alice releases a particle in a definite spin state,  $|+\rangle$  or  $|-\rangle$ , she communicates this to Bob via a classical channel (say, a phone), and Bob prepares and releases a particle of his system in the opposite spin state. Both beams remain separated without interaction.

Eventually,  $N$  pairs of particles with opposite spins have been produced,  $N_1$  pairs  $|+\rangle|-\rangle = |+-\rangle$  and  $N_2$  pairs  $|-\rangle|+\rangle = |--\rangle$  with

$$\frac{N_1}{N} = |f|^2, \quad \frac{N_2}{N} = |g|^2.$$

The total system is then represented by the density operator

$$\rho = |f|^2|+-\rangle\langle+-| + |g|^2|--\rangle\langle--| \quad (3.69)$$

(see Sects. 1.1.3–1.1.5, and in particular (1.20). In fact, we remember from Sect. 1.1.5 that the notation of a density operator describes a preparation procedure and the operator (3.69) contains the full available information on the total system.

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<sup>1</sup>Compare for example (3.84a) and (3.87) below.

In the explicit matrix representation (3.52) we obtain a diagonal matrix with only two non-vanishing elements

$$\langle + - | \rho | + - \rangle = |f|^2,$$

and

$$\langle - + | \rho | - + \rangle = |g|^2.$$

In particular, all coherence terms like  $\langle + - | \rho | - + \rangle$  are zero.

It follows from the method of preparation that any particle in the mixture (3.69) is in a well-defined spin state, either  $|+\rangle$  or  $|-\rangle$ . One is inclined to say that each particle *knows* its spin component. The state of each particle is fixed, but unknown to an external observer prior to a measurement. This case corresponds exactly to classical statistics, but is in sharp contrast to the system described by the state vector (3.49) (or alternatively by the density matrix (3.54)). Here, the state of the individual particles is not only unknown but indeterminate (that is, not even the particles *know* their spin component prior to a measurement).

Both systems, described by (3.49) and (3.69) respectively, can be distinguished experimentally. Let us therefore calculate the polarization properties of the mixture.

If only the first beam (say, Alice's beam) is observed we obtain for its reduced density matrix (3.56a). Similarly, the second beam (Bob's) is characterized by the reduced density matrix (3.56b). Consequently, the components of the individual polarization vectors  $P_z^{(1)}$  and  $P_z^{(2)}$  are given by (3.57), and the  $x$ - and  $y$ -components vanish.

In the next step we calculate the components of the correlation tensor, assuming a sufficiently low intensity so that individual pairs are detected. For the  $zz$ -component we obtain (3.66a):

$$P_z^{(1)} \times P_z^{(2)} = -1. \quad (3.70a)$$

It should be noted that this result differs considerably from the uncorrelated product  $P_z^{(1)} \cdot P_z^{(2)}$ . So far the results for the pure and the mixed state are the same. However, all other components of the correlation tensor vanish for the system (3.69):

$$P_i^{(1)} \times P_j^{(2)} = 0, \quad (3.70b)$$

( $i, j = x$  or  $y$ ). These results for the mixture correspond to classical expectations, but are in sharp contrast to (3.66b) and (3.66c) for the pure state (3.49). While the system (3.69) can explain the perfect anticorrelation if the two analyzers are both oriented parallel to  $z$ , it cannot reproduce the results along other directions.

The particles in Alice's and Bob's beams are correlated because of (3.70a), but this correlation is due to the special method of preparation, namely by a combination of *local operations* and *classical communication* (LOCC). The classical communication is necessary to allow for (classically) correlated systems. Such LOCC-procedures play an important role in quantum teleportation and quantum information theory (see for example [Plenio and Virmani 2007](#)).

We have discussed the difference between LOCC-prepared mixtures and pure states at some length. However, it is important to have a clear perception of the fundamental difference between classical correlations and quantum mechanical entanglement. In order to distinguish between both cases it is necessary to measure all components of the individual polarization vectors and the correlation tensor. In particular, we stress again that systems of particles in different, but definite, states must be described as mixtures and cannot be represented as linear superpositions.

In the last two decades the definition of entanglement has been extended beyond Schrödinger's original conception, in particular, to include mixed states. In order to introduce these new concepts let us first reformulate (3.69). The direct product of the operators  $|+\rangle\langle+|$  and  $|-\rangle\langle-|$  is defined by the expression

$$|+\rangle\langle+| \times |-\rangle\langle-| = |+-\rangle\langle+-|.$$

Equation 3.69 can then be written in the form

$$\rho = |f|^2 (|+\rangle\langle+| \times |-\rangle\langle-|) + |g|^2 (|-\rangle\langle-| \times |+\rangle\langle+|), \quad (3.71)$$

where the first and second factors in the direct product refer to the first and second beam, respectively. Note, that no coherence terms like  $|+\rangle\langle-|$  occur in expression (3.71). Equation 3.71 is a special form of a more general density operator, describing bipartite mixed states

$$\rho = \sum_i p_i \rho_1^{(i)} \times \rho_2^{(i)}, \quad (3.71a)$$

where  $p_i$  denote the respective probabilities, and  $\rho_1^{(i)}$  and  $\rho_2^{(i)}$  refer to subsystems one and two, respectively. For example, comparing with (3.71) we have the relations:

$$\rho_1^{(1)} = |+\rangle\langle+|, \quad \rho_2^{(1)} = |-\rangle\langle-|,$$

and

$$\rho_1^{(2)} = |-\rangle\langle-|, \quad \rho_2^{(2)} = |+\rangle\langle+|.$$

The formulation (3.71a) leads to the following

**Definition.** Any mixed bipartite state  $\rho$  of the general form (3.71a) is said to be separable. Otherwise it is said to be entangled. (see, for example Selleri 1990; Sen et al. 2007; Plenio and Virmani 2007).

Note, that the operator (3.71) cannot be completely factorized as in (3.59a) since both subsystems are classically correlated.

It has been shown that mixtures of the general form (3.71a) are the most general states which can be produced by LOCC methods. These states are all separable

in the sense defined above. Thus, entangled mixtures cannot be obtained by these techniques. In order to produce an entangled state the particles of both beams must be brought closely together and allowed to interact which will then produce the necessary quantum correlations. The state (3.69) is classically correlated but not entangled.

In general, [Popescu and Rohrlich \(1997\)](#) explored analogies between entanglement theory and thermodynamics and stated, what is sometimes called the *fundamental postulate of entanglement*:

**Postulate:** The laws of physics are such that it is impossible to create (or increase) entanglement between remote quantum systems by applying solely local operations and classical communication.

As an example let us reformulate the experiment leading from the initial state (3.48) to the final state (3.49), by considering more general initial conditions. Usually, the initial particles are not completely polarized as in (3.48), but only partially polarized. Suppose that the first beam has been prepared in the mixed state

$$\rho_1 = \sum_M p(M) |M\rangle\langle M|,$$

where  $|M\rangle$  denotes  $|+\rangle$  or  $|-\rangle$ , and  $p(M)$  is the respective probability (see (1.20)). Similarly, the second beam is described by the density operator

$$\rho_2 = \sum_m p(m) |m\rangle\langle m|.$$

Under the premise that both systems have been prepared independently, the joint initial system is described by the direct product

$$\begin{aligned} \rho_{in} &= \rho_1 \times \rho_2, \\ &= \sum_{Mm} p(M) p(m) |Mm\rangle\langle Mm|. \end{aligned} \tag{3.72}$$

Both beams are then allowed to interact and the total system is analyzed after the collision. Any component  $|Mm\rangle$  of the operator (3.72) is transformed into a state  $|\psi(Mm)\rangle$  (similar to the transition from (3.48) to (3.49)), and the initial density operator develops into the final operator  $\rho_{out}$ :

$$\rho_{out} = \sum_{Mm} p(M) p(m) |\psi(Mm)\rangle\langle\psi(Mm)|. \tag{3.73}$$

In general, the states  $|\psi(Mm)\rangle$  are entangled like the state (3.49) and  $\rho_{out}$  can therefore not be factorized similar to the operator (3.71). Equation (3.73) represents an example of an entangled mixture.

The question whether a given mixture is separable or entangled is hard to answer in general and we refer to the relevant papers in [Bruss and Leuchs \(2007\)](#) or [Bouwmeester et al. \(2001\)](#).

### 3.6.5 States with Maximal Entanglement. Entropy of Entanglement. Bell States

At the beginning of the preceding subsection we have discussed some consequences of entanglement for the state (3.49). We have shown the following. Assume that the first analyzer has been set along the  $z$ -axis, and that a particle has been found and registered in a definite spin state with respect to  $z$ , either with spin up or spin down. Then, we can predict with certainty that its collision partner in the second beam has been projected into the opposite spin state with respect to  $z$ , immediately at the end of the first measurement, and before passing its own measuring apparatus. This prediction can be tested experimentally by orienting the second analyzer parallel to  $z$ , and measuring the spin components of the particles in the second beam in coincidence with those in the first beam. The results will always show strict anticorrelation

$$P_z^{(1)} \times P_z^{(2)} = -1.$$

This strong correlation is reduced for all other directions  $\mathbf{a}$  and  $\mathbf{b}$  of the two analyzers, respectively, as follows from (3.68). However, it might be possible to generalize the results if certain restrictions are imposed on the combined state, that is on the amplitudes  $f$  and  $g$ .

Therefore, the following question arises. Assume that the first analyzer has been oriented along an arbitrarily chosen direction  $\mathbf{a}$  (with angles  $\beta$  and  $\alpha$  as specified by (3.51a)). Any particle in the first beam will be found in a definite spin state with respect to  $\mathbf{a}$  after a measurement. Under which conditions will it be possible to find a direction  $\mathbf{b}_0$  for the second analyzer so that there will be either perfect correlation or anticorrelation between both measurements, that is, so that the condition

$$|P_a^{(1)} \times P_{b_0}^{(2)}| = 1 \quad (3.74)$$

will be satisfied? If this condition holds then we can be sure that both particles of the collision pair will always be found in the same or in opposite spin states with respect to  $\mathbf{a}$  and  $\mathbf{b}_0$ , respectively. The result of one measurement can always be predicted with certainty if the result of the other one is known.

If such a direction of  $\mathbf{b}_0$  exists for *any* choice of  $\mathbf{a}$  then we will speak of *maximal entanglement*.

We will first study this problem for the special state (3.49). We have to find:

1. The general conditions under which condition (3.74) holds,
2. The direction  $\mathbf{b}_0$ , that is, the angles  $\beta'_0$  and  $\alpha'_0$  if the angles  $\beta$  and  $\alpha$  of  $\mathbf{a}$  are given (or vice versa).

These problems are discussed in Appendix H.1 and there it is shown that maximal entanglement can only be achieved if the condition

$$2|f||g| = 1, \quad (3.75)$$

is satisfied. In addition, we have to require that either the relation

$$\cos(\alpha'_0 - \alpha + \delta) = 1, \quad (3.76a)$$

or

$$\cos(\alpha'_0 - \alpha + \delta) = -1. \quad (3.76b)$$

is valid, where  $\delta$  is the relative phase between the amplitudes  $f$  and  $g$ . Equations (3.76) represent requirements for the azimuth angle  $\alpha'_0$  of  $\mathbf{b}_0$ . Equation (3.75) is the essential condition and is of key relevance.

Substitution of (3.75) into the general correlation parameter (3.68) yields

$$P_a^{(1)} \times P_b^{(2)} = \sin \beta \sin \beta' \cos(\alpha' - \alpha + \delta) - \cos \beta \cos \beta'. \quad (3.77)$$

Let us choose an azimuth angle

$$\alpha' = \alpha'_0 = \pi + \alpha - \delta, \quad (3.78a)$$

in accordance with condition (3.76b). Setting

$$\beta' = \beta'_0 = \beta, \quad (3.78b)$$

we obtain from (3.77)

$$P_a^{(1)} \times P_{b_0}^{(2)} = -1,$$

where the unit vector  $\mathbf{b}_0$  is defined by (3.78).

If the second analyzer is rotated into direction  $-\mathbf{b}_0$ , corresponding to angles

$$\alpha'_0 = \alpha - \delta, \quad (3.79a)$$

which satisfies condition (3.76a), and

$$\beta'_0 = \pi - \beta, \quad (3.79b)$$

we obtain perfect correlation between the two measurements

$$P_a^{(1)} \times P_{-b_0}^{(2)} = 1,$$

where  $\mathbf{b}_0$  is defined by the angles (3.78). All other orientations  $\mathbf{b}$  of then second analyzer give reduced correlations.

We can summarize and interpret our results as follows. We have chosen an arbitrary direction  $\mathbf{a}$  of the first analyzer, defined by angles  $\beta$  and  $\alpha$ . Give that the essential condition (3.75) holds, then, there exists for *any* choice of  $\mathbf{a}$  a well defined direction  $\mathbf{b}_0$  for the second analyzer, related to  $\mathbf{a}$  by (3.78), so that condition (3.74) is satisfied. That is, if a particle in the first beam has been recorded with spin up (spin down) with respect to  $\mathbf{a}$ , then its partner in the second beam will automatically orient its spin antiparallel (parallel) to  $\mathbf{b}_0$ , immediately at the end of the first measurement. The behaviour of one system is conditioned by the behaviour of the other one. The outcome of a measurement on one system can be predicted with certainty given the results of the appropriate measurement on the other subsystem. The discussion of entanglement, given at the beginning of the preceding subsection, can be repeated here, with  $\mathbf{a}$  and  $\mathbf{b}_0$  instead of  $z$ .

If the direction  $\mathbf{a}$  is changed during a measuring series then the direction  $\mathbf{b}_0$  will adapt itself so that (3.78) hold again. This strong connection between  $\mathbf{a}$  and  $\mathbf{b}_0$  is determined by the intrinsic correlations between the two beams, that is, by the components of the correlation tensor. This will be shown more explicitly below when discussing the Bell states.

We add that the very same conditions (3.78) and (3.79) can be obtained in a different way which gives also additional insight into the general quantum mechanical background, as is shown in Appendix I.1 (see in particular (I.8)).

A special case will be studied in detail in the following subsection and some essential results will be summarized in Table 3.2 later on.

If condition (3.75) is satisfied, or equivalently the relation

$$|f| = |g| = \frac{1}{\sqrt{2}},$$

then (3.49) reduces to the expression

$$|\psi\rangle = \frac{1}{\sqrt{2}}(|+-\rangle + e^{i\delta}|-+\rangle), \quad (3.80)$$

where the physical significance of the relative phase  $\delta$  follows from (3.81d) below, and also from (3.78a) and (3.79a). States of the general form (3.80) are called *maximally entangled* (Le Bellac 2006). From (3.56) follows that the corresponding reduced density matrices  $\rho_1$  and  $\rho_2$  are multiples of the identity matrix  $\mathbf{1}$ :

$$\rho_1 = \rho_2 = \frac{1}{2}\mathbf{1}, \quad (3.81a)$$

and the individually measured polarization vectors vanish:

$$\mathbf{P}^{(1)} = \mathbf{P}^{(2)} = 0. \quad (3.81b)$$

Let us consider the state (3.49). By squaring (3.57) and the normalization condition (3.49a), and by combining both results we obtain

$$(\mathbf{P}^{(1)})^2 = (\mathbf{P}^{(2)})^2 = 1 - (2|f||g|)^2. \quad (3.81c)$$

This relation shows explicitly that the degree of entanglement is restricted by the magnitude of the polarization vector, and vice versa. A more general derivation is given in Appendix J.1 (relations (J.12b) and (J.16) to (J.19)).

Finally, substitution of condition (3.75) into (3.66) yields

$$\begin{aligned} P_x^{(1)} \times P_x^{(2)} &= P_y^{(1)} \times P_y^{(2)} = \cos \delta, \\ P_x^{(1)} \times P_y^{(2)} &= -P_y^{(1)} \times P_x^{(2)} = -\sin \delta, \\ P_z^{(1)} \times P_z^{(2)} &= -1. \end{aligned} \quad (3.81d)$$

These relations give the non-vanishing components of the correlation tensor for maximally entangled states of the form (3.80).

Different states can have stronger or weaker correlations, depending on the values of  $|f|$  and  $|g|$ . For states of the general form (3.49) the parameter

$$E = 2|f||g| \quad (3.82)$$

provides in some sense a measure of the strength of the entanglement. If the normalization (3.49a) is taken into account, we obtain the constraint

$$E \leq 1. \quad (3.82a)$$

$E$  vanishes if  $f$  or  $g$  are zero. The state (3.49) separates then, and there is no entanglement. The maximal possible value of  $E$  is obtained for states with maximal entanglement.

An *operational measure* is introduced by (3.81c). The squares of the individual polarization vectors (which can be measured as functions of scattering energy and angle) are related to the strength of the entanglement, produced during the collision.

So far our discussion of maximal entanglement refers only to the special example (3.49). Let us now consider more general attempts to quantify entanglement. For example, it has been shown that the entanglement of any pure bipartite state is uniquely characterized by the von–Neumann entropy  $S(\rho_i)$ , defined as

$$\begin{aligned} S(\rho_i) &= -\text{tr } \rho_i (\log_2 \rho_i) \\ &= -\sum_n \lambda_n \log_2 \lambda_n, \end{aligned} \quad (3.83)$$

(see e.g., [Popescu and Rohrlich 1997](#)). Here,  $\rho_i$  denotes the reduced density matrix of either of the two subsystems.  $\lambda_n$  are the eigenvalues of  $\rho_i$  (see Appendix [J.1](#)),

$$\rho_i = \begin{pmatrix} \lambda_1 & 0 \\ 0 & \lambda_2 \end{pmatrix}.$$

$\log_2$  denotes the logarithm with basis 2, which is the standard logarithmic basis for information theory. The logarithm of  $\rho_i$  is defined as

$$\log_2 \rho_i = \begin{pmatrix} \log_2 \lambda_1 & 0 \\ 0 & \log_2 \lambda_2 \end{pmatrix},$$

from which follows the second line in [\(3.83\)](#).  $S(\rho_i)$  is usually called the *entropy of entanglement*.

The interpretation of the entropy of entanglement is not obvious, and can be provided by an information-theoretical approach (see e.g., [Nielsen and Chuang 2000](#)). Here, we will restrict ourselves to the following considerations.

The choice of  $S(\rho_i)$  as a measure of entanglement can be motivated by again considering the special example [\(3.49\)](#). If the state  $|\psi\rangle$  is maximally entangled, then condition [\(3.75\)](#) holds, and the individually observed subsystems have necessarily vanishing polarization according to [\(3.81c\)](#), and the reduced density matrices  $\rho_1$  and  $\rho_2$  assume both the form [\(3.81a\)](#). If a spin measurement is performed on either subsystem one finds a random distribution of particles with spin up and spin down, respectively, along any direction we choose for the measurement. In the language of information theory we may express this result by saying that the uncertainty on the outcome of the measurement is largest, or that each subsystem is *maximally mixed*. The von-Neumann entropy achieves its maximum value if the uncertainty is maximal. We obtain by inserting [\(3.81a\)](#) into [\(3.83\)](#) ( $i = 1$  or  $2$ ):

$$S(\rho_i) = -\log_2 \left( \frac{1}{2} \right) = 1. \quad (3.83a)$$

Hence, maximal entanglement in the combined system is characterized by the maximal value of  $S(\rho_i)$ .

On the other hand, if the two subsystems are completely polarized,  $|\mathbf{P}^{(1)}| = |\mathbf{P}^{(2)}| = 1$ , then both subsystems are necessarily in pure states, say

$$\rho_1 = \begin{pmatrix} 1 & 0 \\ 0 & 0 \end{pmatrix}, \quad \text{and} \quad \rho_2 = \begin{pmatrix} 0 & 0 \\ 0 & 1 \end{pmatrix}. \quad (3.83b)$$

The joint state vector is then necessarily separable

$$|\psi\rangle = |+\rangle|-\rangle.$$

Pure states contain the maximal possible information on a system and the entropy vanishes in this case:

$$S(\rho_i) = -\log_2 1 = 0.$$

Hence, a vanishing entropy corresponds to zero entanglement in the joint state.

As an example, consider the state (3.49). The corresponding reduced density matrices are given by (3.56) with eigenvalues  $|f|^2$  and  $|g|^2$ , and the corresponding entropy assumes the form

$$S(\rho_1) = S(\rho_2) = -|f|^2 \log_2 |f|^2 - |g|^2 \log_2 |g|^2.$$

It is of key importance that  $\rho_1$  and  $\rho_2$  have the same set of eigenvalues so that their von–Neumann entropies coincide. It can be shown that, for pure bipartite states, this is always the case so that  $S(\rho_1) = S(\rho_2)$  is ensured (see Appendix J.1).

Finally, we note that the eigenvalues are closely related to the magnitude  $|\mathbf{P}|$  of the corresponding polarization vector by (J.8). Upon substituting this expression into the definition (3.83) we can express the entropy in terms of  $|\mathbf{P}|$ . Both quantities specify the disorder, or the information content, of spin-1/2 systems.

This short discussion may serve as an illustration of the use of the von–Neumann entropy as a measure of entanglement. In the general case of density matrices  $\rho_i$  with dimension  $d$ , the von–Neumann entropy is constrained by the condition

$$0 \leq S(\rho_i) \leq \log_2 d.$$

It has been shown in general, that the upper limit corresponds to the maximally mixed state (maximal entanglement), and the lower limit is reached in case of a pure state (zero entanglement).

The problem of defining entanglement measures has been discussed in much greater generality, and we refer for example to the relevant review papers in [Bruss and Leuchs \(2007\)](#) or [Bouwmeester et al. \(2001\)](#).

Finally, we will consider some examples of conceptual importance. Special cases of (3.80) are the singlet state

$$|\Psi_-\rangle = \frac{1}{\sqrt{2}} (|+-\rangle - |--\rangle), \quad (3.84a)$$

with  $\delta = \pi$ , and the triplet state

$$|\Psi_+\rangle = \frac{1}{\sqrt{2}} (|+-\rangle + |--\rangle), \quad (3.84b)$$

with  $\delta = 0$ . Together with the two states

$$|\Phi_{\pm}\rangle = \frac{1}{\sqrt{2}} (|++\rangle \pm |--\rangle), \quad (3.84c)$$

**Table 3.1** The non-vanishing components of the correlation tensor for the four Bell states  $|\Psi_{\pm}\rangle$  and  $|\Phi_{\pm}\rangle$ , respectively

	$P_x^{(1)} \times P_x^{(2)}$	$P_y^{(1)} \times P_y^{(2)}$	$P_z^{(1)} \times P_z^{(2)}$
$ \Psi_+\rangle$	1	1	-1
$ \Psi_-\rangle$	-1	-1	-1
$ \Phi_+\rangle$	1	-1	1
$ \Phi_-\rangle$	-1	1	1

they form a mutually orthogonal basis system for any two-particle spin-1/2 system. All four states are maximally entangled (see below) and are called *Bell states* (Bohm 1951).

As discussed in Sect. 3.6.3, the spin polarization properties of spin-1/2 systems are uniquely characterized by determining the individual polarization vectors  $\mathbf{P}^{(1)}$  and  $\mathbf{P}^{(2)}$ , and the components of the correlation tensor. It is a simple exercise to calculate these parameters for the four states (3.84). The vectors  $\mathbf{P}^{(1)}$  and  $\mathbf{P}^{(2)}$  vanish, and we give the results for the non-vanishing components of the correlation tensor in Table 3.1. The results show that the four Bell states are characterized by particularly simple properties with vanishing individual polarizations, and with tensor components of maximal magnitudes  $|P_i^{(1)} \times P_i^{(2)}| = 1$ ; ( $i = x, y, z$ ). In other words, the states (3.84) are eigenstates of the three correlation operators  $\sigma_i \times \sigma_i$  with eigenvalues +1 and -1, respectively. Table 3.1 illustrates that the states can be identified by the correlations they exhibit.

The reduced density matrices of all four Bell states are given (3.81a). Hence, the von-Neumann entropy (3.83) achieves its maximum value which proves that the Bell states are maximally entangled.

Alternatively, by inserting the numbers of Table 3.1 into the general equation (3.67c) it can directly be shown that condition (3.74) can be satisfied for *any* direction of  $\mathbf{a}$ . For example, for the singlet state  $|\Psi_-\rangle$  we obtain

$$P_a^{(1)} \times P_b^{(2)} = -\mathbf{a} \cdot \mathbf{b}.$$

The special vector  $\mathbf{b}_0$ , which satisfies (3.74) for given  $\mathbf{a}$ , is obtained by setting  $\mathbf{b} = \mathbf{b}_0 = \mathbf{a}$ , which yields

$$P_a^{(1)} \times P_{b_0}^{(2)} = -1.$$

This example shows directly that  $\mathbf{b}_0$  is determined:

1. By the direction of  $\mathbf{a}$  (that is, by the first measurement), and
2. By the components of the correlation tensor.

We add that the direction of  $\mathbf{b}_0$  follows also from (3.78) by setting the relative phase  $\delta = \pi$ , corresponding to the singlet state.

From Table 3.1 we can read off that the following simple relationship holds for any Bell state:

$$\sum_i \left( P_i^{(1)} \times P_i^{(2)} \right)^2 = 3, \quad (3.85)$$

( $i = x, y, z$ ). It is remarkable that (3.85) follows from general density matrix theory without detailed knowledge of Table 3.1. We refer to Appendix F.1 where also more general relations for the various polarization parameters are given.

It may be appropriate to remark that non-linear relationships like (3.85) do not reduce the number of independent parameters, specifying the system under consideration. For example, in the present case, one obtains no information on the sign of the tensor components.

Finally, we note that (3.84) can be applied to any two-particle system where each particle can be in either of two states (for example polarized photons). The general Bell states play a prominent role in quantum information theory and teleportation schemes where the basis states  $|+\rangle$  and  $|-\rangle$  are usually replaced by  $|0\rangle$  and  $|1\rangle$  (see for example [Bouwmeester et al. 2001](#); [Bruss and Leuchs 2007](#)).

### 3.6.6 Correlations in the Singlet States. Conditional Probabilities

In this subsection we continue our discussion of entanglement by considering the singlet state (3.84a) as an important specific case. Experimentally, a pure singlet state has been prepared by [Cirac and Zoller \(1994\)](#). Another method is in principle the observation of the decay of a spinless particle into a pair of two spin-1/2 particles. [Lamehi-Rachti and Mittig \(1976\)](#) performed an experiment in nuclear physics involving low-energy scattering between protons and hydrogen atoms. In the resulting proton – proton collision the two particles interact predominantly through the singlet channel, and the polarization and correlation parameters were measured.

An important property of the singlet state is its invariance under rotations in spin space (since the total spin is zero). This implies that  $|\Psi_-\rangle$  has the same form in any set of basis states. For example, let us take the general vector  $\mathbf{a}$  (3.51a) as quantization axis. States with spin up and spin down with respect to  $\mathbf{a}$  will be denoted by  $|a(+)\rangle$  and  $|a(-)\rangle$ , respectively. They can be expressed in terms of the basis states  $|+\rangle$  and  $|-\rangle$  similar to (1.10). We will assume throughout this subsection that  $\mathbf{a}$  lies within the  $x$ - $z$ -plane ( $\alpha = 0$ ). We obtain:

$$|a(+)\rangle = |+\rangle \cos \frac{\beta}{2} + |-\rangle \sin \frac{\beta}{2}. \quad (3.86a)$$

The opposite spin state  $|a(-)\rangle$  follows from the orthogonality condition which gives

$$|a(-)\rangle = |+\rangle \sin \frac{\beta}{2} - |-\rangle \cos \frac{\beta}{2}. \quad (3.86b)$$

The rotational invariance of  $|\Psi_-\rangle$  in spin space allows to write down immediately the expansion

$$|\Psi_-\rangle = \frac{1}{\sqrt{2}} (|a(+)\rangle|a(-)\rangle - |a(-)\rangle|a(+)\rangle), \quad (3.87)$$

which has the same structure as (3.84a) although involving different states. (By substituting (3.86) into (3.87) the expansion (3.84a) can be directly rederived).

Both expressions, (3.84a) and (3.87), contain of course the same information on the combined system. That makes it again evident that, prior to a measurement, it is not possible to assign a definite spin state to one subsystem.

As shown by (3.81a) the reduced density matrices of both individually measured beams are proportional to the identity matrix. Hence, if the spins of only one beam are observed, each measurement series will give a random sequence of results, either spin up or spin down. If both beams are observed in coincidence one detects the correlation. In order to find out the amount of correlation between the two measurements we calculate the parameters  $P_a^{(1)} \times P_b^{(2)}$  which follow from the general equation (3.67c) and Table 3.1 as follows:

$$P_a^{(1)} \times P_b^{(2)} = -\mathbf{a} \cdot \mathbf{b}. \quad (3.88a)$$

Throughout this and the following subsection it will always be assumed that  $\mathbf{a}$  and  $\mathbf{b}$  are coplanar and are both contained within the  $x$ - $z$ -plane. We have then the alternative form

$$P_a^{(1)} \times P_b^{(2)} = -\cos(\beta - \beta'). \quad (3.88b)$$

This equation gives the extent of the correlation between the two measurements as a function of the relative orientation  $\beta - \beta'$  of the two measuring devices.

For example, if the orientations  $\mathbf{a}$  and  $\mathbf{b}$  of the two spin analyzers are parallel we obtain

$$P_a^{(1)} \times P_b^{(2)} = -1. \quad (3.89a)$$

Both particles of a collision pair are always found in opposite spin states along whichever direction  $\mathbf{a}$  we choose to measure.

If both analyzers are set along opposite directions ( $\beta - \beta' = \pi$ ) we have strict correlation

$$P_a^{(1)} \times P_b^{(2)} = 1. \quad (3.89b)$$

Halfway between, for  $\beta - \beta' = \pi/2$ , the correlation parameter vanishes

$$P_a^{(1)} \times P_b^{(2)} = 0. \quad (3.89c)$$

It is instructive to rederive (3.88) and (3.89) in a more direct way by calculating the probabilities  $W(\mathbf{a}, \mathbf{b})_{Mm}$ . As explained in Sect. 3.6.3,  $W(\mathbf{a}, \mathbf{b})_{Mm}$  denotes the joint probability that the first particle of a collision pair is found with spin component  $M$  with respect to  $\mathbf{a}$ , and the second particle with spin component  $m$  with respect to  $\mathbf{b}$ . For example, the probability  $W(\mathbf{a}, \mathbf{b})_{++}$  that a

particle in the first beam is found in state  $|a(+)\rangle$ , and its partner in the second beam in state  $|b(+)\rangle$  follows from general quantum mechanical rules:

$$\begin{aligned} W(\mathbf{a}, \mathbf{b})_{++} &= |\langle a(+)b(+)|\Psi_-\rangle|^2 \\ &= \frac{1}{2} |\langle a(+)|+\rangle\langle b(+)|-\rangle - \langle a(+)|-\rangle\langle b(+)|+\rangle|^2, \end{aligned} \quad (3.90)$$

where we substituted (3.84a) for the singlet state and applied (A.7). The two factors containing  $|a(+)\rangle$  can be obtained immediately from (3.86a), and the results for  $|b(+)\rangle$  are obtained by replacing the polar angle  $\beta$  of  $\mathbf{a}$  by the polar angle  $\beta'$  of  $\mathbf{b}$  in (3.86). This yields

$$\begin{aligned} W(\mathbf{a}, \mathbf{b})_{++} &= \left| \cos \frac{\beta}{2} \sin \frac{\beta'}{2} - \sin \frac{\beta}{2} \cos \frac{\beta'}{2} \right|^2 \\ &= \frac{1}{2} \sin^2 \left( \frac{\beta - \beta'}{2} \right). \end{aligned} \quad (3.91a)$$

We can apply similar arguments to the other cases and we summarize the results as follows:

$$W(\mathbf{a}, \mathbf{b})_{+-} = \frac{1}{2} \cos^2 \left( \frac{\beta - \beta'}{2} \right), \quad (3.91b)$$

$$W(\mathbf{a}, \mathbf{b})_{-+} = \frac{1}{2} \cos^2 \left( \frac{\beta - \beta'}{2} \right), \quad (3.91c)$$

$$W(\mathbf{a}, \mathbf{b})_{--} = \frac{1}{2} \sin^2 \left( \frac{\beta - \beta'}{2} \right). \quad (3.91d)$$

Using (3.63) we rediscover the solutions (3.88) and (3.89). For example, for  $\beta = \beta'$  we obtain

$$W(\mathbf{a}, \mathbf{b})_{++} = W(\mathbf{a}, \mathbf{b})_{--} = 0, \quad (3.92a)$$

and

$$W(\mathbf{a}, \mathbf{b})_{+-} = W(\mathbf{a}, \mathbf{b})_{-+} = \frac{1}{2}, \quad (3.92b)$$

which gives perfectly anticorrelated measuring results. If the second analyzer is rotated into a direction  $\beta' = \beta \pm \pi/2$  we obtain that all four probabilities (3.91) are equal to 1/4. All combinations of particle pairs are then equally likely and we have no correlation between the measurements.

Let us further analyze the results (3.91) in order to make the connection with entanglement more explicit. Suppose the first observer chooses an arbitrary direction  $\mathbf{a}$  as orientation for his analyzer, and keeps  $\mathbf{a}$  fixed. This detection direction can be decided after the interaction of the two beams, when the particles have separated again (delayed choice mechanism). The coincident measurement can be split into two parts, such that the measurement on the first beam takes place first. Each particle in the first beam is then projected into one of the two eigenstates of the analyzer,  $|a(+)\rangle$  and  $|a(-)\rangle$ , respectively.

For example, assume that a particle has been found in state  $|a(+)\rangle$ . Quantum mechanics predicts by means of (3.87) that its distinct collision partner in the second beam, which has not yet interacted with any analyzer, is projected into the *definite* spin state  $|a(-)\rangle$  at the moment of the first measurement. Subsequently this particle enters then the second analyzer, oriented along direction  $\mathbf{b}$ , and is projected into one of the two eigenstates of the analyzer,  $|b(+)\rangle$  or  $|b(-)\rangle$ , with probability  $|\langle b(+)|a(-)\rangle|^2$  or  $|\langle b(-)|a(-)\rangle|^2$ , respectively.

These probabilities will be evaluated by rederiving the joint probabilities (3.91) in a slightly different way, for example

$$\begin{aligned} W(\mathbf{a}, \mathbf{b})_{++} &= |\langle a(+)|b(+)|\Psi_-\rangle|^2 \\ &= \frac{1}{2} |\langle b(+)|a(-)\rangle|^2, \end{aligned} \quad (3.93a)$$

where we have substituted (3.87) for  $|\Psi_-\rangle$  and used the orthonormality of the states  $|a(+)\rangle$  and  $|a(-)\rangle$ . Equation 3.93a suggests an interesting interpretation of the joint probabilities. For example, the first factor in (3.93a) (and (3.91a)) represents the probability  $W(\mathbf{a})_+ = 1/2$  of detecting a particle in the first beam in state  $|a(+)\rangle$  (before the second particle has been detected). The second factor in (3.93a) (and (3.91a)) is the probability that the other member of the collision pair, which with certainty has been projected into state  $|a(-)\rangle$  at the end of the measurement of the first particle, is detected in state  $|b(+)\rangle$  in the subsequent measurement by the second analyzer.

The other joint probabilities can be interpreted accordingly:

$$W(\mathbf{a}, \mathbf{b})_{+-} = \frac{1}{2} |\langle b(-)|a(-)\rangle|^2, \quad (3.93b)$$

$$W(\mathbf{a}, \mathbf{b})_{-+} = \frac{1}{2} |\langle b(+)|a(+)\rangle|^2, \quad (3.93c)$$

$$W(\mathbf{a}, \mathbf{b})_{--} = \frac{1}{2} |\langle b(-)|a(+)\rangle|^2. \quad (3.93d)$$

This reinterpretation of the probabilities has the advantage that the expressions can be directly related to the main conceptions of entanglement, and gives perhaps a more intuitive feeling for the contents of the preceding results.

By comparing (3.91) and (3.93), or by direct calculation, we obtain the explicit expressions:

$$|\langle b(+)|a(-)\rangle|^2 = \sin^2\left(\frac{\beta - \beta'}{2}\right), \quad (3.94a)$$

$$|\langle b(-)|a(-)\rangle|^2 = \cos^2\left(\frac{\beta - \beta'}{2}\right), \quad (3.94b)$$

$$|\langle b(+)|a(+)\rangle|^2 = \cos^2\left(\frac{\beta - \beta'}{2}\right), \quad (3.94c)$$

$$|\langle b(-)|a(+)\rangle|^2 = \sin^2\left(\frac{\beta - \beta'}{2}\right). \quad (3.94d)$$

The probabilities on the left-hand side of (3.94) are called *conditional probabilities* in statistics. They are probabilities for one measurement conditional on the result of another measurement. For example,  $|\langle b(+)|a(-)\rangle|^2$  is the probability of finding a particle in the second beam in the state  $|b(+)\rangle$  after the second measurement, under the condition, that its collision partner in the first beam has before been found and registered in state  $|a(+)\rangle$  (projecting the second particle in state  $|a(-)\rangle$ ). The relations (3.93) represent special cases of a more general relationship between joint and conditional probabilities.

General probability theory requires that the conditional probabilities are normalized, for example

$$|\langle b(+)|a(-)\rangle|^2 + |\langle b(-)|a(-)\rangle|^2 = 1, \quad (3.95a)$$

$$|\langle b(+)|a(+)\rangle|^2 + |\langle b(-)|a(+)\rangle|^2 = 1. \quad (3.95b)$$

Similarly, we must have

$$|\langle b(+)|a(-)\rangle|^2 + |\langle b(+)|a(+)\rangle|^2 = 1, \quad (3.95c)$$

$$|\langle b(-)|a(-)\rangle|^2 + |\langle b(-)|a(+)\rangle|^2 = 1. \quad (3.95d)$$

These conditions are satisfied by (3.94), so that there remains only one independent probability.

It is perhaps appropriate to summarize the various possibilities for the singlet state in Table 3.2. For example, the first two lines read that particle one has been found and registered with spin up with respect to the orientation  $\mathbf{a}$  of the first analyzer – detector set, with probability  $W(\mathbf{a})_+$ . Immediately afterwards its former collision partner in the second beam is projected with certainty into state  $|a(-)\rangle$ ; that is with conditional probability unity. (This is the essential point of entanglement theory which is responsible for the correlation of the first and the second measurement.) Subsequently, this particle passes the second analyzer – detector assembly, oriented

**Table 3.2** The various possibilities for the singlet state

	Result of first measurement	Second particle projected into state	Result of second measurement	Joint probability
State vector	$ a(+)\rangle$	$ a(-)\rangle$	$ b(+)\rangle$	
Probability	$W(\mathbf{a})_+ = 1/2$	1	$ \langle b(+) a(-)\rangle ^2$	$W(\mathbf{a}, \mathbf{b})_{++}$
State vector			$ b(-)\rangle$	
Probability			$ \langle b(-) a(-)\rangle ^2$	$W(\mathbf{a}, \mathbf{b})_{+-}$
State vector	$ a(-)\rangle$	$ a(+)\rangle$	$ b(+)\rangle$	
Probability	$W(\mathbf{a})_- = 1/2$	1	$ \langle b(+) a(+)\rangle ^2$	$W(\mathbf{a}, \mathbf{b})_{-+}$
State vector			$ b(-)\rangle$	
Probability			$ \langle b(-) a(+)\rangle ^2$	$W(\mathbf{a}, \mathbf{b})_{--}$

parallel to **b**, and is projected into one of the two eigenstates of the analyzer, either  $|b(+)\rangle$  or  $|b(-)\rangle$ , with the corresponding probabilities. The last column relates to the joint probabilities for the combined measurements.

Other cases than the singlet state can be treated similarly, for example following the procedures in Appendix I.1 and using equations like (I.8). Care must be taken if states with less than maximal entanglement are considered.

It is interesting that between the two measurements the second particle is in a definite quantum mechanical state, whether it is observed or not. This represents an *element of reality* in the sense of the EPR–paper to be discussed in the following subsection.

### 3.6.7 Entanglement and Non-Locality. Bell Inequalities

The discussion in the preceding subsection has shown the characteristic trait of entangled states. By performing an experiment on only one of the particles, not only can this particle's state vector be established by the measurement, but also that of its partner can be inferred without interfering with it. Quantum mechanics tells us that the result, obtained for a particle in one of the beams, depends on the choice made for the setting of the analyzer – detector assembly for the other beam, independent of how large their spatial separation is. This extraordinary feature of quantum mechanics is usually referred to as non-locality.

These quantum mechanical predictions for entangled states are in sharp contrast to classical expectations and have led to many controversial discussions, starting with the famous EPR–paper (Einstein et al. 1935). The authors argued that physics should combine

1. **Locality:** that is, the result of a measurement on one system should be unaffected by operations on a distant system, which it has interacted with in the past.
2. **Realism:** that is, particles should possess definite properties whether or not they are observed.

This led eventually to so-called *hidden-variable* theories. The hope was that by introducing hidden variables it might be possible to reproduce the quantum mechanical results within a local–realistic theory. Einstein found entanglement between spatially well-separated systems unbelievable.

However, in 1965 Bell derived a remarkable theorem which might be stated as follows:

**Theorem.** *There exists no local–realistic theory which reproduces all quantum mechanical results (Bell 1964).*

This is a crucial result. It shows that quantum theory and the common-sense assumption of local–realistic theories cannot both be right.

Bell derived a set of inequalities for measurable quantities for which quantum mechanical predictions differ from those of *any* local–realistic theory. The important point is that a more *philosophical* question (quantum mechanics versus EPR) can thus be settled by experiment in a very direct way. And if quantum mechanics is correct then non-locality is an important feature of our world.

A detailed discussion of these topics is outside the scope of this book and we refer to the literature cited below. We will only give two examples.

Consider the following combination of correlation parameters

$$\Delta = |P_a^{(1)} \times P_b^{(2)} - P_a^{(1)} \times P_{b'}^{(2)}| + |P_{a'}^{(1)} \times P_b^{(2)} + P_{a'}^{(1)} \times P_{b'}^{(2)}|, \quad (3.96)$$

where  $\mathbf{a}$ ,  $\mathbf{a}'$ ,  $\mathbf{b}$ , and  $\mathbf{b}'$  are four unit vectors. It has been shown that in *any* local–realistic theory, which uses hidden variables, the following inequality must hold for any arrangement of the four vectors:

$$\Delta \leq 2. \quad (3.97)$$

This is one of a family of inequalities collectively called *Bell inequalities*. The result (3.97) has been derived by [Clauser et al. \(1969\)](#). The inequality shows that in any local–realistic theory there is an upper limit to the strength of correlation of distant events.

Consider now the quantum mechanical predictions for  $\Delta$ . Consider two particles in a singlet state, far away from each other. Substitution of (3.88a) into (3.96) yields

$$\Delta = |\mathbf{a} \cdot \mathbf{b} - \mathbf{a} \cdot \mathbf{b}'| + |\mathbf{a}' \cdot \mathbf{b} + \mathbf{a}' \cdot \mathbf{b}'|. \quad (3.98)$$

Assume that the four vectors are coplanar and that the angles between  $\mathbf{a}$  and  $\mathbf{b}$ ,  $\mathbf{b}$  and  $\mathbf{a}'$ , and  $\mathbf{a}'$  and  $\mathbf{b}'$  are equal to  $\pi/4$  (with cosine  $1/\sqrt{2}$ ). The angle between  $\mathbf{b}'$  and  $\mathbf{a}$  is then  $3\pi/4$  (with cosine  $-1/\sqrt{2}$ ).

We obtain from (3.98)

$$\Delta = 2\sqrt{2}. \quad (3.99)$$

This result violates the inequality (3.97) by about 40%. This is an example of a special situation where the quantum mechanical predictions cannot be reproduced by local-realistic theories. There are of course many other arrangements of the four vectors for which the quantum theoretical results are in accordance with (3.97). Nevertheless, the result (3.99) is of great importance. It shows that it is impossible to understand *all* results of quantum theory within a local framework. The quantum mechanical correlations can be stronger than could ever exist between classical systems.

Next we will discuss the mixed state, described by the density operator (3.69). The only non-vanishing component of its correlation tensor is  $P_z^{(1)} \times P_z^{(2)}$  according to (3.70). Substitution of this result into (3.67c), and use of (3.51) yields

$$\begin{aligned} P_a^{(1)} \times P_b^{(2)} &= a_z b_z (P_z^{(1)} \times P_z^{(2)}) \\ &= -\cos \beta \cos \beta', \end{aligned} \quad (3.100)$$

which is independent of  $f$  and  $g$ .

Employing this result we check the validity of the inequality (3.97). Let us denote the polar angles of  $\mathbf{a}$  and  $\mathbf{b}$  by  $\beta$  and  $\beta'$  as before, and the polar angles of  $\mathbf{b}'$  and  $\mathbf{a}'$  by  $\beta(b')$  and  $\beta(a')$ , respectively. Calculating the parameter (3.96) by adapting a more general derivation by [Selleri \(1990\)](#), we obtain

$$\begin{aligned} \Delta &= |- \cos \beta \cos \beta' + \cos \beta \cos \beta(b')| \\ &\quad + |- \cos \beta(a') \cos \beta' + \cos \beta(a') \cos \beta(b')| \\ &= |\cos \beta| |- \cos \beta' + \cos \beta(b')| + |\cos \beta(a')| |\cos \beta' + \cos \beta(b')| \\ &\leq |- \cos \beta' + \cos \beta(b')| + |\cos \beta' + \cos \beta(b')| \\ &\leq 2. \end{aligned} \quad (3.101)$$

The last step follows from the general result, that  $x, y$  with  $|x| \leq 1, |y| \leq 1$  satisfy always the inequality

$$|x - y| + |x + y| \leq 2.$$

Hence, the mixed state (3.69) does not violate the inequality (3.97). This is not surprising if one remembers the classical nature of the mixture. Any particle is in a *definite* quantum state,  $|+\rangle$  or  $|-\rangle$ , (because of the method of preparation), independently of whether the particles are observed or not. This property corresponds to an element of reality in the sense defined in the EPR-paper. Furthermore, the two constituent beams of the mixture are correlated, but only because of classical communication during the preparation process. Hence, the mixture should behave similar to a classical system and the result (3.101) was to be expected.

More generally, it has been shown that any mixture of factorizable states satisfies Bells inequalities ([Selleri 1990](#)).

The ultimate proof of entanglement in a system is to show that Bell's inequalities are violated. In addition, any entangled state detected in this way violates *local realism*.

### 3.6.8 Experimental Tests. Conclusions

In the preceding subsections we have discussed the phenomenon of entanglement, or non-separability, and derived some of its surprising consequences. The apparent non-locality of the quantum mechanical conclusions is in sharp contrast to the *common sense* view of the classical local-realistic theories that whatever happens in some place cannot instantaneously affect what happens at distant locations. This point of view was particularly advocated in the EPR-paper mentioned above.

The discussion of these discrepancies was for many years considered as merely of philosophical interest. This changed when Bell derived in 1965 his famous theorem and pointed out the remarkable fact that the use of entanglement systems allow decisive experimental tests between the quantum mechanical and the local-realistic world-views by measuring certain combinations of correlation parameters, and checking the validity limits of Bells inequalities as discussed in the preceding subsection.

So far there has been only one experiment in which entanglement between spin-1/2 particles has been tested and to which we have referred in Sect. 3.6.6 ([Lamehi-Racht and Mittig 1976](#)). In this experiment correlated pairs of protons in the singlet state were observed and their spin correlations measured. Overcoming large difficulties the authors could show that the results were in agreement with quantum mechanical predictions.

Most experiments have been performed with pairs of polarized photons, pioneered by [Freedman and Clauser \(1972\)](#), and followed by a large number of experimental studies with increasing precision and efficiency. For example [Aspect et al. \(1982\)](#) designed polarizers whose direction in space could be changed at such high speed that the change could be made while the two correlated photons were still in flight. Furthermore, [Tittel et al. \(1998\)](#) reported about experiments where it had been possible to preserve entanglement over distances of about 10 km, in spite of the ever present danger of decoherences because of interactions with the environment (see for example Chap. 8 for a discussion of such decoherence processes). More recently, several groups have succeeded to prepare atoms in entangled states ([Hagley et al. 1997](#)).

In all experiments clear violation of Bells inequalities have been found. For example, ([Kwiat et al. 1995](#)) reported a violation by 100 standard deviations in a few minutes. In spite of some loopholes all experiments strongly suggest that nature behaves quantum mechanically and non-locally. All experiments have confirmed that entanglement is real and does not dissipate with increasing separation. It is not appropriate to think of an entangled pair as two particles with their own individual properties. Rather, an entangled system must be considered as a single entity even

when they are widely separated from each other. In this entanglement [Schrödinger \(1935\)](#) saw the characteristic trait of quantum mechanics, *the one that enforces its entire departure from classical line of thought*.

Furthermore, entanglement of three and more particles has been studied theoretically and experimentally and it has been shown that such systems offer a powerful and conceptually simpler approach to prove Bells theorem without using inequalities ([Greenberger et al. 1990](#)). Such correlated states show a strikingly non-classical behaviour.

There have been more discoveries with surprising and important consequences. It was realized that these fundamentally non-classical states can be used to perform tasks that cannot be achieved with classical systems. The basic concepts of superposition and entanglement (in particular multi-particle entanglement) play a crucial role in developments which offer new ways to technological advances. One can mention here the developments in quantum information, quantum cryptography, and quantum teleportation.

For detailed discussions and more references we must refer to the literature. We list here a few books and review papers, starting with introductory texts: [Selleri \(1990\)](#), [Le Bellac \(2006\)](#), [Aspect \(2001\)](#), [Duncan et al. \(2001\)](#), [Auletta \(2000\)](#), [Nielsen and Chuang \(2000\)](#), [Bouwmeester et al. \(2001\)](#), [Bruss and Leuchs \(2007\)](#). A very readable historical account has been given by [Aczel \(2003\)](#).

# Chapter 4

## Irreducible Components of the Density Matrix

### 4.1 Introduction

As discussed in Chaps. 1 and 2 it is often useful to expand  $\rho$  in terms of a conveniently chosen operator set  $Q_i$ . This method has two main advantages. First of all, it gives a more satisfactory definition of  $\rho$  (see, for example, Sect. 1.1.7), and secondly by using explicitly the algebraic properties of the basis operators the calculations are often greatly simplified (see Sect. 2.5). The usefulness of this method depends on the choice of the basis operator set. When the angular symmetries of the ensemble of interest are important it is convenient to expand  $\rho$  in terms of irreducible tensor operators. This method provides a well-developed and efficient way of using the inherent symmetry of the system. It also enables the consequences of angular momentum conservation to be simply allowed for and enables dynamical and geometrical factors in the equation of interest to be separated from each other.

The systematic use of tensor operators was first suggested by Fano (1953). Since then they have been applied extensively, for example in angular correlation theory in nuclear physics (Steffen and Alder 1975) and atomic physics (Blum and Kleinpoppen 1979), in optical pumping work (Happer 1972; Omont 1977), descriptions of quantum beat experiments (Fano and Macek 1973; Macek and Burns 1976; Andrä 1979) and experiments with laser-excited atoms (Hertel and Stoll 1978). The material presented in this and the following chapters is directly derived from these papers.

In this chapter the theory which is central to the subsequent discussions in this book will be presented and illustrated. In Sects. 4.2 and 4.3 spherical tensor operators and state multipoles will be introduced and their main properties derived. Extensive use will be made of angular momentum theory, but for the convenience of the reader some of the basic concepts are derived in the text and all the formulas which are used are listed in Appendix C.1. Readers who are not too familiar with the relevant mathematical techniques may omit the details of the calculations in a first reading.

The abstract theory will be illustrated by various examples. In Sect. 4.4 it will be shown that the state multipole description of spin systems is but a generalization of the approach of Sect. 1.1 which used the polarization vector. The discussion of spin-1 particles will illustrate the necessity of introducing tensors of higher rank than vectors.

In the following two sections it will be shown that the symmetry properties of a system can often be exploited more directly by using the multipole components than in terms of the density matrix elements. In Sect. 4.5 axially and spherically symmetric ensembles will be considered. In Sect. 4.6 the consequences of reflection invariance with respect to a given plane will be investigated.

In Sect. 4.6 we will continue with the discussion of the excited state density matrix introduced in Sect. 3.5 and consider another important aspect of the multipole expansion of  $\rho$ . The elements of  $\rho$  contain the full information on the scattering process; however, it is difficult to interpret these elements in terms of a physical picture and it is in this connection that the multipole components of  $\rho$  play an important role. It is often possible to anticipate the properties of the multipole components by considering the physics of the collision and we will illustrate this using the orientation vector as an example.

Finally, in Sect. 4.7, the time evolution of state multipoles in the presence of an internal or external perturbation will be considered.

The results obtained in this chapter will then be applied in Chaps. 5 and 6 where the full power of the irreducible tensor method will become evident.

## 4.2 The Definition of Tensor Operators

### 4.2.1 The General Construction Rule

Consider two ensembles of particles, the first with angular momenta  $J'$  and the second with angular momenta  $J$ . If the two ensembles interact it is convenient to classify the possible states in terms of the total angular momentum and its  $z$  component, which we will denote here by  $K$  and  $Q$ . Applying the usual angular momentum coupling rules gives

$$(|J'J)KQ\rangle = \sum_{M'M} (J'M', JM | KQ) |J'M')|JM\rangle \quad (4.1)$$

The states  $|JM\rangle$  are orthonormal since

$$\langle J'M'|JM\rangle = \delta_{M'M} \delta_{J'J} \quad (4.2)$$

Let us now consider the set of operators  $|J'M'\rangle\langle JM|$  defined as outer products of the angular momentum states as in (1.24). The state  $|JM\rangle$  can be represented by

a  $(2J + 1)$ -dimensional column vector with a unit element in the  $M$ th row and zeros elsewhere, and the corresponding adjoint state  $\langle JM|$  is then represented by a row vector with a unit element in the  $M$ th column and zeros elsewhere. The outer product can then be represented by matrices using the rule (1.24).

It is convenient to combine the operators  $|J'M'\rangle\langle JM|$  in a way similar to (4.1). A set of operators  $T(J'J)_{KQ}$  is defined by the relation<sup>1</sup>

- $$T(J'J)_{KQ} = \sum_{M'M} (-1)^{J-M} (J'M', J - M | KQ) | J'M' \rangle \langle JM | \quad (4.3)$$

The Clebsch-Gordan coefficient vanishes unless the usual angular momentum coupling rules are satisfied:

- $$|J' - J| \leq K \leq J' + J, \quad -K \leq Q \leq K \quad (4.4)$$

As a consequence, for any given pair of angular momenta  $J'$  and  $J$  the number of operators (4.3) is limited; thus, for example, if  $J' = J = 1$  the possible operators are one with  $K = 1$  (and  $Q = 0, \pm 1$ ), and five with  $K = 2$  (and  $Q = \pm 2, \pm 1, 0$ ).

An explicit matrix representation of the operators (4.3) can be obtained by “sandwiching” (4.3) between states  $\langle J'N'|$  and  $|JN\rangle$  ( $N' = J', \dots, -J'$ ,  $N = J, \dots, -J$ ) and applying condition (4.2):

$$\begin{aligned} \langle J'N' | T(J'J)_{KQ} | JN \rangle &= \sum_{M'M} (-1)^{J-M} (J'M', J - M | KQ) \langle J'N' | J'M' \rangle \langle JM | JN \rangle \\ &= (-1)^{J-N} (J'N', J - N | KQ) \end{aligned} \quad (4.5)$$

The set of all elements of a given operator  $T(J'J)_{KQ}$  defines a matrix with  $(2J' + 1)$  rows and  $(2J + 1)$  columns:

$$T(J'J)_{KQ} = \begin{pmatrix} \langle J'J' | T(J'J)_{KQ} | JJ \rangle & \langle J'J' | T(J'J)_{KQ} | J, J-1 \rangle & \dots & \langle J'J' | T(J'J)_{KQ} | J, -J \rangle \\ \langle J', J' - 1 | T(J'J)_{KQ} | JJ \rangle & \langle J', J' - 1 | T(J'J)_{KQ} | J, J-1 \rangle & \dots & \langle J', J' - 1 | T(J'J)_{KQ} | J, -J \rangle \\ \langle J', -J' | T(J'J) | JJ \rangle & \langle J', -J' | T(J'J)_{KQ} | J, J-1 \rangle & \dots & \langle J', -J' | T(J'J)_{KQ} | J, -J \rangle \end{pmatrix} \quad (4.6)$$

If  $J' = J$  this gives a  $(2J + 1)$ -dimensional square matrix.

The inverse form of (4.3) is obtained by multiplying both sides with a Clebsch-Gordan coefficient  $(J'N', J - N | KQ)$ , summing over all values of  $K$  and  $Q$ , and using the orthogonality properties of the Clebsch-Gordan coefficients (see Appendix C.1):

---

<sup>1</sup>We will only consider operators with integer  $K$ .

$$\begin{aligned}
& \sum_{KQ} (J'N', J - N | KQ) T(J'J)_{KQ} \\
&= \sum_{M'M} (-1)^{J-M} \left[ \sum_{KQ} (J'N', J - N | KQ) (J'M', J - M | KQ) \right] |J'M'\rangle \langle JM| \\
&= (-1)^{J-N} |J'N'\rangle \langle JN|
\end{aligned}$$

or

$$|J'N'\rangle \langle JN| = \sum_{KQ} (-1)^{J-N} (J'N', J - N | KQ) T(J'J)_{KQ} \quad (4.7)$$

Finally, if the  $3j$ -symbol notation is used for the coupling coefficient the definition (4.3) can be rewritten as

$$\bullet \quad T(J'J)_{KQ} = \sum_{M'M} (-1)^{J'-M'} (2K + 1)^{1/2} \begin{pmatrix} J' & J & K \\ M' & -M & -Q \end{pmatrix} |J'M'\rangle \langle JM| \quad (4.8)$$

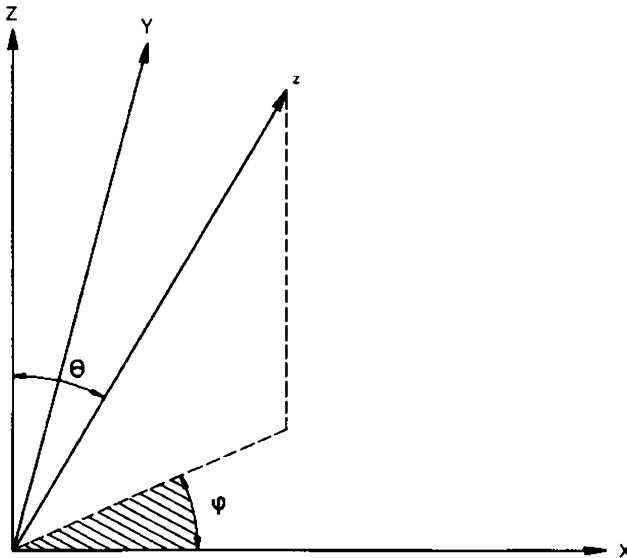
which gives

$$\bullet \quad \langle J'M' | T(J'J)_{KQ} | JM \rangle = (-1)^{J'-M'} (2K + 1)^{1/2} \begin{pmatrix} J' & J & K \\ M' & -M & -Q \end{pmatrix} \quad (4.9)$$

This particular form is of great utility since the special symmetry properties of the  $3j$  symbol (C.5) allow the corresponding symmetry properties of the tensor operators to be treated in the most direct way.

#### 4.2.2 Transformation Properties Under Rotations. The Rotation Matrix

In order to clarify the meaning of (4.3) we will now consider the transformation properties of the tensor operators under rotations. The angular momentum states (4.1) and the operators (4.3) are defined with respect to a fixed coordinate system, for example, with axes  $X$ ,  $Y$ ,  $Z$ . Suppose that a second system with axes  $x$ ,  $y$ ,  $z$  is obtained by the following two consecutive rotations: (1) a rotation of angle  $\varphi$  about the  $Z$  axis (the new axes are then  $x'$ ,  $y$ ,  $Z$ ), and (2) a rotation of angle  $\theta$  about the  $y$  direction (which transforms  $x'$  and  $Z$  into  $x$  and  $z$ , respectively). These rotations are counterclockwise when looking down the rotation axis toward the origin. The Euler angles as defined by Edmonds (1957) are then given by  $\alpha = \varphi$ ,  $\beta = \theta$ ,  $\gamma = 0$ .  $\theta$  and  $\varphi$  are the polar angles of the  $z$  axis with respect to the  $XYZ$  system (see Fig. 4.1). The  $x$  axis has polar angles



**Fig. 4.1** Illustration of the rotation defined by the angles  $\Theta$  and  $\varphi$

$(\theta + 90^\circ, \varphi)$  and the  $y$  axis is specified by  $(90^\circ, \varphi + 90^\circ)$

The angular momentum operator  $\mathbf{J}$  has a component  $J_z$  with respect to the  $Z$  axis and a component  $J_z$  with respect to the  $z$  axis. We will denote the eigenvalues of  $J_z$  by  $M$  and the eigenvalues of  $J_z$  by  $m$ . An eigenstate  $|JM\rangle$  of  $J_z$  is not an eigenstate for  $J_z$  for  $Z \neq z$  because in general the two operators do not commute. Using the superposition principle (2.1) the state  $|JM\rangle$  can be written as a linear superposition of the eigenstates  $|Jm\rangle$  of  $J_z$  with expansion coefficients which will depend on the angular momentum quantum numbers and the Euler angles  $\omega = (\gamma, \beta, \alpha)$ . It is customary to denote the expansion coefficients by  $D(\omega)_{mM}^{(J)}$ :

$$|JM\rangle = \sum_m |Jm\rangle D(\omega)_{mM}^{(J)} \quad (4.10)$$

We can interpret the coefficients as the probability amplitudes of finding a state  $|Jm\rangle$  in a given state  $|JM\rangle$  if the latter system is related to the former by the Euler angles  $\omega$ . For fixed  $J$  the set of all coefficients can be written in the form of a matrix, call the *rotation matrix* the elements of which are the amplitudes  $D(\omega)_{mM}^{(J)}$ . Explicit expressions for various  $J$  are given, for example, in [Edmonds \(1957\)](#) (see also Appendix C.1).

The transformation law for the adjoint state  $\langle JM|$  is [see (2.5)]

$$\langle JM| = \sum_m D(\omega)_{mM}^{(J)*} \langle Jm| \quad (4.11)$$

Let us now relate the operators  $T(J'J)_{KQ}$ , defined in the *XYZ* system, to operators  $T(J'J)_{Kq}$  which are defined in the *xyz* system. In order to do this (4.10) and (4.11) are inserted into (4.3) and the symmetry property

$$D_{mM}^{(J)*} = (-1)^{m-M} D_{-m-M}^{(J)}$$

of the rotation matrix. Since  $m - M$  is an integer  $(-1)^{m-M} = (-1)^{M-m}$  and we obtain

$$\begin{aligned} T(J'J)_{KQ} &= \sum_{M'M} (-1)^{J'-M} (J'M', J - M | KQ) \\ &= \sum_{m'm} |J'm'\rangle \langle JM| \sum_{M'M} (J'M', J - M | KQ) \\ &\quad \times (-1)^{J-m} D(\omega)_{m'M'}^{(J')} D(\omega)_{-m-M}^{(J)} \\ &= \sum_{m'm} (-1)^{J-m} |J'm'\rangle \langle Jm| \sum_{kqq'} (J'm', J - m | kq) \\ &\quad \times \left[ \sum_{M'M} (J'M', J - M | KQ) (J'M', J - M | kq') D_{qq'}^{(k)} \right] \\ &= \sum_q \left[ \sum_{m'm} (-1)^{J-m} (J'm', J - m | Kq) |J'm'\rangle \langle Jm| \right] D(\omega)_{qQ}^{(K)} \quad (4.12) \end{aligned}$$

which finally gives

$$\bullet \quad T(J'J)_{KQ} = \sum_q T(J'J)_{Kq} D(\omega)_{qQ}^{(K)} \quad (4.13)$$

In obtaining (4.13) the product  $D(\omega)_{m'M'}^{(J')} D(\omega)_{-m-M}^{(J)}$  has been written as a linear combination of matrices  $D(\omega)_{qq'}^{(k)}$  [see (C.17)], performed the sum over  $M'$  and  $M$  using the orthonormality relations of the Clebsch-Gordan coefficients, and finally the definition (4.3) applied. Equation 4.13 expresses the operators  $T(J'J)_{KQ}$  defined in the *XYZ* system, in terms of the operators  $T(J'J)_{Kq}$ , defined in the *xyz* system.

Operators which transform under rotations according to (4.13) are called *irreducible tensor operators of rank K and component Q*. Equation 4.13 shows that the rank of a tensor operator remains invariant under a rotation. We will discuss some examples of the use of this equation in the following section.

### 4.2.3 Examples

In this section we will consider the case of sharp angular momentum ( $J' = J$ ) and denote the corresponding tensor operators by  $T(J)_{KQ}$ . First of all we will show that the operator with rank  $K = 0$  is a scalar operator, that is, it remains invariant under all rotations. This can be demonstrated by showing that  $T(J)_{00}$  is proportional to the  $(2J + 1)$ -dimensional unit matrix  $\mathbf{1}$ . From the definition (4.8) and (C.6) we have

$$\begin{aligned} T(J)_{00} &= \sum_{M'M} (-1)^{J' - M'} \begin{pmatrix} J' & J & 0 \\ M' & -M & 0 \end{pmatrix} |JM'\rangle \langle JM| \\ &= \frac{1}{(2J + 1)^{1/2}} \sum_M |JM\rangle \langle JM| \\ &= \frac{1}{(2J + 1)^{1/2}} \mathbf{1} \end{aligned} \quad (4.14)$$

where the completeness relation  $\sum_M |JM\rangle \langle JM| = \mathbf{1}$  has been used.

Tensor operators of rank  $K = 1$  are called *vector operators*. The three vector components  $T(J)_{1Q}$  can be related to the components of the angular momentum vectors  $\mathbf{J}$  with respect to the fixed *XYZ* system,  $J_X$ ,  $J_Y$ ,  $J_Z$ , as follows. We introduce the *spherical vector components* defined as

$$J_{\pm} = \mp \frac{1}{2^{1/2}} (J_X \pm iJ_Y), \quad J_0 = J_Z \quad (4.15)$$

Thus

$$J_0 |JM\rangle = M |JM\rangle$$

and, for sharp  $J$ ,  $J_0$  can be represented by a  $(2J + 1)$ -dimensional diagonal matrix with elements

$$\langle JM' | J_0 | JM \rangle = M \delta_{M'M} \quad (4.16a)$$

$T(J)_{10}$  is represented by the matrix

$$\begin{aligned} \langle JM' | T(J)_{10} | JM \rangle &= (-1)^{J-M} (3)^{1/2} \begin{pmatrix} J & J & 1 \\ M' & -M & 0 \end{pmatrix} \\ &= \left[ \frac{3}{(2J + 1)(J + 1)J} \right]^{1/2} M \delta_{M'M} \end{aligned} \quad (4.16b)$$

which satisfies (4.8). Similarly, using the standard results of angular momentum theory:

$$J_{\pm 1} |JM\rangle = \mp \frac{1}{2^{1/2}} [(J \mp M)(J \pm M + 1)]^{1/2} |JM \pm 1\rangle$$

the matrix representations of the other components are

$$\langle JM' | J_{\pm 1} | JM \rangle = \mp \frac{1}{2^{1/2}} [J \mp M)(J \pm M + 1)]^{1/2} \delta_{M', M \pm 1} \quad (4.17a)$$

On the other hand, using (4.9)

$$\begin{aligned} \langle JM' | T(J)_{1,\pm 1} | JM \rangle &= (-1)^{J-M'} 3^{1/2} \begin{pmatrix} J & J & 1 \\ M' & -M & \mp 1 \end{pmatrix} \\ &= \mp \frac{3^{1/2}}{2^{1/2}} \left[ \frac{(J \mp M)(J \pm M + 1)}{(2J + 1)(J + 1)J} \right]^{1/2} \delta_{M', M \pm 1} \end{aligned} \quad (4.17b)$$

By composing (4.16a) and (4.17a) with (4.16b) and (4.17b), respectively, we obtain the operator relation:

$$T(J)_{1Q} = \left[ \frac{3}{(2J + 1)(J + 1)J} \right]^{1/2} J_Q \quad (4.18)$$

Thus the vector operators  $T(J)_{1Q}$  are proportional to the spherical components of the angular momentum operator.

Similarly, the second-rank tensor  $T(J)_{2Q}$  can be related to quadratic combinations of the angular momentum vector components. The spherical components  $T(J)_{2Q}$  of the second-rank tensor are related to the Cartesian components by the following equations (which are given without proof):

$$\begin{aligned} T(J)_{20} &= \frac{N_2}{6^{1/2}} (3J_Z^2 - \mathbf{J}^2) \\ T(J)_{2\pm 1} &= \mp \frac{N_2}{2} [(J_X J_Z + J_Z J_X) \pm i(J_Y J_Z + J_Z J_Y)] \\ T(J)_{2\pm 2} &= \frac{N_2}{2} [J_X^2 - J_Y^2 \pm i(J_X J_Y + J_Y J_X)] \end{aligned} \quad (4.19)$$

with

$$N_2 = \left[ \frac{30}{(2J + 3)(2J + 1)J(2J - 1)(J + 1)} \right]^{1/2} \quad (4.20)$$

It should be noted that relations (4.18) and (4.19) hold only in the case of sharp angular momentum. The matrix elements of  $J_Q$  vanish between states  $\langle J'M' |$  and  $|JM \rangle$  with  $J' \neq J$ , whereas the elements of  $T(J'J)_{KQ}$  are in general nonzero for  $J' \neq J$ . We will return to this point in the following section.

#### 4.2.4 Some Important Properties of the Tensor Operators

The adjoint  $T(J'J)_{KQ}^\dagger$  of an operator  $T(J'J)_{KQ}$  is defined by expressing its matrix elements in terms of the elements (4.9):

$$\langle JM | T(J'J)_{KQ}^\dagger | J'M' \rangle = \langle J'M' | T(J'J)_{KQ} | JM \rangle^* \quad (4.21)$$

In this case the star denoting the complex conjugate is superfluous because the elements (4.9) are real. Equation 4.21 defines a matrix representation of  $T(J'J)_{KQ}^\dagger$ . This is a matrix with  $(2J + 1)$  rows and  $(2J' + 1)$  columns which is obtained by interchanging the rows and columns of the matrix (4.9). In order to obtain a relation between the operators the right-hand side of (4.21) is transformed into a matrix with  $(2J + 1)$  rows and  $(2J' + 1)$  columns. Substituting (4.9) into (4.21) and using the symmetry property (C.5a) of the  $3j$  symbol yields

$$\begin{aligned} \langle JM | T(J'J)_{KQ}^\dagger | J'M' \rangle &= (-1)^{J'-M'} \begin{pmatrix} J' & J & K \\ M' & -M & -Q \end{pmatrix} (2K + 1)^{1/2} \\ &= (-1)^{J'-M'} (2K + 1)^{1/2} \begin{pmatrix} J & J' & K \\ M & -M' & Q \end{pmatrix} \\ &= (-1)^{J'-J+Q} \langle JM | T(JJ')_{K-Q} | J'M' \rangle \end{aligned} \quad (4.22)$$

where the  $3j$  symbol in the second line has been expressed in terms of the elements (4.9). From (4.22) it follows that

- $T(J'J)_{KQ}^\dagger = (-1)^{J'-J+Q} T(JJ')_{K-Q}$  (4.23)

where now both operators are represented by matrices with  $(2J + 1)$  rows and  $(2J' + 1)$  columns.

Equation 4.23 can be used to derive an important result. With the help of (4.9) and (4.21) and the orthonormality condition of the  $3j$  symbols we obtain

$$\begin{aligned} \bullet \quad \text{tr } T(J'J)_{KQ} T(J'J)_{K'Q'} &= \sum_{M'M} \langle J'M' | T(J'J)_{KQ} | JM \rangle \langle JM | T(J'J)_{K'Q'}^\dagger | J'M' \rangle \\ &= \delta_{K'K} \delta_{Q'Q} \end{aligned} \quad (4.24)$$

It should be noted that the product  $T(J'J)_{KQ} T(J'J)_{K'Q'}^\dagger$ , corresponds to a square matrix with  $(2J' + 1)$  rows and columns and hence the trace of the product is well defined. It follows from (4.24) that

$$\text{tr } T(J)_{KQ} = \text{tr } T(J)_{KQ} \cdot 1 = (2J + 1)^{1/2} \delta_{K0} \delta_{Q0} \quad (4.25)$$

where we used the relation (4.14). All tensors  $T(J)_{KQ}$  therefore have zero trace except the monopole.

Finally, we recall from angular momentum theory that all irreducible tensor operators  $V_{KQ}$  satisfy the Wigner-Eckart theorem:

- $\langle J'M' | V_{KQ} | JM \rangle = (-1)^{J'-M'} \begin{pmatrix} J' & K & J \\ -M' & Q & +M \end{pmatrix} \langle J' | V_K | J \rangle$  (4.26)

It is important to note that the “reduced” matrix element  $\langle J' \| V_K \| J \rangle$  is a scalar and independent of  $M'$ ,  $M$ , and  $Q$ . The  $3j$  symbol, on the other hand, is a well-defined number which reflects the geometry of the interaction. The Wigner-Eckart theorem therefore separates out those quantities which depend explicitly on the dynamics of the interaction from those which are purely geometrical.

Applying (4.26) to the tensor operators  $T(J'J)_{KQ}$  gives

$$\langle J'M'|T(J'J)_{KQ}|JM\rangle = (-1)^{J'-M'} \begin{pmatrix} J' & K & J \\ -M' & Q & M \end{pmatrix} \langle J' \| T_K \| J \rangle \quad (4.27)$$

where  $\langle J' \| T_K \| J \rangle$  is the corresponding reduced matrix element. Comparing (4.27) with (4.9) and using the symmetry property of the  $3j$  symbol (C5) it can be seen that

$$\langle J' \| T_K \| J \rangle = (2K + 1)^{1/2} \quad (4.28)$$

Inserting (4.28) back into (4.27) shows that the tensor operators  $T(J'J)_{KQ}$  are purely geometrical quantities.

## 4.3 State Multipoles (Statistical Tensors)

### 4.3.1 Definition of State Multipoles

Consider an ensemble of particles in various angular momentum states  $|JM\rangle$  characterized by a density matrix  $\rho$  with elements  $\langle J'M'|\rho|JM\rangle$  [see, for example, (2.30)]. The density operator in the  $\{|JM\rangle\}$  representation can then be written in the form

$$\rho = \sum_{J'JM'M} \langle J'M'|\rho|JM\rangle |J'M'\rangle \langle JM| \quad (4.29)$$

according to (2.10) and (2.11). Substitution of (4.7) into (4.29) yields

$$\begin{aligned} \rho = \sum_{J'JKQ} \left[ \sum_{M'M} \langle J'M'|\rho|JM\rangle (-1)^{J'-M'} \begin{pmatrix} J' & J & K \\ M' & -M & -Q \end{pmatrix} \right. \\ \left. \times (2K + 1)^{1/2} \right] T(J'J)_{KQ} \end{aligned} \quad (4.30)$$

The *state multipoles* or *statistical tensors* are defined as

$$\begin{aligned} \bullet \quad \left\langle T(J'J)_{KQ}^\dagger \right\rangle = \sum_{M'M} (-1)^{J'-M'} (2K + 1)^{1/2} \begin{pmatrix} J' & J & K \\ M' & -M & -Q \end{pmatrix} \\ \langle J'M'|\rho|JM\rangle \end{aligned} \quad (4.31)$$

Using (4.31) in (4.30) gives the expansion of the density operator in terms of irreducible tensor operators:

- $\rho = \sum_{J'JKQ} \langle T(J'J)_{KQ}^\dagger \rangle T(J'J)_{KQ}$  (4.32)

Multiplying both sides of (4.32) by  $T(J'J)_{K'Q'}^\dagger$ , taking the trace, and using the relation (4.24) gives

- $\langle T(J'J)_{KQ}^\dagger \rangle = \text{tr } \rho T(J'J)_{KQ}^\dagger$  (4.33)

which is equivalent to (4.31). The expression (4.31) can be inverted by multiplying both sides by

$$(2K+1)^{1/2} \begin{pmatrix} J' & J & K \\ N' & -N & -Q \end{pmatrix}$$

and summing over all values of  $K$  and  $Q$ . This gives

- $\langle J'N'|\rho|JN\rangle = \sum_{KQ} (-1)^{J'-N'} (2K+1)^{1/2} \begin{pmatrix} J' & J & K \\ N' & -N & -Q \end{pmatrix} \times \langle T(J'J)_{KQ}^\dagger \rangle$  (4.34)

*The two descriptions of a system, in terms of density matrix elements and in terms of state multipoles, are therefore equivalent.* They can be transformed into each other by applying (4.31) and (4.34). Equations 4.31–4.34 are of great importance in all problems where angular momentum properties play a role, for example in angular correlation theory, optical pumping work, and spin-polarization phenomena. The utility of the state multipoles will become evident through the examples and discussions in the following chapters of this book.

If the ensemble of interest is an incoherent mixture of  $J$  states the density matrix is diagonal in  $J$  according to Sect. 2.3:

$$\langle J'M'|\rho|JM\rangle = \langle JM'|\rho|JM\rangle \delta_{J'J}$$

and from (4.31) follows

$$\langle T(J'J)_{KQ}^\dagger \rangle = \langle T(J)_{KQ}^\dagger \rangle \delta_{J'J}$$

Equation 4.32 then reduces to

$$\rho = \sum_{JKQ} \langle T(J)_{KQ}^\dagger \rangle T(J)_{KQ} \quad (4.35)$$

This result shows that multipoles  $T(J'J)_{KQ}$  with  $J' \neq J$  describe the coherence between states of different angular momentum  $J$ .

If the ensemble of interest is an incoherent superposition of states with different quantum numbers  $M$ , then the density matrix is diagonal in  $M$  and (4.31) shows that all multipoles with  $Q \neq 0$  vanish. The corresponding density operator is then given by

$$\rho = \sum_{J'JK} \langle T(J'J)_{K0}^{\dagger} T(J'J)_{K0} \rangle \quad (4.36)$$

Hence the coherence between states with different quantum number  $M$  is characterized by the nonvanishing multipoles with  $Q \neq 0$ .

### 4.3.2 Basic Properties of State Multipoles

The hermiticity condition (2.12) becomes

$$\langle J'M'|\rho|JM\rangle = \langle JM|\rho|J'M'\rangle^* \quad (4.37)$$

for the case under discussion here. By taking the complex conjugate of (4.31), using (4.37) we obtain

- $\langle T(J'J)_{KQ}^{\dagger} \rangle^* = (-1)^{J'-J+Q} \langle T(JJ')_{K-Q}^{\dagger} \rangle \quad (4.38)$

For sharp angular momentum  $J' = J$  (4.38) implies

- $\langle T(J)_{KQ}^{\dagger} \rangle^* = (-1)^Q \langle T(J)_{K-Q}^{\dagger} \rangle \quad (4.39)$

which relates the multipoles of components  $Q$  and  $-Q$  to each other. In particular (4.39) ensures that the multipoles  $\langle T(J)_{KQ}^{\dagger} \rangle$  are real numbers.

In many cases an alternative set of parameters is used:

$$\langle T(J'J)_{KQ} \rangle = \text{tr } \rho T(J'J)_{KQ} \quad (4.40a)$$

[employing the operator  $T(J'J)_{KQ}$  instead of its adjoint]. Substitution of (4.23) into (4.40a) and use of the definition (4.33) yields

$$\langle T(J'J)_{KQ}^{\dagger} \rangle = (-1)^{J'-J+Q} \langle T(JJ')_{K-Q} \rangle \quad (4.40b)$$

Applying (4.38) the two parametrizations can be seen to be related to each other by

$$\langle T(J'J)_{KQ}^{\dagger} \rangle^* = \langle T(J'J)_{KQ} \rangle \quad (4.40c)$$

In order to see the significance of (4.31) we will consider the transformation properties of the state multipoles under rotations. A set of multipoles  $\langle T(J'J)_{KQ}^\dagger \rangle$  can be defined with respect to a coordinate system with axes  $X$ ,  $Y$ ,  $Z$  with corresponding quantum numbers  $M'$ ,  $M$ ,  $Q$  in (4.31). A second set of multipoles  $\langle T(J'J)_{Kq}^\dagger \rangle$  can be defined with respect to the coordinate system  $x$ ,  $y$ ,  $z$  shown in Fig. 4.1. Using (4.40c) and (4.13),

$$\begin{aligned}\langle T(J'J)_{KQ}^\dagger \rangle &= \langle T(J'J)_{KQ} \rangle^* = [\text{tr } \rho T(J'J)_{KQ}]^* \\ &= \left[ \sum_q D(\omega)_{qQ}^{(K)} \text{tr } \rho T(J'J)_{Kq} \right]^*\end{aligned}$$

Using (4.40a, c) then gives

- $$\langle T(J'J)_{KQ}^\dagger \rangle = \sum_q \langle T(J'J)_{Kq}^\dagger \rangle D(\omega)_{qQ}^{(K)*} \quad (4.41)$$

*This result shows that the state multipoles transform as irreducible tensors of rank  $K$  and component  $Q$ .*

### 4.3.3 Physical Interpretation of State Multipoles. The Orientation Vector and Alignment Tensor

The irreducible components  $\langle T_{KQ}^\dagger \rangle$  of the density matrix in general have a deeper physical significance than the elements of  $\rho$ . In this section we will discuss the physical interpretation of the lower-rank tensors in the case of sharp angular momentum.

The tensor with rank  $K = 0$  is merely a normalization constant. Taking the trace of (4.32) and using (4.25) gives

$$\langle T(J)_{00}^\dagger \rangle = \frac{\text{tr } \rho}{(2J+1)^{1/2}} \quad (4.42)$$

The three components with  $K = 1$  and  $Q = \pm 1, 0$  transform as the components of a vector. From (4.18) and the definition (4.33) it is readily found that

$$\begin{aligned}\langle T(J)_{1Q}^\dagger \rangle &= \left[ \frac{3}{(2J+1)(J+1)J} \right]^{1/2} \text{tr } \rho J_Q^\dagger \\ &= \left[ \frac{3}{(2J+1)(J+1)J} \right]^{1/2} \langle J_Q^\dagger \rangle \text{tr } \rho \quad (4.43)\end{aligned}$$

where the expectation value  $\langle J_Q^\dagger \rangle$  of the operator  $J_Q^\dagger$  is defined by (2.19a). Taking the complex conjugate of (4.43) and using the relation (4.40c) we obtain the alternative form:

$$\langle T(J)_{1Q} \rangle = \left[ \frac{3}{(2J+1)(J+1)J} \right]^{1/2} \langle J_Q \rangle \operatorname{tr} \rho \quad (4.44a)$$

The three parameters  $\langle T(J)_{1Q}^\dagger \rangle$  with  $Q = \pm 1, 0$  are often called the components of the “orientation vector.” As shown by (4.43) the orientation vector is proportional to the net angular momentum  $\langle \mathbf{J} \rangle$  of the ensemble under discussion. Since

$$\langle \boldsymbol{\mu} \rangle = -g\mu_B \langle \mathbf{J} \rangle \quad (4.45)$$

where  $\langle \boldsymbol{\mu} \rangle$  denotes the magnetic dipole vector averaged over the ensemble under consideration, it can be seen that *the orientation vector is proportional to the net magnetic dipole vector of the given system* ( $g$  is the Landé factor,  $\mu_B$  the Bohr magneton).

In a similar way the components  $\langle T(J)_{2Q}^\dagger \rangle$  of the second-rank tensor can be expressed in terms of quadratic combinations of the angular momentum components using (4.19) and (4.33). For example,

$$\langle T(J)_{20}^\dagger \rangle = \frac{N_2}{6^{1/2}} \langle 3J_Z^2 - \mathbf{J}^2 \rangle \operatorname{tr} \rho \quad (4.46)$$

The tensor  $\langle T(J)_{2Q}^\dagger \rangle$  is called the *alignment tensor*. Its physical significance follows from the fact that *the components  $\langle T(J)_{2Q}^\dagger \rangle$  are proportional to the spherical components  $\langle Q_{2Q} \rangle$  of the electric quadrupole tensor*. This can be seen in the following way. The expectation value  $\langle Q_{2Q} \rangle$  is defined by (2.19a). Applying the Wigner-Eckart theorem to the matrix elements of  $Q_{2Q}$  gives

$$\begin{aligned} \langle Q_{2Q} \rangle \operatorname{tr} \rho &= \operatorname{tr} \rho Q_{2Q} \\ &= \sum_{M'M} \langle JM' | \rho | JM \rangle \langle Q_{2Q} | JM' \rangle \\ &= \langle J \| Q_2 \| J \rangle \sum_{M'M} \langle JM' | \rho | JM \rangle (-1)^{J-M} \begin{pmatrix} J & 2 & J \\ -M & Q & M' \end{pmatrix} \end{aligned}$$

Using the symmetry properties of the  $3j$  symbols and substitution of (4.31) then gives

$$\langle Q_{2Q} \rangle \operatorname{tr} \rho = \frac{\langle J \| Q_2 \| J \rangle}{5^{1/2}} \langle T(J)_{2Q} \rangle \quad (4.47)$$

where the reduced matrix element is proportional to the quadrupole moment of the system (see, for example, [Edmonds 1957](#)).

Equation [4.47](#) illustrates how the expansion of  $\rho$  in terms of irreducible components, combined with the Wigner-Eckart theorem, enables the geometrical and dynamical properties of the system to be separated. The reduced matrix element contains all information on the dynamics while the tensor  $\langle T(J)_{2Q} \rangle$  describes the geometrical properties of the relevant ensemble. This aspect of the theory will be of increasing importance to our subsequent discussions.

The components of the alignment tensor can be expressed in terms of Cartesian components. From [\(4.19\)](#) we obtain, for example,

$$\langle T_{20} \rangle = \frac{N_2}{(6)^{1/2}} \langle 3J_Z^2 - J^2 \rangle \quad (4.48)$$

assuming that  $\text{tr}\rho = 1$ .

Relations like [\(4.43\)](#) and [\(4.48\)](#) provide a physical interpretation of state multipoles that may be useful in depicting the ensemble. In the classical limit they become moments of spatial angular momentum distributions. We will study the classical interpretation in Sects. [4.5](#) and, in particular, [7.2](#). Furthermore, in Sect. [4.6.5](#) we will show that there is a close relation between the alignment components and shape and spatial orientation of atomic charge clouds.

- Finally, we give the following definition. A system is *oriented* if at least one multipole with  $K$  odd is nonvanishing. The system is said to be *aligned* if at least one tensor component with  $K$  even is different from zero.

The results given in this subsection hold only for sharp  $J$ . Multipoles  $\langle T(J'J)_{KQ}^\dagger \rangle$  describe the coherence between states of different momenta within a system, or the joint multipoles of two systems with angular momenta  $J'$  and  $J$  respectively (for example, orbital angular momentum and spin). Applications will be given in subsequent chapters (for example in Sect. [4.6](#)).

## 4.4 Examples: Spin Tensors

### 4.4.1 Spin Tensors for Spin-1/2 Particles

We start by reexamining the description of spin-1/2 particles characterized by a density matrix  $\rho$  with elements  $\langle m'|\rho|m\rangle$ . We define a set of stat multipoles  $\langle T(S)_{KQ}^\dagger \rangle$ , the *spin tensors*, by means of [\(4.31\)](#). Thus, for  $S = 1/2$ , we write

$$\langle T(1/2)_{KQ}^\dagger \rangle = \sum_{m'm} (-1)^{(1/2)-m'} (2K+1)^{1/2} \begin{pmatrix} 1/2 & 1/2 & K \\ m' & -m & -Q \end{pmatrix} \langle m'|\rho|m\rangle \quad (4.49)$$

Because of condition (4.4) only terms with  $K = 0$  and  $K = 1$  are allowed in (4.49). The monopole with  $K = 0$  is a normalization constant. If the spin-1/2 density matrix is normalized so that  $\text{tr } \rho = 1$  as in Sect. 1.1, then using (4.42) the monopole term is given by

$$\langle T(1/2)_{00} \rangle = 1/2^{1/2} \quad (4.50)$$

The three vector components  $\langle T(1/2)_{1Q}^\dagger \rangle$  are related to the corresponding components of the spin vector by (4.44a):

$$\langle T(1/2)_{1Q}^\dagger \rangle = 2^{1/2} \langle S_Q \rangle^* \quad (4.51a)$$

where  $S_Q$  denotes the  $Q$ th spherical component of the spin operator  $S$  as defined by (4.15). Using the definition of the Pauli matrices  $(1/2)\sigma_i = S_i (i = x, y, z)$  and of the polarization vector  $\mathbf{P}$  we obtain

$$\langle T(1/2)_{1Q}^\dagger \rangle = P_Q^*/2^{1/2} \quad (4.51b)$$

Thus the state multipoles (spin tensors)  $\langle T(1/2)_{1Q}^\dagger \rangle$  are proportional to the spherical components of the polarization vector defined by (4.15):

$$P_{\pm 1} = \mp(1/2^{1/2})(P_x \pm iP_y), \quad P_0 = P_z \quad (4.52)$$

The expansion of the spin-1/2 density matrix in terms of spin tensors can be obtained by applying (4.32):

$$\begin{aligned} \rho &= \sum_{KQ} \langle T(1/2)_{KQ}^\dagger \rangle T(1/2)_{KQ} \\ &= (1/2)\mathbf{1} + \sum_Q \langle T(1/2)_{1Q}^\dagger \rangle T(1/2)_{1Q} \end{aligned} \quad (4.53)$$

which is simply a reformulation of (1.48).

#### 4.4.2 Description of Spin-1 Particles

Spin-1 particles are described by three basic states corresponding to the three possible eigenvalues of the operator  $S_z$ . These states can be represented in form of the three-dimensional column vectors

$$\begin{pmatrix} 1 \\ 0 \\ 0 \end{pmatrix}, \quad \begin{pmatrix} 0 \\ 1 \\ 0 \end{pmatrix}, \quad \begin{pmatrix} 0 \\ 0 \\ 1 \end{pmatrix} \quad (4.54a)$$

In the standard representation (4.54a) the operators  $S_x$ ,  $S_y$ ,  $S_z$  are given by the matrices

$$S_x = \frac{1}{2^{1/2}} \begin{pmatrix} 0 & 1 & 0 \\ 1 & 0 & 1 \\ 0 & 1 & 0 \end{pmatrix}, \quad S_y = \frac{i}{2^{1/2}} \begin{pmatrix} 0 & -1 & 0 \\ 1 & 0 & -1 \\ 0 & 1 & 0 \end{pmatrix}, \quad S_z = \begin{pmatrix} 1 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & -1 \end{pmatrix}, \quad (4.54b)$$

The components of the polarization vector of spin- $S$  particles are defined by the relation

$$P_i = \frac{\langle S_i \rangle}{S} \quad (4.55)$$

( $i = x, y, z$ ). For  $S = 1/2$  (4.55) reduces to (1.5). For  $S = 1$  we have

$$P_i = \langle S_i \rangle \quad (4.56a)$$

It is instructive to calculate  $\mathbf{P}$  for the three basis states  $|+1\rangle$ ,  $|0\rangle$ ,  $| -1\rangle$ . Using the explicit representations (4.54a) and (4.54) and performing the calculations in the same way as in Sect. 1.1.2 it is found that  $P_x = P_y = 0$  in all three cases and  $P_z = 1$ ,  $P_z = 0$ ,  $P_z = -1$  for the states  $|+1\rangle$ ,  $|0\rangle$ ,  $| -1\rangle$ , respectively.

It is important to note that the state  $|0\rangle$  has a polarization vector of zero magnitude. This shows a fundamental difference between spin-1/2 and spin-1 particles: For  $S = 1$  it is impossible to have a pure spin state which does not have a preferred direction (that is, there need not be a direction in which the spins are “pointing”). This is easily understood in terms of the semiclassical vector model. The state  $M = 0$  is represented by a spin vector perpendicular to the  $z$  axis and precessing around it. Clearly, in this case there can be a preferred axis ( $z$  axis) but it is not possible to specify a *direction* along this axis. *It is this property in particular which makes it necessary to consider quantities of higher rank than the polarization vector.* The quantities which are required must not depend on the direction of the  $z$  axis, and hence quadratic combinations like  $\langle S_z^2 \rangle$  or, more generally, components of second-rank tensors can be used.

Furthermore, if a beam of particles in the pure state  $|0\rangle$  is compared with a mixture of  $N_+ = N/2$  particles in the state  $|+1\rangle$  and  $N_- = N/2$  particles in the state  $| -1\rangle$ , then in both cases  $\mathbf{P} = 0$ . Thus knowledge of the polarization vector alone is insufficient for a complete specification of spin-1 particles and additional parameters must be introduced.

The most systematic way to obtain all the necessary parameters is to construct the relevant spin tensors  $\langle T(S)_{KQ}^\dagger \rangle$  for  $S = 1$ . If the elements of the spin-1 density matrix are denoted by  $\langle M'|\rho|M\rangle$ , then from (4.31)

$$\langle T(1)_{KQ}^\dagger \rangle = \sum_{M'M} (-1)^{1-M'} (2K+1)^{1/2} \begin{pmatrix} 1 & 1 & K \\ M' & -M & -Q \end{pmatrix} \langle M'|\rho|M\rangle \quad (4.57)$$

Because of condition (4.4) it is necessary to construct a monopole, a vector, and a second-rank tensor. The monopole is specified by the normalization:

$$\langle T(1)_{00}^\dagger \rangle = 1/3^{1/2} \quad (4.58)$$

The corresponding density matrix can then be written in the form

$$\rho = (1/3)\mathbf{1} + \sum_Q \langle T(1)_{1Q}^\dagger \rangle T(1)_{1Q} + \sum_Q \langle T(1)_{2Q}^\dagger \rangle T(1)_{2Q} \quad (4.59)$$

Consequently, if the hermiticity condition (4.39) is taken into account, the most general spin-1 density matrix is completely specified in terms of eight real parameters (nine if the normalization  $\text{tr } \rho = 1$  is dropped and  $\text{tr } \rho$  considered as a parameter to be determined experimentally).

As an example consider an incoherent mixture of  $N_+$  particles in the state  $|+1\rangle$ ,  $N_-$  particles in the state  $| -1\rangle$ , and  $N_0$  particles in the state  $|0\rangle$ . In this case the density matrix is diagonal in the representation (4.53):

$$\langle M' | \rho | M \rangle = W_M \delta_{M'M} \quad (4.60)$$

where  $W_M = N_M/N$  and  $N$  is the total number of particles. Substitution of (4.60) into (4.57) yields

$$\langle T(1)_{20}^\dagger \rangle = (1/6^{1/2})(W_{+1} + W_{-1} - 2W_0) = \frac{N_{+1} + N_{-1} - 2N_0}{N(6)^{1/2}} \quad (4.61)$$

for the tensor polarization and

$$\langle T(1)_{10}^\dagger \rangle = \frac{W_{+1} - W_{-1}}{2^{1/2}} = \frac{N_+ - N_-}{2^{1/2}N} \quad (4.62)$$

for the vector polarization. (All components with  $Q \neq 0$  are zero).

The components  $\langle T(S)_{1Q}^\dagger \rangle$  are proportional to the spherical components of the polarization vector. Substituting  $\mathbf{S}$  for  $\mathbf{J}$  into (4.44a) and taking definition (4.56a) into account gives

$$\langle T(1)_{1Q}^\dagger \rangle = (1/2^{1/2})P_Q^* \quad (4.63)$$

where the spherical components of  $\mathbf{P}$  are defined by (4.52). The five components of the second-rank tensor  $\langle T(S)_{2Q}^\dagger \rangle$  can be constructed from quadratic combinations of the spin operators  $S$  as in (4.19) with  $J_i = S_i$  and  $N_2 = 1$ .

The use of Cartesian tensors in actual calculations can have some advantages but the spherical tensors  $\langle T(S)_{KQ}^\dagger \rangle$  have a simpler algebra, which in general considerably simplifies the calculations.

Finally, let us consider the consequences of condition (2.22). Substitution of (4.59) for  $\rho$  and use of (4.25) yields  $\text{tr } \rho = 1$  and

$$\begin{aligned}\text{tr}(\rho)^2 &= \sum_{\substack{KQ \\ K'Q'}} \left\langle T(1)_{K'Q'}^\dagger \right\rangle \left\langle T(1)_{KQ}^\dagger \right\rangle \text{tr} [T(1)_{K'Q'} T(1)_{KQ}] \\ &= \sum_{KQ} (-1)^Q \left\langle T(1)_{KQ}^\dagger \right\rangle \left\langle T(1)_{K-Q}^\dagger \right\rangle \\ &= \sum_{KQ} \left| \left\langle T(1)_{KQ}^\dagger \right\rangle \right|^2\end{aligned}$$

where (4.23), (4.24), and (4.39) have been used. Thus the spin tensors are restricted such that

$$\sum_{KQ} \left| \left\langle T(1)_{KQ}^\dagger \right\rangle \right|^2 \leq 1 \quad (4.64)$$

If (and only if)  $\rho$  characterizes a pure state then

$$\sum_{KQ} \left| \left\langle T(1)_{KQ}^\dagger \right\rangle \right|^2 = 1 \quad (4.65)$$

In the literature a beam of spin-1 particles is usually referred to as *completely polarized* if the beam is in a pure state, that is, if (and only if) condition (4.65) is satisfied. In this case the state of the beam can be represented by a single state vector  $|\chi\rangle$  which can be expanded in terms of the basic states (4.54a):

$$|\chi\rangle = a_{+1}|+1\rangle + a_0|0\rangle + a_{-1}|-1\rangle \quad (4.66)$$

Equation 4.66 shows that in general a completely polarized beam of spin-1 particles is specified by five real parameters, for example the magnitudes of the coefficients,  $a_M$ , and their relative phases.

The formalism which has been developed here is of considerable interest in the description of scattering processes involving polarized particles. This topic will not be discussed in this book except for a few relevant formulas which are given in Appendixes A and B. Detailed accounts can be found in textbooks on scattering theory, for example in the books by [Rodberg and Thaler \(1967\)](#). Discussion of scattering experiments using polarized electrons, including many experimental details, can be found in [Kessler \(1976\)](#). The more formal aspects of the theory have been discussed by [Robson \(1974\)](#) (see also [Blum and Kleinpoppen 1981](#)).

## 4.5 Symmetry Properties. Relation Between Symmetry and Coherence

### 4.5.1 Axially Symmetric Systems

The excitation of an ensemble of particles (atoms or nuclei) can be achieved in several ways: by the interaction of external fields, by absorption of radiation, by impact by other particles, and so on. Let us assume that the excitation process is axially symmetric with respect to some axis. This axis can be, for example, the direction of an external field. In excitation by electron impact, in which the scattered electrons are not detected, the symmetry axis would be defined by the direction of the initial electron beam.

Throughout this section we will always take the symmetry axis as the  $Z$  axis of our coordinate system (quantization axis). The choice of the  $X$  and  $Y$  axes perpendicular to  $Z$  is arbitrary and *the physical properties of the ensemble must therefore be independent of this choice* (the particles cannot “know” how the  $X$  and  $Y$  axes are defined). In particular, the real and imaginary parts of the state multipoles are directly measurable quantities (see Chap. 5) and hence must have the *same numerical values* in the  $XYZ$  system and in any  $xyZ$  system which can be obtained by a rotation about the  $Z$  axis through an arbitrary angle  $\gamma$ . This gives the following *symmetry condition*:

$$\langle T(J'J)_{KQ}^\dagger \rangle = \langle T(J'J)_{KQ}^\dagger \rangle_{\text{rot}} \quad (4.67)$$

where  $\langle T(J'J)_{KQ}^\dagger \rangle$  and  $\langle T(J'J)_{KQ}^\dagger \rangle_{\text{rot}}$  are defined in the fixed  $XYZ$  and the rotated  $xyZ$  systems, respectively. Equation 4.67 relates two complex quantities and hence real and imaginary parts are equal.

On the other hand, from the transformation law (4.41), the multipoles are related by

$$\langle T(J'J)_{KQ}^\dagger \rangle = \sum_q \langle T(J'J)_{Kq}^\dagger \rangle_{\text{rot}} \cdot D(00\gamma)_{qQ}^{(K)*} \quad (4.68)$$

where  $\gamma$  denotes the angle between the  $X$  and the  $x$  axes. The elements of the rotation matrix specifying the rotation around  $Z$  are given by

$$D(00\gamma)_{qQ}^{(K)*} = \exp(-iQ\gamma)\delta_{qQ} \quad (4.69)$$

[see (C.12)]. Substitution of (4.69) into (4.68) yields

$$\langle T(J'J)_{KQ}^\dagger \rangle = \langle T(J'J)_{KQ}^\dagger \rangle_{\text{rot}} \exp(-iQ\gamma) \quad (4.70)$$

Equation 4.70 is the general transformation law which holds for *any* angle  $\gamma$ . In addition, because of the axial symmetry, the condition (4.67) must also be satisfied

for any angle  $\gamma$ . This is only possible if  $Q = 0$ . Thus *axially symmetric systems are characterized by multipole components  $\langle T(J'J)_{K0}^\dagger \rangle$* , all components with  $Q \neq 0$  are necessarily zero because they violate the symmetry condition (4.67). The density operator characterizing systems with axial symmetry is therefore given by

$$\rho = \sum_{J'JK} \langle T(J'J)_{K0}^\dagger \rangle T(J'J)_{k0} \quad (4.71)$$

It follows from (4.36) that  $\rho$  is diagonal in  $M$ . We therefore have the following general result. If an ensemble of particles has been excited by a process, which is axially symmetric with respect to a preferred axis, *then states with different components of angular momentum are necessarily incoherently excited* (provided the quantization axis coincides with the symmetry axis). *The production of a coherent superposition of states with different angular momentum components requires an excitation process which is not axially symmetric.*

### 4.5.2 Classification of Axially Symmetric Systems

In this and the following section we will consider states with sharp angular momentum  $J' = J$ .

Axially symmetric systems can be classified by their transformation properties under a reversal of the symmetry axis:  $Z \rightarrow (-Z)$ . This corresponds to a rotation around the  $Y$  axis by an angle  $\pi$ . The corresponding rotation matrix elements are given by (C.12) and (C.15):

$$D(0\pi0)_{qQ}^{(K)} = (-1)^{K+Q} \delta_{q-Q} \quad (4.72)$$

Inserting (4.72) into the general relation (4.41) and accounting for the axial symmetry we obtain

$$\begin{aligned} \langle T(J)_{K0}^\dagger \rangle &= \sum_q \langle T(J)_{Kq}^\dagger \rangle_{\text{rot}} (-1)^{K-1} \delta_q 0 \\ &= (-1)^K \langle T(J)_{K0}^\dagger \rangle_{\text{rot}} \end{aligned} \quad (4.73)$$

where  $\langle T(J)_{K0}^\dagger \rangle$  and  $\langle T(J)_{K0}^\dagger \rangle_{\text{rot}}$  are defined with respect to the  $Z$  and  $-Z$  axes.

If a given ensemble is invariant with respect to the transformation  $Z \rightarrow -Z$ , that is, the values of all measurable quantities remain unchanged under this operation, then this requires that

$$\langle T(J)_{K0}^\dagger \rangle = \langle T(J)_{K0}^\dagger \rangle_{\text{rot}} \quad (4.74)$$

The expressions (4.73) and (4.74) can only be simultaneously satisfied by multipoles of even rank  $K$ . As a result an axially symmetric system which is invariant under the reversal of the symmetry axis is characterized by multipoles of even rank  $K$  and all

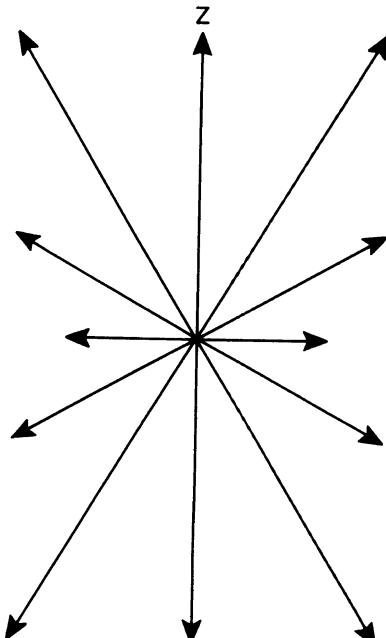
tensors with  $K$  odd are necessarily zero. In particular the orientation vector vanishes. It follows that the system under consideration is a special case of an *aligned system* as defined in Sect. 4.3.3.

Let us consider the effect of the symmetry condition (4.74) on the density matrix elements. Applying (4.34) and the symmetry properties of the  $3j$  symbols we have

$$\begin{aligned}\langle J - M | \rho | J - M \rangle &= \sum_K \langle T(J)_{K0}^\dagger \rangle (2K + 1)^{1/2} (-1)^{J+M} \begin{pmatrix} J & J & K \\ -M & M & 0 \end{pmatrix} \\ &= \langle JM | \rho | JM \rangle\end{aligned}\quad (4.75)$$

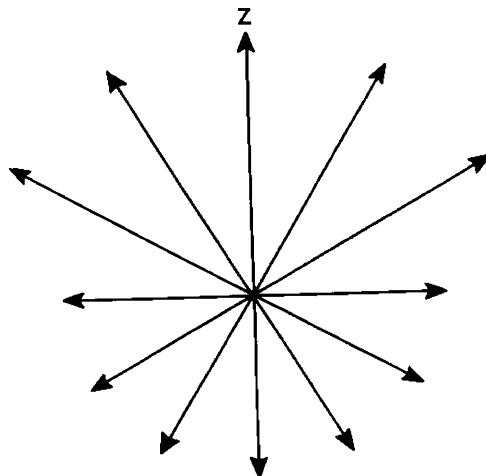
since only multipoles with even  $K$  contribute. The diagonal elements of  $\rho$  are proportional to the populations of the state  $|JM\rangle$  and the proportionality constant is specified by the normalization. Equation 4.75 shows that the states  $|JM\rangle$  and  $|J-M\rangle$  are *equally populated*.

It will be useful to discuss these results from a more physical viewpoint. Semiclassically, with a state  $|JM\rangle$  is associated a vector of length  $[J(J + 1)]^{1/2}$  with its  $Z$  component  $M$  precessing around  $Z$ . The length of the vectors can be changed without altering their directions in space, in such a way that the length is made proportional to the number of particles in the corresponding state  $|JM\rangle$ . In terms of this model a system satisfying (4.75) can be represented diagrammatically by Fig. 4.2 where the arrows represent the angular momentum vectors, pointing



**Fig. 4.2** Aligned axially symmetric system

**Fig. 4.3** Oriented axially symmetric system



into those directions of space which are allowed. The figure is axially symmetric and invariant under the operation  $Z \rightarrow -Z$ , that is, vectors pointing in opposite directions have the same length. In particular, the figure shows that the net angular momentum  $\langle \mathbf{J} \rangle$  of an aligned system is zero.

The condition (4.75) is trivially fulfilled for an atomic ensemble where all the particles are in the same state  $|J, M = 0\rangle$ . A system of this kind is a particularly simple example of an aligned system without orientation.

An axially symmetric system being not invariant against a reversal of the symmetry ( $Z$ ) axis is illustrated in Fig. 4.3. In this case, the length of vectors pointing in opposite directions is different. The figure shows that the system possesses a nonvanishing net angular momentum component. The excess of angular momentum vectors pointing in one direction can be described either by  $\langle J_z \rangle$  or  $\langle T(J)_{10} \rangle$ . This is an example of an oriented system.

Let us normalize according to  $\text{tr } \rho = 1$  and  $\langle JM | \rho | JM \rangle = W(M)$  where  $W(M)$  is the probability of finding a particle in the state  $|JM\rangle$ . Using (4.31) and inserting explicit values of the  $3j$  symbols we obtain for the orientation vector

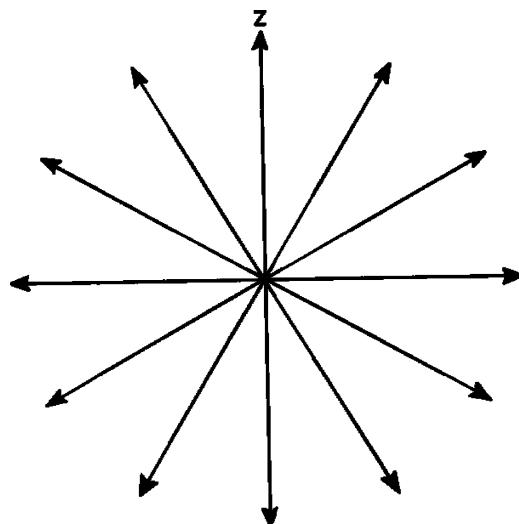
$$\langle T(J)_{10} \rangle = \left( \frac{3}{(2J+1)(J+1)J} \right)^{1/2} \sum_M M W(M) \quad (4.76a)$$

and for the nonvanishing component of the alignment tensor

$$\langle T(J)_{20} \rangle = \left( \frac{5}{(2J+3)(J+1)2J+1J(J-1)} \right)^{1/2} \sum_M [3M^2 - J(J+1)] W(M) \quad (4.76b)$$

In the special case that all  $W(M)$  are equal we obtain from (4.31) that all multipoles with  $K \neq 0$  vanish and (4.32) reduces to

**Fig. 4.4** Isotropic angular distribution



$$\rho = \langle T_{00} \rangle T_{00} = \left( \frac{1}{2J+1} \right)^{1/2} 1 \quad (4.77)$$

where we have used (4.14) and (4.42). The corresponding system is *isotropic* as illustrated by Fig. 4.4.

It is often useful to apply slightly different criteria for the classification of axially symmetric systems. Let us first assume that the symmetry axis is defined by a *polar* vector. This is the case for focusing molecules in electric fields  $\mathbf{E}$ , or by exciting atoms or molecules with linearly polarized light where the symmetry axis is defined by the  $\mathbf{E}$  vector. Another case is provided by excitation of atoms or molecules by particle impact. If the scattered projectiles are not observed then the process is axially symmetric with respect to the incoming beam direction. *Any polar vector remains unchanged under reflection through any plane which contains the vector.* Hence, starting with an initially isotropic target system, the total system must remain invariant under these reflections. Since states  $|JM\rangle$  are transformed into states  $|J-M\rangle$  it follows from the invariance condition that states with different signs of  $M$  (but the same  $|M|$ ) are necessarily equally populated. The system is aligned *but no orientation can be produced*. This result has important consequences for attempts to orient molecules in electric fields (see Chap. 7).

Secondly, let us assume that the symmetry axis is defined by an *axial* vector. This is the case, for example, in excitation processes by circularly polarized light where the direction of light propagation represents the symmetry axis. *Axial vectors change their sign under reflections in planes containing the vector.* Hence, the invariance condition derived for polar vectors does not apply. States with opposite signs of  $M$  will be unequally populated and both, orientation and alignment, can be produced.

In conclusion, axially symmetric systems will be aligned (but not oriented) if the symmetry axis is defined by a polar vector; they can also be oriented if the symmetry axis transforms as an axial vector. Equivalently, applying (4.75), we can state that the system is aligned if at least some states with different  $|M|$  are unequally populated, and oriented if at least some states with opposite signs of  $M$  (but the same  $|M|$ ) have been differently populated. The two situations are illustrated by Figs. 4.2 and 4.3 respectively. A more detailed semiclassical interpretation of the corresponding state multipoles can be found in Sect. 7.2.

Finally we note that the symmetry properties are not always correctly discussed in the literature. Sometimes the following statement is given: “A distribution of vectors is aligned or oriented if the distribution is symmetric or nonsymmetric under reflections in a plane perpendicular to the symmetry axis.” This statement is correct for polar vectors (e.g., the axes distribution of diatomic molecules) *but incorrect for a distribution of axial vectors like  $\mathbf{J}$ .* For example, Figs. 4.2 and 4.3 *both* remain invariant if every  $\mathbf{J}$ -vector is reflected in the  $X - Y$  plane.

### 4.5.3 Examples: Photoabsorption by Atoms (Nuclei)

We will now illustrate the theory described in the preceding sections with some examples. Consider an ensemble of atoms or nuclei which is initially in a state with angular momentum  $J_0 = 0$ , and is then excited by photon absorption to a state with  $J = 1$ . We will first discuss the case in which the incident light is *unpolarized*. The total system is axially symmetric with respect to the direction of propagation  $\mathbf{n}$  of the light, and it is therefore convenient to choose this as the quantization axis. Consequently, the excited state density matrix is diagonal:  $\langle M'|\rho|M\rangle = \langle M|\rho|M\rangle \delta_{M'M}$  with respect to  $\mathbf{n}$ . The incident light beam can be considered as an incoherent mixture of the two helicity states each with equal intensity, and hence only atomic states with  $M = \pm 1$  can be excited and  $\langle 0|\rho|0\rangle = 0$ . Furthermore, as a consequence of angular momentum conservation and the fact that the light beam has equal components of the two helicity states, the atomic states  $|+1\rangle$  and  $| -1\rangle$  are equally populated, i.e.,  $\langle +1|\rho|+1\rangle = \langle -1|\rho|-1\rangle$ , and the net angular momentum component of the atomic states is zero. Thus no net angular momentum is transferred to the atoms and the state is aligned but not oriented. In terms of state multipoles, the atomic state can be completely specified by two parameters only, the monopole  $\langle T_{00} \rangle$  and the alignment parameter  $\langle T_{20}^\dagger \rangle$ .

Consider now the case that the incident radiation is *linearly polarized*. The  $Z$  axis can be chosen in such a way that  $Z$  is parallel to the electric vector  $\mathbf{E}$ . Absorption of this light will occur through  $\pi$  transitions ( $\Delta M = 0$ ) which will produce an alignment but no orientation in the excited atoms. Thus *with the quantization axis parallel to E* the excited ensemble is again characterized in terms of two parameters,  $\langle T_{00} \rangle$  and  $\langle T_{20}^\dagger \rangle$ .

Finally, if the incident light is *circularly polarized* and the direction of motion is chosen as the quantization axis, then the states  $|+1\rangle$  and  $| -1\rangle$  will not be equally populated. The light will produce an orientation and the atomic density matrix is specified by three parameters,  $\langle T_{00} \rangle$ ,  $\langle T_{10}^\dagger \rangle$ ,  $\langle T_{20}^\dagger \rangle$  where  $\langle T_{10}^\dagger \rangle$  gives the net amount of angular momentum which is transferred to the atoms.

## 4.6 Excitation of Atoms by Electron Impact II: State Multipoles

### 4.6.1 Collisional Production of Atomic Orientation

In Sect. 3.5 an expression was derived for the density matrix  $\rho$  describing an atomic ensemble excited by electrons which were “scattered” in a fixed direction (with momentum  $\mathbf{p}_1$ ). We will now give a description of the excited atoms in terms of state multipoles. This will be a convenient starting point for the discussions in Chap. 6.

The elements of the density matrix, averaged over all spins, are given by (3.42). Using (4.31) we can define multipole components  $\langle T(L)_{KQ}^\dagger \rangle$  which describe the orbital states alone:

$$\begin{aligned} \langle T(L)_{KQ}^\dagger \rangle &= \sum_{M'M} (-1)^{L-M'} (2K+1)^{1/2} \begin{pmatrix} L & L & K \\ M' & -M & -Q \end{pmatrix} \langle LM' | \rho | LM \rangle \\ &= \sum_{M'M} (-1)^{L-M'} (2K+1)^{1/2} \begin{pmatrix} L & L & K \\ M' & -M & -Q \end{pmatrix} \langle f_{M'} f_M^* \rangle \end{aligned} \quad (4.78)$$

In accordance with condition (4.4), for a given orbital angular momentum  $L$  all tensors of rank  $K = 0, 1, \dots, 2L$  and components  $|Q| \leq K$  must be constructed in order to obtain a complete description of the atomic ensemble.

As discussed in Sect. 3.5.2 the atomic system under consideration must be invariant under reflections in the scattering  $X - Z$  plane. In order to see the consequences of this symmetry requirement on the state multipoles we will first consider the orientation vector which is proportional to the net angular momentum  $\langle \mathbf{L} \rangle$  of the atomic subensemble. Since initially the atoms were assumed to be unoriented  $\langle \mathbf{L} \rangle$  is the net angular momentum transferred to the atoms during the scattering. We will now discuss the transformation properties of  $\mathbf{L}$ .

Suppose the orientation vector has a nonvanishing component  $\sim \langle L_X \rangle$  in the  $X$  direction as shown in Fig. 4.5a. A reflection in the  $X - Z$  plane can be generated by rotating the system around the  $Y$  axes by an angle  $\pi$  followed by an inversion through the origin. Angular momentum vectors transform as *axial* vectors. Polar vectors, such as momentum, and axial vectors have the same transformation properties under rotating but behave differently under inversion: polar vectors change their sign, whereas axial vectors do not. Under reflection in the scattering

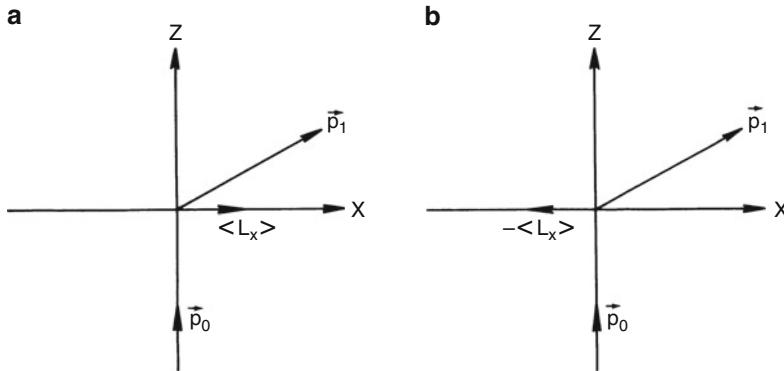


Fig. 4.5 Reflection of  $\langle \mathbf{L} \rangle$  in the scattering plane

plane Fig. 4.5a is therefore transformed into Fig. 4.5b. Since the atomic ensemble must be invariant under reflection in the scattering plane the situations depicted in Fig. 4.5a, b must occur with equal probability. The net component  $\langle L_x \rangle$  must therefore vanish. The same argument holds for the component  $\langle L_z \rangle$ . In this case only  $\langle L_y \rangle$ , which is perpendicular to the scattering plane, can be nonzero.

In general the excited atomic system can therefore be expected to be oriented. A suggestive classical model of the mechanism responsible for the atomic orientation is that of a grazing impact illustrated in Fig. 4.6. The diagrams suggest that the atoms obtain an angular momentum perpendicular to the scattering plane which is opposite for a repulsive force (Fig. 4.6a) and for an attractive one (Fig. 4.6b).

This relation between the sign of the orientation, the deflection of the scattered particles, and the effective interactions was further studied by [Fano and Komoto \(1977\)](#) and [Herman and Hertel \(1979\)](#). They succeeded in showing that the orientation is reversed by a sign reversal of the interaction.

These results enable some conclusions to be made on the behavior of the orientation vector with respect to the scattering angle  $\theta$  at fixed energy. Consider, for example, the excitation of  ${}^1P$  states of helium. Electrons scattered in the forward or backward direction cannot transfer a net angular momentum to the atoms and  $\langle \mathbf{L} \rangle = 0$  for  $\theta^\circ = 0^\circ = 180^\circ$ . Scattering into small angles is dominated by the long-range attractive force due to the atomic polarizability, while large-angle scattering is dominated by the short-range repulsive force caused by the atomic electrons.  $\langle \mathbf{L} \rangle$  can therefore be expected to have opposite signs at small and large angles and to vanish at an intermediate angle where the contributions from the attractive and repulsive forces are equal in magnitude. These conclusions are confirmed by the recent measurements of [Holywood et al. \(1979\)](#) and [Steph and Golden \(1980\)](#). A summary of further experimental and theoretical results has been given by [Andersen and Bartschat \(1996\)](#).

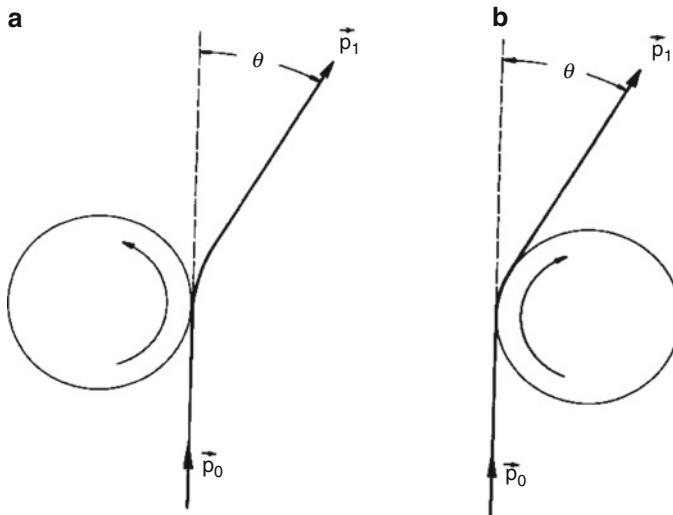


Fig. 4.6 Model for orientation by collisions

#### 4.6.2 General Consequences of Reflection Invariance

We will now discuss the transformation properties of the state multipoles (4.78) under reflection in the  $X - Z$  plane. Reflection invariance of the atomic system under consideration implies that the elements of  $\rho$  must satisfy condition (3.36b):

$$\langle LM'|\rho(L)|LM\rangle = (-1)^{M'+M}\langle L-M'|\rho(L)|L-M\rangle \quad (4.79)$$

In particular, for the diagonal elements we have

$$\sigma(M) = \sigma(-M) \quad (4.80a)$$

Substituting condition (4.79) into (4.78) gives

$$\begin{aligned} \langle T(L)_{KQ}^\dagger \rangle &= \sum_{M'M} (-1)^{L-M'} (2K+1)^{1/2} \binom{L \quad L \quad K}{M' \quad -M \quad -Q} \\ &\quad \times (-1)^{M'+M} \langle L-M'|\rho|L-M\rangle \end{aligned} \quad (4.81a)$$

Since all the values of  $M'$  and  $M$  are summed over in (4.81a) we can replace  $(+M')$  and  $(+M)$  by  $(-M')$  and  $(-M)$ , respectively. Applying the symmetry property (C.5c) (from Appendix C.1), then gives

$$\begin{aligned}
\langle T(L)_{KQ}^\dagger \rangle^* &= (-1)^{K+Q} \sum_{M'M} (-1)^{L-M'} (2K+1)^{1/2} \binom{L}{M'} \binom{L}{-M} \binom{K}{-Q} \\
&\quad \times \langle LM' | \rho(L) | LM \rangle \\
&= (-1)^{K+Q} \langle T(L)_{K-Q}^\dagger \rangle
\end{aligned} \tag{4.82}$$

From this relation and the hermiticity condition (4.39) it follows that

$$\langle T(L)_{KQ}^\dagger \rangle = (-1)^K \langle T(L)_{KQ}^\dagger \rangle^* \tag{4.83}$$

In this case of the atomic system under consideration reflection in the  $X - Z$  plane has the following consequences on the state multipoles: *for even  $K$  the tensors  $\langle T(L)_{KQ}^\dagger \rangle$  are real and for  $K$  odd the tensors  $\langle T(L)_{KQ}^\dagger \rangle$  are imaginary. The components with  $Q = 0$  vanish if  $K$  is odd.*

The components of orientation vector and alignment tensor are related to the corresponding angular momentum tensors by (4.43) and (4.19). Because of the symmetry condition (4.83) the real or imaginary part of these expressions is zero depending on whether  $K$  is odd or even. Applying the normalization (3.33)

$$\text{tr } \rho = \sigma$$

we have for the components of the orientation vector

$$-i \langle T(L)_{1\pm 1}^\dagger \rangle = \frac{3^{1/2}}{[2(2L+1)(L+1)L]^{1/2}} \sigma \langle L_Y \rangle \tag{4.84a}$$

$$\langle T(L)_{10}^\dagger \rangle = 0 \tag{4.84b}$$

and for the components of the alignment tensor

$$\begin{aligned}
\langle T(L)_{20}^\dagger \rangle &= \frac{N_2}{6^{1/2}} \sigma \langle 3L_Z^2 - \mathbf{L}^2 \rangle \\
\langle T(L)_{2\pm 1}^\dagger \rangle &= \mp \frac{N_2}{2} \sigma \langle L_X L_Z + L_Z L_X \rangle \\
\langle T(L)_{2\pm 2}^\dagger \rangle &= \frac{N_2}{2} \sigma \langle L_X^2 - L_Y^2 \rangle
\end{aligned} \tag{4.85}$$

It should be noted that the hermiticity condition (4.39) restricts the number of independent multipoles. The orientation is specified in terms of one parameter [for example,  $\langle T(L)_{1,+1}^\dagger \rangle$ ] and the alignment is completely characterized in terms of three independent parameters [for example, the components  $\langle T(L)_{2Q}^\dagger \rangle$  with  $Q = 0, +1, +2$ ].

The parameters (4.84) and (4.85) are closely related to a set of quantities introduced by [Fano and Macek \(1973\)](#):

$$\begin{aligned} 0_{1-} &= \frac{\langle L_Y \rangle}{L(L+1)}, & A_{1+} &= \frac{\langle L_X L_Z + L_Z L_X \rangle}{L(L+1)} \\ A_0 &= \frac{\langle 3L_Z^2 - L^2 \rangle}{L(L+1)}, & A_{2+} &= \frac{\langle L_X^2 - L_Y^2 \rangle}{L(L+1)} \end{aligned} \quad (4.86)$$

where  $0_{1-}$  characterizes the orientation and the three other ones the alignment. Note, however, that the use of the relations (4.71), (4.85), and (4.86) is only meaningful if atomic states with sharp angular momentum  $L$  have been excited.

If atomic states with different  $L$  have been coherently excited then it is necessary to construct state multipoles  $\langle T(L'L)_{KQ}^\dagger \rangle$  in order to describe completely the atomic ensemble. The transformation properties of the tensors  $\langle T(L'L)_{KQ}^\dagger \rangle$  under reflection and inversion depend on whether  $L' + L$  is even or odd. For example, if  $L' + L$  is odd the vector  $\langle T(L'L)_{1Q}^\dagger \rangle$  transforms as a polar vector and must therefore lie in the scattering plane in order to be invariant under reflection in this plane. By applying the Wigner-Eckart theorem it can be shown that this vector is related to the components  $\langle r_Q \rangle$  of the net electric dipole vector induced in the atomic ensemble. We will not go further into the details of this analysis here but a more complete treatment can be found in Sect. 4.4 of the review by [Blum and Kleinpoppen \(1979\)](#).

### 4.6.3 Axially Symmetric Atomic Systems

We will now specialize the results of the preceding sections to the case in which the scattered electrons are not observed. In this case a single axis (the direction of  $\mathbf{p}_0$ ) is defined by the geometry of the experiment. Consequently, the excited atomic ensemble must be invariant with respect to rotations around this axis and the results of Sect. 4.5.2 apply: All multipoles with  $Q \neq 0$  vanish. Denoting the corresponding density matrix by  $\rho$  then

$$\langle LM | \rho | LM \rangle = Q(M) \quad (4.87)$$

where  $Q(M)$  is the total cross section for excitation of the substate with magnetic quantum number  $M$ . From relation (4.80a) it follows that

$$Q(M) = Q(-M) \quad (4.88)$$

The monopole is given by

$$\langle T(L)_{00} \rangle = \frac{Q}{(2L+1)^{1/2}} \quad (4.89)$$

where  $Q = \sum_M Q(M)$  is the total cross section. Substituting (4.87) into (4.78) and using (4.88) gives

$$\langle T(L)_{10}^\dagger \rangle = 0 \quad (4.90a)$$

which is a consequence of (4.88) and

$$\begin{aligned} \langle T(L)_{20}^\dagger \rangle &= 5^{1/2} \sum_M (-1)^{L-M} \begin{pmatrix} L & L & 2 \\ M & -M & 0 \end{pmatrix} Q(M) \\ &= \frac{5^{1/2}}{[(2L+3)(L+1)(2L+1)(2L-1)L]^{1/2}} \sum_M [3M^2 - L(L+1)] Q(M) \end{aligned} \quad (4.91)$$

where explicit values for the  $3j$  symbols have been used. In particular, if  $L = 1$ , the atomic system under consideration is completely specified by two parameters, the monopole or the total cross section and the alignment parameter  $\langle T(1)_{20}^\dagger \rangle$ . No net angular momentum  $\langle \mathbf{L} \rangle$  is transferred to the system.

#### 4.6.4 Symmetry Relations in the “Natural System”

Let us further consider an atomic ensemble described by a density matrix  $\rho$ , which possesses a plane of symmetry. In Sect. 4.6.2 we have chosen this plane as the  $X - Z$  plane of our coordinate system. There are many advantages to a coordinate frame with axes  $X_N$ ,  $Y_N$ ,  $Z_N$ , where the  $X_N - Y_N$  plane coincides with the symmetry plane and where  $Z_N$  is perpendicular to it. This frame is the “natural system” which has become very popular in atomic collision physics (see, for example, the reviews by [Andersen et al. \(1988\)](#), and [Andersen and Bartschat \(1996\)](#)).

In this subsection we will choose  $Z_N$  as quantization axis and it will be understood that the state multipoles  $\langle T(2)_{KQ}^\dagger \rangle$  refer to the natural system. Let us first consider the transformation properties of (orbital) angular momentum states under reflections in the  $X_N - Y_N$  plane. This operation can be performed as a consecutive application of two symmetry operations, an inversion (operator  $S$ ) followed by a rotation  $R(\pi)_z$  around the  $Z_N$  axis by an angle  $\pi$ . The reflection operator  $R$  therefore has the form

$$R = S_0 R(\pi)_z \quad (4.92)$$

The states  $|LM\rangle$  transform according to

$$S_0|LM\rangle = (-1)^L|LM\rangle$$

and

$$R(\pi)_z|LM\rangle = e^{iM\pi}|LM\rangle = (-1)^M|LM\rangle$$

which results in the expression

$$R|LM\rangle = (-1)^{L+M}|LM\rangle \quad (4.93)$$

We will now assume that the ensemble under consideration possesses a symmetry plane ( $X_N - Y_N$  plane). Mathematically, this is expressed by the condition that the corresponding density matrix  $\rho$  is invariant under reflection in this plane; that is,

•

$$R^+ \rho R = \rho \quad (4.94)$$

Taking matrix elements we obtain

•

$$\begin{aligned} \langle LM' | \rho | LM \rangle &= \langle LM' | R^+ \rho R | LM \rangle \\ &= (-1)^{M'-M} \langle LM' | \rho | LM \rangle \end{aligned} \quad (4.95)$$

where we have applied  $R^\dagger$  and  $R$  to the bra and Ket vectors of the matrix element, and have used (4.93).

From the general definition (4.31) of state multipoles, and (4.95) we obtain

•

$$\langle T(L)_{KQ}^\dagger \rangle = (-1)^Q \langle T(L)_{KQ}^\dagger \rangle \quad (4.96)$$

Equation 4.96 is the condition which must be satisfied by the multipoles if the  $X_N - Y_N$  plane is a symmetry plane of the system. In particular, we have the requirement

•

$$\langle T(L)_{KQ}^\dagger \rangle = 0 \quad (4.97a)$$

for  $Q$  odd. Combining (4.96) with the general hermiticity condition (4.39) we obtain

•

$$\langle T(L)_{KQ}^\dagger \rangle = \langle T(L)_{K-Q}^\dagger \rangle^* \quad (4.97b)$$

The results show that the symmetry relations of the multipoles can be expressed in a simple way if the natural system is used. Consider, for example,  $^1P$ -excitation. If (4.96) apply then the excited atomic ensemble is characterized by the parameters  $\langle T_{00}^\dagger \rangle$ ,  $\langle T_{10}^\dagger \rangle$ ,  $\langle T_{20}^\dagger \rangle$  (which are all real), and  $\langle T_{22}^\dagger \rangle$  (which is complex).  $\langle T_{11}^\dagger \rangle$  and  $\langle T_{21}^\dagger \rangle$  vanish because of condition (4.97a).

Finally, let us consider systems which possess two symmetry planes orthogonal to each other, say, the  $X_N - Y_N$  and  $X_N - Z_N$  planes. In this case the symmetry conditions (4.82) and (4.83) hold in addition to the requirements (4.96).

### 4.6.5 Coordinate Representation of the Density Matrix. Shape and Spatial Orientation of Atomic Charge Clouds

#### 4.6.5.1 General Equations

In the present section, and also in Sect. 4.3.2, we have discussed some applications of the concept of orientation and alignment. In order to obtain a more physical picture we will consider in this subsection the geometric properties of the charge clouds of excited atoms. It will be shown that shape and spatial orientation of the charge distributions are described by the components of the alignment tensor (for  $l \leq 1$ ) and by multipole components of even rank in general cases ( $l > 1$ ).

The spatial properties of atomic charge distributions have been discussed in the reviews by [Andersen et al. \(1988\)](#) and [Hertel and Stoll \(1978\)](#), where many examples can be found. Here, we will derive some general equations with the main aim of further illustrating the importance particularly of the alignment tensor. We will consider a general case where the charge cloud of an ensemble of excited atoms has an arbitrary orientation relative to a given laboratory system (XYZ system). In particular, it will not be assumed that the excitation process possesses a plane of symmetry. In order to concentrate on the essentials we will, however, consider atoms in singlet states. More general cases have been discussed by [Sohn and Hanne \(1992\)](#) and by [Raeker et al. \(1993\)](#).

$\rho$  may be the density matrix describing the excited atomic ensemble of interest. Assuming that the atoms are in states with arbitrary but definite orbital angular momentum  $L$  we can write  $\rho$  in the form (4.29):

$$\rho = \sum_{M'M} \langle LM' | \rho | LM \rangle | LM' \rangle \langle LM |$$

Expressing the density matrix elements in terms of state multipoles similarly to (4.34), it follows that

$$\rho = \sum_{\substack{KQ \\ M'M}} (-1)^{L-M'} (2K+1)^{1/2} \begin{pmatrix} L & L & K \\ M' & -M & -Q \end{pmatrix} \left\langle T(L)_{KQ}^{\dagger} \right| | LM' \rangle \langle LM | \quad (4.98)$$

We transform to the coordinate representation by remembering the relation

$$\langle \mathbf{r} | LM \rangle = \psi(\mathbf{r})_{LM} = R(r)_L Y(\Theta\varphi)_{LM} \quad (4.99)$$

where  $Y(\Theta\varphi)_{LM}$  denotes a spherical harmonic and where the radial part  $R(r)_L$  may depend on further quantum numbers.  $\Theta$  and  $\varphi$  are polar and azimuth angles of the radius vector  $\mathbf{r}$  respectively. The charge density of atoms in the state  $|LM\rangle$  is then given by  $e|\psi(\mathbf{r})_{LM}|^2$  where  $e$  is the electron charge. Since the corresponding density matrix is  $\rho = |LM\rangle \langle LM|$ , we have  $e\langle \mathbf{r} | \rho | \mathbf{r} \rangle = e|\psi(\mathbf{r})_{LM}|^2$ . Hence, the element  $e$

$\langle \mathbf{r} | \rho | \mathbf{r} \rangle$  can be interpreted as charge density of an atomic ensemble described by the density matrix  $\rho$ .

More generally, “we sandwich” (4.98) between states  $\langle \mathbf{r} |$  and  $\langle \mathbf{r} \rangle$ , and inserting (4.99) we obtain

$$\begin{aligned} e \langle \mathbf{r} | \rho | \mathbf{r} \rangle &= \sum_{\substack{KQ \\ M'M}} (-1)^{L-M'} (2K+1)^{1/2} \begin{pmatrix} L & L & K \\ M' & -M & -Q \end{pmatrix} \\ &\quad \times \left\langle T(L)_{KQ}^\dagger \right\rangle e \psi(\mathbf{r}) LM' \psi(\mathbf{r})_{LM}^* \\ &= e |R(r)_L|^2 W(\Theta\varphi) \end{aligned}$$

where

$$\begin{aligned} W(\Theta\varphi) &= \sum_{\substack{KQ \\ M'M}} (-1)^{L-M'} (2K+1)^{1/2} \begin{pmatrix} L & L & K \\ M' & -M & -Q \end{pmatrix} \\ &\quad \left\langle T(L)_{KQ}^\dagger \right\rangle Y(\Theta\varphi)_{LM'} Y(\Theta\varphi)_{LM}^* \end{aligned} \quad (4.100)$$

This expression can be simplified by applying the addition theorem of the spherical harmonics. Substituting (C.22) into (4.100), and performing the sum over  $M'$  and  $M$  by using relation (C4b) we obtain finally

$$\begin{aligned} W(\Theta\varphi) &= \left( \frac{1}{4\pi} \right)^{1/2} \sum_{KQ} (-1)^L (2L+1) \begin{pmatrix} L & L & K \\ 0 & 0 & 0 \end{pmatrix} \\ &\quad \left\langle T(L)_{KQ}^\dagger \right\rangle Y(\Theta\varphi)_{KQ} \end{aligned} \quad (4.101)$$

Equation 4.101 describes the angular dependence of the charge cloud. The angles  $\Theta$ ,  $\varphi$ , define a certain direction in the  $XYZ$  system, and  $W(\Theta\varphi)$  is the “length” of the charge cloud in this particular direction. The total set of all values of this function then defines the surface” of the charge distribution.

Equation 4.96 shows that every nonvanishing state multipole gives rise to a particular angular dependence described by the corresponding spherical harmonic with the same rank  $K$  and component  $Q$ . Furthermore, since the  $3j$  symbol vanishes for odd  $K$  [(C.5c)], it follows that only tensors with even rank contribute to the expansion (4.101). This result was to be expected since the tensors with odd rank are proportional to the corresponding magnetic multipoles (as discussed in Sect. 4.3.3) and describe the distribution of electric currents within the atoms.

Specializing (4.101) to states with  $L = 1$  we obtain that only terms with  $K = 0$  and  $K = 2$  contribute. Applying the hermiticity property (4.39) it follows that one can choose the real parameters  $\langle T_{20} \rangle$ ,  $\text{Re} \langle T_{21}^\dagger \rangle$ ,  $\text{Re} \langle T_{22}^\dagger \rangle$  and the imaginary parts

$\text{Im} \langle T_{21}^\dagger \rangle$ ,  $\text{Im} \langle T_{22}^\dagger \rangle$  as independent parameters. Inserting the explicit expressions for the spherical harmonics and applying the normalization (4.42) with  $\text{tr } \rho = 1$ , we obtain

- $$W(\Theta\varphi) = \frac{1}{4\pi} \left[ 1 - 3 \left[ \text{Re} \langle T_{22}^\dagger \sin^2 \Theta \cos 2\varphi - \text{Re} \langle T_{21}^\dagger \rangle \sin 2\Theta \cos \varphi \right. \right. \\ \left. \left. + \left( \frac{1}{6} \right)^{1/2} \langle T_{20}^\dagger \rangle (3 \cos^2 \Theta - 1) - \text{Im} \langle T_{22}^\dagger \rangle \sin^2 \Theta \sin 2\varphi \right. \right. \\ \left. \left. + \text{Im} \langle T_{21}^\dagger \rangle \sin 2\Theta \cos \varphi \right] \right] \quad (4.102)$$

According to (4.102) the charge distribution can be thought of as being composed of two incoherent parts, an isotropic contribution and an anisotropic one (corresponding to the second-rank tensor  $\langle T_{20}^\dagger \rangle$ ).

If the  $X - Z$  plane is a symmetry plane of the system then the alignment components are real according to (4.83). Two of the principal axes of the charge cloud must lie within this plane, and the third is perpendicular to it. The imaginary parts of  $\langle T_{21}^\dagger \rangle$  and  $\langle T_{22}^\dagger \rangle$  in (4.102) characterize therefore the amount by which the charge cloud is tilted out of the  $X - Z$  plane in more general situations.

A geometric interpretation can also be given to  $\langle T_{21}^\dagger \rangle$  if the  $X - Z$  plane is a symmetry plane.  $\langle T_{21}^\dagger \rangle$  is related to the “alignment angle”  $\gamma$ , that is, the angle between the main principal axes of the charge distribution and the  $Z$  axis:

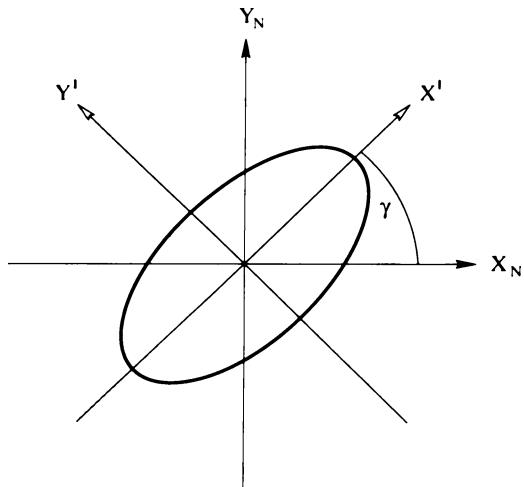
- $$\tan 2\gamma = \frac{2 \langle T_{21}^\dagger \rangle}{\langle T_{22}^\dagger \rangle - (frac{3}{2})^{1/2} \langle T_{20}^\dagger \rangle} \quad (4.103a)$$

(Hertel and Stoll 1978; Raeker et al. 1993).  $\langle T_{21}^\dagger \rangle$  is zero for  $\gamma = 0$  and  $\gamma = \pi/2$ . The charge cloud is tilted with respect to both the  $Z$  and the  $X$  axes if  $\langle T_{21}^\dagger \rangle$  is different from zero. The alignment angle is shown in Fig. 4.7, where  $X_N - Y_N$  plane of the “natural system” has been chosen as symmetry plane.  $Z_N$  is perpendicular to the plane,  $X_N$  corresponds to  $Z$ , and  $Y_N$  to the  $X$  axis.

#### 4.6.5.2 Geometric Interpretation of State Multipoles

So far we have not fixed the coordinate system. Equations 4.101 and 4.102 hold therefore in any frame. We will now assume that the atomic ensemble

**Fig. 4.7** Schematic representation of a charge cloud in the  $X_N Y_N$  plane



under consideration possesses a symmetry plane, and at this point we have to choose explicitly a coordinate system. It is convenient to choose the “natural frame”  $X_N Y_N Z_N$ , introduced in Sect. 4.6.4, where  $Z_N$  is perpendicular to the symmetry plane.

We will now assume that the parameters  $\langle T_{KQ}^+ \rangle$  are defined with respect to  $Z_N$  as quantization axis, and that (4.101) and (4.102) refer to the natural frame. The symmetry properties of the state multipoles under reflection in the  $X_N - Y_N$  plane have been derived in Sect. 4.6.4. In particular, from (4.97a) it follows that the multipoles with  $Q$  odd vanish so that only tensors with  $Q$  even contribute to  $W(\Theta, \varphi)$ . We write

$$\langle T_{KQ}^+ \rangle = |\langle T_{KQ}^+ \rangle| e^{i\gamma(KQ)} \quad (4.104)$$

where  $\gamma(KQ)$  is the phase of the multipole with rank  $K$  and component  $Q$ . From condition (4.97b) follows  $\gamma(K - Q) = -\gamma(KQ)$ .

Using (4.104) and the relation (C.16b) and (C.12)

$$Y(\Theta\varphi)_{KQ} = \left( \frac{2K+1}{4\pi} \right)^{1/2} d(\Theta)_{0Q}^{(K)} e^{iQ\varphi} \quad (4.105)$$

we combine the terms with  $\pm Q$  in (4.101) in the following way:

$$\begin{aligned} \langle T_{KQ}^+ \rangle Y_{KQ} + \langle T_{K-Q}^+ \rangle Y_{K-Q} &= 2 \left( \frac{2K+1}{4\pi} \right)^{1/2} \\ &\quad \langle T_{KQ}^+ \rangle d(\Theta)_{0Q}^{(K)} \cos[\gamma(KQ) + Q\varphi] \end{aligned} \quad (4.106)$$

Substitution of (4.106) into (4.101) yields

$$\begin{aligned}
W(\Theta\varphi) = & \times \frac{1}{2\pi} \sum_{KQ} (-1)^L (2L+1) (2K+1)^{1/2} \begin{pmatrix} L & L & K \\ 0 & 0 & 0 \end{pmatrix} \\
& |\langle T_{KQ}^+ \rangle| d(\Theta)_{0Q}^{(K)} \cos[\gamma(KQ) + Q\varphi]
\end{aligned} \tag{4.107}$$

where the sum contains only terms with  $Q$  even, and  $Q \geq 0$ .

Let us consider in particular a cut through the charge cloud along the  $X_N - Y_N$  plane, obtained from (4.107) by setting  $\Theta = \pi/2$ . The  $\varphi$ -dependence then has the general form

$$\begin{aligned}
W\left(\Theta = \frac{\pi}{2}, \varphi\right) = & A + B \cos[\gamma(22) + 2\varphi] + C \cos[\gamma(42) + 2\varphi] \\
& + D \cos[\gamma(44) + 4\varphi] + \dots
\end{aligned} \tag{4.108a}$$

and higher terms up to  $K = 2L$  and  $Q = 2L$ . The parameters  $A, B, \dots$  contain all  $\gamma$ -independent factors of (4.107). In particular, for  $L = 1$ , we obtain

$$W\left(\Theta = \frac{\pi}{2}, \varphi\right) = A + B \cos[2\varphi - 2\gamma] \tag{4.108b}$$

where  $\gamma = -\frac{1}{2}\gamma(22)$  is the “alignment angle”, that is, the angle between  $X_N$  and the principal  $X'$  axis of the charge cloud as shown in Fig. 4.7.  $\varphi$  is the angle between radius vector and  $X_N$ .

The phase of the multipole  $\langle T_{22}^+ \rangle$  therefore has a simple geometric importance. In order to discuss the magnitudes of the multipoles let us consider the case  $L = 1$  in more detail. We define the “eigenframe”  $X'Y'Z'$  of the charge cloud in such a way that  $Z'$  coincides with  $Z_N$ , and  $X'$  and  $Y'$  are parallel to the other two principal axes as shown in Fig. 4.7. With  $X_N - Y_N$  as symmetry plane one principal axis is always parallel to  $Z_N$ .

The eigenframe is obtained by rotating the natural system around  $Z_N$  by the alignment angle  $\gamma$ .

Consequently, the state multipoles  $\langle T_{KQ}^+ \rangle'$ , defined with respect to the eigenframe, are related to the multipoles  $\langle T_{KQ}^+ \rangle$  in the natural frame by relation (4.70):

$$\langle T_{KQ}^+ \rangle = \langle T_{KQ}^+ \rangle' e^{iQ\gamma}$$

Furthermore, the  $X' - Y'$ ,  $X' - Z'$ , and  $Y' - Z'$  planes are symmetry planes of the charge cloud. It follows that the state multipoles have to satisfy the symmetry conditions (4.83) and (4.96). Hence, the charge cloud is characterized by three real parameters:  $\langle T_{00} \rangle$ ,  $\langle T_{20}^+ \rangle'$ , and  $\langle T_{22}^+ \rangle'$ . By adapting the general (4.102) we obtain

$$\bullet \quad W'(\Theta\varphi') = \frac{1}{2\pi} \sum_{KQ} (-1)^L 3(2K+1)^{1/2} \begin{pmatrix} 1 & 1 & K \\ 0 & 0 & 0 \end{pmatrix} \langle T_{KQ}^+ \rangle' d(\Theta)_{0Q}^{(K)} \cos Q\varphi' \quad (4.109)$$

where now  $\Theta$  and  $\varphi'$  are the polar and azimuth angles of the radius vector with respect to the eigenframe. In particular, for  $\Theta = \pi/2$ , the radius vector lies in the  $X' - Y'$  plane, and  $\varphi'$  is the angle between the radius vector and  $X'$ .  $\Theta$  remains unchanged under the transformation from the natural frame to the eigenframe. Substitution of the explicit forms of the  $d$ -functions yields

$$\bullet \quad W(\Theta\varphi')' = \frac{1}{4\pi} - \frac{3}{4\pi} \left[ \langle T_{22}^+ \rangle' \sin^2 \Theta \cos 2\varphi' + \left( \frac{1}{2} \right)^{1/2} \langle T_{20}^+ \rangle' (3 \cos^2 \Theta - 1) \right] \quad (4.110)$$

The lengths of the principal axes are then given by  $2W(\Theta = 0, \varphi' \text{ arbitrary})'$ ,  $2W(\Theta = 90^\circ, \varphi' = 0)'$ , and  $2W(\Theta = 90^\circ, \varphi' = 90^\circ)'$ , respectively, and can be expressed in terms of the multipoles  $\langle T_{00} \rangle$ ,  $\langle T_{22}^+ \rangle'$ , and  $\langle T_{20}^+ \rangle'$ . From (4.110) we obtain

$$W(0)' = \frac{1}{4\pi} [1 - 6^{1/2} \langle T_{20} \rangle'] \quad (4.111a)$$

$$W(90^\circ, 0^\circ)' = \frac{1}{\pi} \left[ 1 - 3 \langle T_{22}^+ \rangle' + \left( \frac{3}{2} \right)^{1/2} \langle T_{20}' \rangle \right] \quad (4.111b)$$

$$W(90^\circ, 90^\circ)' = \frac{1}{\pi} \left[ 1 + 3 \langle T_{22}^+ \rangle' + \left( \frac{3}{2} \right)^{1/2} \langle T_{20}' \rangle \right] \quad (4.111c)$$

From the last two equations follows

$$\langle T_{22}^+ \rangle' = \frac{2\pi}{3} [W(90^\circ, 90^\circ)' - W(90^\circ, 0)'] \quad (4.112a)$$

The alignment component  $\langle T_{22}^+ \rangle'$  is therefore proportional to the difference between height and width of the charge cloud. If  $\langle T_{22}^+ \rangle'$  vanishes then the charge distribution is axially symmetric around  $z'$  and the angular distributions become independent of  $\varphi'$ . In this case we obtain, from (4.111),

$$W(0)' - W(90^\circ, 0)' = - \left( \frac{1}{2} \right)^{1/2} \langle T_{20}^+ \rangle' \quad (4.112b)$$

The distribution is disclike if  $\langle T_{20}^+ \rangle'$  is positive and cigar-shaped if  $\langle T_{20}^+ \rangle'$  is negative.

Our results show that the parameters  $\langle T_{20}^+ \rangle'$  and  $\langle T_{22}^+ \rangle'$ , defined in the eigenframe, are directly related to the geometric properties of the charge cloud. The relations (4.111) give a simple geometric interpretation to these multipoles.

A more detailed discussion of the description of charge distribution has been given by [Andersen et al. \(1988\)](#), where another convenient set of parameters has been introduced which are closely related to experimental observables (see Sect. 6.1.1).

The formalism developed here will further be applied in Sect. 6.3 where the rotation of the charge cloud in magnetic fields will be discussed. The influence of electric fields is the topic of Sect. 6.4. In Sect. 7.7 we will consider shape and spatial orientation of molecular charge distributions.

## 4.7 Time Evolution of State Multipoles in the Presence of an External Perturbation

### 4.7.1 The Perturbation Coefficients

The time evolution of state multipoles can be obtained from (2.50) or (2.52) and (4.33). Of particular interest for our subsequent discussion is the following situation. Consider an ensemble of atoms (nuclei) which has been excited to states which can be described by a Hamiltonian  $H = H_0 + H'$ , where  $H'$  denotes a perturbation which is assumed to be weak and unimportant during the excitation process. The term  $H'$  can then be neglected during the excitation. Assuming that the eigenstates of  $H_0$  can be identified in terms of angular momentum numbers we will denote the relevant states by  $|JM\rangle$ . After the excitation, however, the time evolution of the states is governed by the total Hamiltonian  $H$  and the corresponding time evolution operator  $U(t)$ .

Suppose that an atomic ensemble has been excited instantaneously at time  $t = 0$  where by “instantaneously” is meant that the excitation time is much shorter than all characteristic transition times caused by the perturbation  $H'$  (see Sect. 3.5.1). Immediately after the excitation the ensemble can then be represented by a density matrix  $\rho(0)$ . Tensor operators can be constructed using the eigenstates  $|JM\rangle$  of  $H_0$  in (4.8). Expanding  $\rho(0)$  in terms of these tensors gives

$$\rho(0) = \sum_{\substack{J'J \\ KQ}} \left\langle T(J'J)_{KQ}^\dagger \right\rangle T(J'J)_{KQ} \quad (4.113)$$

where the state multipoles are given by

$$\left\langle T(J'J)_{KQ}^\dagger \right\rangle = \text{tr } \rho(0) T(J'J)_{KQ}^\dagger \quad (4.114)$$

[see (4.33)]. We will henceforth denote the multipoles describing the atomic states at time  $t = 0$  by  $\left\langle T(J'J)_{KQ}^\dagger \right\rangle$ . The sum in Eq. (4.113) includes all angular momenta  $J'$ ,  $J$  which are present at time  $t = 0$ .

The density matrix  $\rho(0)$  evolves under the influence of the total Hamiltonian  $H$  into the density matrix

$$\rho(t) = U(t)\rho(0)U(t)^\dagger \quad (4.115)$$

During the time interval  $0 \dots t$  the states which were initially excited are disturbed and mixed by the perturbation  $H'$ . Any state  $|JM\rangle$  will evolve into a state  $|\varphi(t)\rangle = U(t)|JM\rangle$  which can be expanded in terms of a full set of eigenstates  $|jm\rangle$  of the Hamiltonian  $H_0$ . Tensor operators can be constructed from these states  $|jm\rangle$  and used to expand  $\rho(t)$ :

$$\rho(t) = \sum_{\substack{j'j \\ kq}} \left\langle T(j'j)_{kq}^\dagger \right\rangle T(j'j)_{kq} \quad (4.116)$$

where the sum includes all angular momenta  $j'$  and  $j$  in which the atoms can be found at time  $t$ . From (4.113), (4.115), and (4.116)

$$\begin{aligned} \left\langle T(j'j)_{kq}^\dagger \right\rangle &= \text{tr } \rho(t) T(j'j)_{kq}^\dagger \\ &= \text{tr } U(t)\rho(0)U(t)^\dagger T(j'j)_{kq}^\dagger \\ &= \sum_{\substack{J'J \\ KQ}} \left\langle T(J'J)_{KQ}^\dagger \right\rangle \text{tr} \left[ U(t)T(J'J)_{KQ}U(t)^\dagger T(j'j)_{kq}^\dagger \right] \\ &= \sum_{\substack{J'J \\ KQ}} \left\langle T(J'J)_{KQ}^\dagger \right\rangle G(J'J, j'j; t)_{Kk}^{Qq} \end{aligned} \quad (4.117)$$

where we introduced the *perturbation coefficients*

- 

$$G(J'J, j'j; t)_{Kk}^{Qq} = \text{tr} \left[ U(t)T(J'J)_{KQ}U(t)^\dagger T(j'j)_{kq}^\dagger \right] \quad (4.118)$$

In (4.117) the multipoles  $\left\langle T(j'j, t)_{kq}^\dagger \right\rangle$  characterizing the atomic states at time  $t$ , are expressed in terms of their counterparts at time  $t = 0$ . *The perturbation coefficients are simply the coefficients in this expansion.*

### 4.7.2 Perturbation Coefficients for the Fine and Hyperfine Interactions

In order to clarify the concepts introduced in the preceding section we will now consider the time evolution of atomic states, excited at  $t = 0$ , under the influence of the fine-structure interaction. We will not specify the excitation mechanism. The basic assumptions which will be made are that during the excitation the orbital and spin angular momentum of the atoms are uncoupled and that the atomic spins are unpolarized immediately after the excitation. With these assumptions the atomic states immediately after the excitation can then be represented in the uncoupled representation  $|LMS_1 M_{s_1}\rangle$  where the spin states are equally populated. We will assume sharp values of  $L$  and  $S_1$ .

These assumptions apply, for example, in the case of excitation of light atoms by electron impact as discussed in Sect. 3.5. They are also assumed to be valid for atoms which have been excited by beam-foil excitation.

Immediately after the excitation the atomic ensemble can be represented by a density matrix  $\rho(0)$  with elements  $\langle LM' S_1 M' S_1 | \rho(0) | LMS_1 M_{s_1} \rangle$ . In the following we will be interested only in the properties of the orbital states and hence we will define a reduced density matrix  $\rho(L)$  with elements

$$\langle LM' | \rho(L) | LM \rangle = \sum_{M_{s_1}} \langle LM' S_1 M_{s_1} | \rho(0) | LMS_1 M_{s_1} \rangle \quad (4.119)$$

For example, in the case of excitation by electron impact, the elements (4.119) are given by (3.31) in terms of the scattering amplitudes.

The reduced density matrix can be expanded in terms of state multipoles as in (4.113):

$$\rho(L) = \sum_{KQ} \langle T(L)_{KQ}^\dagger \rangle T(L)_{KQ} \quad (4.120)$$

where the tensors  $\langle T(L)_{KQ} \rangle$  characterize the orbital states at time  $t = 0$ , that is, immediately after the excitation.

The states  $|LMS_1 M_{s_1}\rangle$  can be considered as eigenstates of a Hamiltonian  $H_0$ . After the excitation the atoms are assumed to relax into the  $JM$ -coupling scheme under the influence of the fine-structure interaction  $H' \sim LS$  which perturbs the initially excited states. In terms of the vector model this distortion can be interpreted as a precession of the angular momentum vectors  $\mathbf{L}$  and  $\mathbf{S}_1$  around the total angular momentum  $\mathbf{J}$  (this precession is neglected during the excitation). The fine-structure interaction is assumed to be weak, and hence transitions between states with different  $L$  and  $S_1$  can be neglected and  $L$  and  $S_1$  can be considered to be conserved.

The time development of the atomic state is governed by the operator

$$U(t) = \exp(-iHt/\hbar)$$

where the total Hamiltonian  $H = H_0 + H'$  includes the interaction term  $H'$  which couples the spin and orbital systems. Thus  $U(t)$  acts on both systems and it is therefore necessary to consider the total density matrix  $\rho(0)$  instead of the matrix (4.120), which only describes the orbital states. A convenient form of  $\rho(0)$  can be obtained as follows: Since orbital and spin systems are uncorrelated at time  $t = 0$  and the spins unpolarized,  $\rho(0)$  is given by

$$\rho(0) = \rho(L) \times \frac{1}{2S_1 + 1} \mathbf{1} \quad (4.121a)$$

where (2.24) and (A.11) have been used and where  $\mathbf{1}$  is the unit operator in spin space. Substituting (4.120) into (4.121a) gives

$$\rho(0) = \frac{1}{2S_1 + 1} \sum_{KQ} \left\langle T(L)_{KQ}^\dagger \right\rangle [T(L)_{KQ} \times \mathbf{1}] \quad (4.121b)$$

At time  $t$  the system is represented by a density matrix which has evolved from the matrix  $\rho(0)$  and satisfies (2.50):

$$\begin{aligned} \rho(t) &= U(t)\rho(0)U(t)^\dagger \\ &= \frac{1}{2S_1 + 1} \sum_{KQ} \left\langle T(L)_{KQ}^\dagger \right\rangle U(t)(T(L)_{KQ} \times \mathbf{1})U(t)^\dagger \end{aligned} \quad (4.122)$$

We define state multipoles  $\left\langle T(L, t)_{kq}^\dagger \right\rangle$  describing the orbital states at time  $t$  as the irreducible components of the corresponding reduced density matrix  $\rho(L, t)$ :

$$\left\langle T(L, t)_{kq}^\dagger \right\rangle = \text{tr } \rho(L, t) T(L)_{kq}^\dagger \quad (4.123a)$$

where the elements of  $\rho(L, t)$  are given by

$$\langle LM' | \rho(L, t) | LM \rangle = \sum_{M_{S_1}} \langle LM' S_1 M_{S_1} | \rho(t) | LMS_1 M_{S_1} \rangle$$

Alternatively, and more conveniently for the present discussion, the multipole components can be represented by

$$\left\langle T(L, t)_{kq}^\dagger \right\rangle = \text{tr } \rho(t) \left[ T(L)_{kq}^\dagger \times \mathbf{1} \right] \quad (4.123b)$$

where  $\mathbf{1}$  is the unit operator in spin space. The equivalence of (4.123a) and (4.123b) can be shown by calculating the trace (4.123) using the uncoupled states  $|LMS_1 M_{S_1}\rangle$  (see Appendix A.1).

Substituting (4.122) into (4.123) gives

$$\begin{aligned}
 & \left\langle T(L, t)_{kq}^\dagger \right\rangle \\
 &= \frac{1}{2S_1 + 1} \sum_{KQ} \left\langle T(L)_{KQ}^\dagger \right\rangle \text{tr} \left\{ U(t) [T(L)_{KQ} \times \mathbf{1}] U(t)^\dagger \left[ T(L)_{kq}^\dagger \times \mathbf{1} \right] \right\} \\
 &= \sum_{KQ} \left\langle T(L)_{KQ}^\dagger \right\rangle G(L; t)_{Kk}^{Qq}
 \end{aligned} \tag{4.124}$$

where the perturbation coefficients  $G(L; t)_{Kk}^{Qq}$  are the coefficients in this new multipole expansion:

$$G(L; t)_{Kk}^{Qq} = \frac{1}{2S_1 + 1} \text{tr} \left\{ U(t) [T(L)_{KQ} \times \mathbf{1}] U(t)^\dagger \left[ T(L)_{kq}^\dagger \times \mathbf{1} \right] \right\} \tag{4.125}$$

We will now derive an explicit expression for the quantities (4.125). Because the elements of  $U(t)$  are diagonal in the eigenstate representation  $|(LS_1)JM\rangle$  of the total Hamiltonian  $H$  the matrix representation of  $U(t)$  in this representation has elements

$$\langle (LS_1)J'M' | U(t) | (LS_1)JM \rangle = \exp(-iE_J t / \hbar) \delta_{JJ'} \delta_{MM'} \tag{4.126}$$

(where  $E_J$  is the energy of the level  $LS_1J$ ). using (4.126) the trace in (4.125) can be calculated in the coupled representation:

$$\begin{aligned}
 G(L; t)_{Kk}^{Qq} &= \frac{1}{2S_1 + 1} \sum_{\substack{J'M' \\ JM}} \exp \left[ \frac{+i(E_J - E_{J'})t}{\hbar} \right] \\
 &\quad \times \langle (LS_1)J'M' | T(L)_{KQ} \times \mathbf{1} | (LS_1)JM \rangle \left\langle (LS_1)JM \left| T(L)_{kq}^\dagger \right. \right. \\
 &\quad \times \mathbf{1} \left. \left. | (LS_1)J'M' \right\rangle \right. \tag{4.127a}
 \end{aligned}$$

The remaining elements can be obtained by using the fact that  $T(L)_{KQ} \times \mathbf{1}$  is a tensor operator of rank  $K$  and components  $Q$ . Applying the Wigner–Eckart theorem

$$\begin{aligned}
 & \langle (LS_1)J'M' | T(L)_{KQ} \times \mathbf{1} | (LS_1)JM \rangle \\
 &= (-1)^{J'-M'} \begin{pmatrix} J' & K & J \\ -M' & Q & M \end{pmatrix} \langle (LS_1)J' | T_K \times \mathbf{1} | (LS_1)J \rangle
 \end{aligned} \tag{4.127b}$$

and a standard formula of angular momentum theory [(C.20)] gives

$$\begin{aligned} & \langle (LS_1)J' \| T_K \times \mathbf{1} \| (LS_1)J \rangle \\ &= (-1)^{L+S_1+J+K} [(2J'+1)(2J+1)(2K+1)]^{1/2} \begin{Bmatrix} L & J' & S_1 \\ J & L & K \end{Bmatrix} \end{aligned} \quad (4.127c)$$

where (4.28) has been used to give the explicit value of the reduced matrix element  $\langle L \| T(L)_K \| L \rangle$ . A similar formula holds for the matrix element of the operator  $T(L)_{Kq}^\dagger \times \mathbf{1}$ . Inserting the resultant expressions into (4.127a) and summing over  $M'$  and  $M$  with the help of the orthogonality relations of the  $3j$  symbols give

$$\begin{aligned} G(L; t)_{Kk}^{Qq} &= \frac{1}{2S_1 + 1} \sum_{J'J} (2J'+1)(2J+1) \\ &\times \begin{Bmatrix} L & J' & S_1 \\ J & L & K \end{Bmatrix}^2 \exp \left[ \frac{-i(E_{J'} - E_J)t}{\hbar} \right] \delta_{Kk} \delta_{Qq} \end{aligned} \quad (4.128)$$

The Kronecker symbols indicate that multipoles with different ranks and components cannot be mixed by the interaction. Furthermore, the perturbation coefficients are independent of  $Q$  and can hence be written in the form

$$G(L; t)_{Kk}^{Qq} = G(L; t)_K \delta_{Kk} \delta_{Qq} \quad (4.129)$$

The coefficients (4.128) are real numbers. This can be shown by taking the complex conjugate of the bracket in (4.128), interchanging  $J$  and  $J'$ , and using the symmetry property (C.8) of the  $6j$  symbols. The imaginary part of the complex exponential function in (4.128) therefore vanishes as a result of summing over all  $J$  and  $J'$  and only the real part survives:

$$\bullet \quad G(L; t) = \frac{1}{2S_1 + 1} \sum_{J'J} (2J'+1)(2J+1) \begin{Bmatrix} L & J' & S_1 \\ J & L & K \end{Bmatrix}^2 \cos \left[ \frac{E_{J'} - E_J)t}{\hbar} \right] \quad (4.130)$$

From (4.124) and (4.129) we obtain finally

$$\bullet \quad \langle T(L; t)_{KQ}^\dagger \rangle = G(L; t)_K \langle T(L)_{KQ}^\dagger \rangle \quad (4.131)$$

which describes the time evolution of the state multipoles under the influence of the fine-structure interaction.

It is sometimes convenient to represent the coefficients  $G(L; t)_K$  in the form

$$\begin{aligned} G(L; t)_K &= \overline{G(L)_K} \\ &+ \frac{1}{2S_1 + 1} \sum_{J' \neq J} (2J'+1)(2J+1) \begin{Bmatrix} L & J' & S_1 \\ J & L & K \end{Bmatrix}^2 \cos \left[ \frac{(E_{J'} - E_J)t}{\hbar} \right] \end{aligned} \quad (4.132)$$

where terms with  $J = J'$  and terms with  $J \neq J'$  have been separated and where the time-independent part is defined by

$$\overline{G(L)_K} = \frac{1}{2S_1 + 1} \sum_J (2J + 1)^2 \left\{ \begin{smallmatrix} L & J & S_1 \\ J & L & K \end{smallmatrix} \right\}^2 \quad (4.133)$$

The hyperfine interaction can be treated by using the same method as has been used for the fine-structure interaction. Suppose that at time  $t = 0$  atomic states with electronic angular momentum  $J$  are excited with the nuclear spin  $I$  unaffected. Constructing state multipoles  $\langle T(J)_{KQ}^\dagger \rangle$  and  $\langle T(J; t)_{KQ}^\dagger \rangle$  from the states  $|JM\rangle$  at times  $t = 0$  and  $t$ , respectively, it can be shown that these tensors are related by an expression similar to (4.131):

$$\langle T(J; t)_{KQ}^\dagger \rangle = G(J; t)_K \langle T(J)_{KQ}^\dagger \rangle$$

where the perturbation coefficients  $G(J; t)$  are given by (4.130) with  $L$  replaced by  $J$ ,  $S_1$  replaced by  $I$ , and  $J(J')$  replaced by  $F(F')$ , where  $F$  denotes the total angular momentum:

$$G(J; t)_K = \frac{1}{2I + 1} \sum_{F'F} (2F' + 1)(2F + 1) \left\{ \begin{smallmatrix} J & F' & I \\ F & J & K \end{smallmatrix} \right\}^2 \cos \left[ \frac{(E_{F'} - E_F)t}{\hbar} \right] \quad (4.134)$$

Finally, we will consider the case in which both fine and hyperfine interaction must be taken into account. When the hyperfine interaction is much weaker than the fine-structure interaction the angular momentum of the electronic state,  $J$ , remains a good quantum number and the relevant perturbation coefficients can be calculated by a similar method to that used above and are given by

$$\begin{aligned} G(t)_K^H &= \frac{1}{(2S_1 + 1)(2I + 1)} \sum_{J'J} (2J + 1)(2J' + 1)(2F' + 1) \\ &\quad \times (2F + 1) \left\{ \begin{smallmatrix} J' & F' & I \\ F & J & K \end{smallmatrix} \right\}^2 \left\{ \begin{smallmatrix} L & J' & S_1 \\ J & L & K \end{smallmatrix} \right\}^2 \\ &\quad \times \exp \left[ \frac{i(E_{J'} - E_J)t}{\hbar} - \frac{(\gamma_1 + \gamma_{J'})t}{2} \right] \end{aligned} \quad (4.135)$$

In deriving (4.135) it is again assumed that  $S_1$  and  $I$  are unaffected by the excitation and decay process. The energies  $E_1$  and decay constants  $\gamma_1$  refer to states with angular momenta  $J$  and  $F$ .

If the fine and hyperfine splittings are comparable a more elaborate calculation is necessary since  $J$  is no longer a good quantum number. This is discussed in more detail, for example, by [Fano and Macek \(1973\)](#).

### 4.7.3 An Explicit Example

We will now discuss the physical significance of the perturbation coefficients (4.130), following [Fano and Macek \(1973\)](#), using an explicit example. Let us take the case with  $L = 1$ ,  $S_1 = 1/2$ , and  $J = 1/2, 3/2$ , and discuss the time evolution of the orientation vector:

$$\langle T(L; t)_{1Q}^\dagger \rangle = G(L; t)_1 \langle T(L)_{1Q}^\dagger \rangle \quad (4.136)$$

The numerical values of the relevant  $6j$  symbols are given by

$$\begin{aligned} \left\{ \begin{array}{ccc} 1 & \frac{1}{2} & \frac{1}{2} \\ \frac{1}{2} & 1 & 1 \end{array} \right\} &= -\frac{1}{3}, & \left\{ \begin{array}{ccc} 1 & \frac{3}{2} & \frac{1}{2} \\ \frac{3}{2} & 1 & 1 \end{array} \right\} &= \frac{5^{1/2}}{6(2^{1/2})}, \\ \left\{ \begin{array}{ccc} 1 & \frac{1}{2} & \frac{1}{2} \\ \frac{3}{2} & 1 & 1 \end{array} \right\} &= -\frac{1}{6} \end{aligned}$$

Substituting these values into (4.130) gives

$$G(L; t)_1 = \frac{7}{9} + \frac{2}{9} \cos[(E_{1/2} - E_{3/2})t/\hbar] \quad (4.137)$$

Equation 4.137 shows that in this case  $G(L; t)_1$  oscillates around the mean value  $G(L)_1 = 7/9$  with a frequency  $\omega = (E_{1/2} - E_{3/2})/\hbar$ , which in the semiclassical model is just the precession period of the vectors  $\mathbf{S}_1$  and  $\mathbf{L}$  around  $\mathbf{J}$ . From (4.136) and (4.137) it can be seen that the orientation vector  $\langle T(L)_{1Q}^\dagger \rangle$  varies periodically with  $t$ . This behavior is a consequence of angular momentum coupling. During the excitation the orbital system acquires a certain orientation while the spins remain unpolarized. Because of the spin-orbit coupling, which is assumed to be “switched on” immediately after the excitation, there is a transfer of orientation between orbital and spin systems. The spins become oriented and there is a resultant loss of orientation in the orbital states. In each period  $\langle T(L)_{1Q}^\dagger \rangle$  decreases, reaches a minimum (when the spins have obtained the maximum possible orientation), and then rises again to its initial value when the spins are again unoriented. *This exchange of orientation is periodic and reversible*, reflecting the fact that the spin-orbit coupling  $H' \sim LS$  is symmetric in  $L$  and  $S$ . These results can be generalized to any multipole component.

In conclusion, the state multipoles  $\langle T(Lt)_{KQ}^\dagger \rangle$  oscillate about a mean value  $\overline{G(L)_K} \langle T(L)_{KQ}^\dagger \rangle$ . This behavior is a consequence of the fine-structure interaction between orbital and spin angular momentum which results in a *periodic and reversible* exchange of polarization between the two systems. The observable consequences of these time variations will be considered in detail in Chaps. 5 and 6.

#### 4.7.4 Influence of an External Magnetic Field

We will now consider a situation in which an ensemble of atoms (or nuclei) has been excited at time  $t = 0$  in the presence of a magnetic field,  $\mathbf{H}_m$ . The total Hamiltonian is given by  $H = H_0 + H'$ , where  $H' = -g\mu_B \mathbf{J} \mathbf{H}_m$  describes the interaction with the field. The eigenstates of  $H_0$  are chosen to be  $|JM\rangle$ . The magnetic field induces splittings between levels with the same  $J$  and different  $M$ . Transitions between the split levels are characterized by a transition time  $T \sim 1/\Delta E$ , where  $\Delta E$  is the largest energy splitting of a level with angular momentum  $J$ . It will be assumed that  $T$  is large compared to the excitation time. In this case the influence of the magnetic field can be neglected during the excitation and the atoms can be assumed to be excited into states  $|JM\rangle$ . The field will disturb the states immediately after the excitation and we will consider the time development of the initial multipoles  $\langle T(J)_{KQ}^\dagger \rangle$  under the influence of the time evolution operator

$$U(t) = \exp(-iHt)/\hbar \quad (4.138)$$

The relevant perturbation coefficients are given by

$$G(J; t) \frac{\partial^q}{\partial k^q} = \text{tr} [U(t) T(J)_{KQ} U(t)^\dagger T(J)_{KQ}^\dagger] \quad (4.139)$$

The initial multipoles are defined with respect to a coordinate system  $XYZ$  and the field  $\mathbf{H}_m$  is taken to be parallel to a direction  $z$ . With  $z$  as the quantization axis

$$H' = -g\mu_B J_z H_m \quad (4.140)$$

and relating the eigenstates of  $H_0$  to  $z$  the elements of  $H$  are given by

$$\langle Jm' | H | JM \rangle = (E_J - g\mu_B B_m) \delta_{m'm} \quad (4.141)$$

Transforming the tensor operators to the  $xyz$  system using (4.13), calculating the trace (4.139) in terms of the states  $|Jm\rangle$ , and using (4.138) and (4.141) gives, after some manipulations,

$$\begin{aligned}
G(J; t)_{Kk}^{Qq} &= \sum_{Q'q'} (-1)^q \left[ D(0\beta\alpha)_{Q'Q}^{(K)} \right] \left[ D(0\beta\alpha)_{q'q}^{(k)} \right] \\
&\quad \times \text{tr} [U(t)T(J)_{KQ'}U(t)^\dagger T(J)_{kq'}] \\
&= \sum_{Q'q'} (-1)^q \left[ D(0\beta\alpha)_{Q'Q}^{(K)} \right] \left[ D(0\beta\alpha)_{q'q}^{(k)} \right] \\
&\quad \times \sum_{m'm} \langle Jm' | T(J)_{KQ'} | Jm \rangle \\
&\quad \times \langle Jm | T(J)_{kq'} | Jm' \rangle \exp(-i\omega_L Q't) \tag{4.142}
\end{aligned}$$

where  $\beta$  is the angle between  $Z$  and  $z$  and  $\alpha$  is the azimuthal angle of  $z$  in the  $XYZ$  system,  $\omega_L$  denotes the Larmor frequency.

Using (4.9) in the  $xyz$  system, performing the sum over  $m'$  and  $m$  by using the orthogonality relations of the  $3j$  symbols, we obtain

$$G(J; t)_{Kk}^{Qq} = \delta_{Kk} \sum_{Q'} \exp(-i\omega_L Q't) D(0\beta\alpha)_{Q'Q}^{(K)} D(0\beta\alpha)_{Qq}^{(K)*} \tag{4.143}$$

Using (C.12),  $\exp(-i\omega_L Qt)$  can be interpreted as a rotation of  $-\omega_L t$  about  $z$ .

In the simple case where the field direction  $z$  coincides with  $Z$  we have  $\beta = \alpha = 0$  and (4.143) reduces to

$$G(J, t)_{Kk}^{Qq} = \delta_{Kk} \delta_{Qq} \exp(-i\omega_L Qt) \tag{4.144}$$

In this case the field cannot alter the multipoles but merely causes their phases to change in time:

$$\langle T(J; t)_{KQ}^\dagger \rangle = \exp(-i\omega_L Qt) \langle T(J)_{KQ}^\dagger \rangle \tag{4.145}$$

Equations 4.143 and 4.144 will be used in Sect. 6.3.

## 4.8 Notations Used by Other Authors

Unfortunately many notations are used for the tensor operators and state multipoles. We list here a few of the notations used in the literature.

Our tensor operator  $T(J'J)_{KQ}$  is written as

$$\begin{aligned}
T_Q^{(K)}(\alpha J', \beta J) &\quad \text{by Omont (1977),} \\
T_Q^{(K)}(J', J) &\quad \text{by Happer (1972), and}
\end{aligned}$$

$T_{KQ}$  by Brink and Satchler (1962) and Lamb and ter Haar (1971).

[Dynakov et al. \(1965\)](#) use a different normalization so that the operator  $T_Q^{(K)}$  of these authors is equal to

$$[(2K + 1)/(2J + 1)]^{1/2}(-1)^Q T(J)_{KQ}$$

in our notation.

Our state multipole  $\langle T(J'J)_{KQ}^\dagger \rangle$  is written as

$\rho_Q^{(K)}(\alpha J', \beta J)$	by <a href="#">Omont (1977)</a> ,
$\rho_{KQ}(J'J)$	by <a href="#">Happer (1972)</a> ,
$\rho(JJ')_{KQ}^*$	by <a href="#">Brink and Satchler (1962)</a> and Lamb and ter Haar (1971),
$(-1)^{J'+J+Q} \rho_Q^{:(K)}(J'J)$	by <a href="#">Steffen and Alder (1975)</a> .

The convention for the  $D$  matrices adopted here is that of [Landau and Lifschitz \(1965\)](#). Edmonds' (1957) notation is obtained by interchanging  $\alpha$  and  $\gamma$  in all equations. For the functions  $d(\beta)_{n'n}^{(J)}$  the convention of Edmonds is the same as that employed here. The relation between our notation and that of [Zare \(1988\)](#) is

$$D(\gamma\beta\alpha)_{M'M}^{(J)} = \left( D(\alpha\beta\gamma)_{MM'}^{(J)*} \right)_{\text{Zare}}$$

That is, we can use Zare's equations by interchanging  $M$  and  $M'$ ,  $\alpha$  and  $\gamma$ , and taking the complex conjugate. Note the relation for the  $d$  matrices:

$$\left( d(\Theta)_{MM'}^{(J)} \right)_{\text{Zare}} = \left( d(-\Theta)_{MM'}^{(J)} \right)_{\text{Edmonds}} = \left( d(\Theta)_{M'M}^{(J)} \right)_{\text{Edmonds}}$$

Further conventions have been listed by Edmonds.

# Chapter 5

## Radiation from Polarized Atoms. Quantum Beats

### 5.1 General Theory I: Density Matrix Description of Radiative Decay Processes

In this chapter we will consider the decay of an ensemble of excited atoms by photon emission. We will discuss the following case. We assume that an ensemble of atoms has been excited “instantaneously” at time  $t = 0$ . As usual, “instantaneous” implies that the excitation time is short compared to the mean lifetime of the excited states and any characteristic precession frequency (see Sects. 3.5 and 4.7.1).

The excitation mechanism can be of any kind and the atoms may have been excited, for example, by electron impact, photon absorption, or by beam–foil techniques. Our main objective will be the derivation of (5.18) and (5.19), which will then be used in the subsequent sections. Readers who are not so much interested in mathematical details of the proofs may proceed directly to formulas (5.18) and (5.19).

The excited atoms may be considered as a (coherent or incoherent) superposition of states  $|\alpha_1 J_1 M_1\rangle$ , where  $\alpha_1$  denotes collectively the set of quantum numbers which are needed to describe the states in addition to the angular momentum quantum numbers  $J_1$  and  $M_1$ .

The atoms are assumed to decay to lower levels  $|\alpha_2 J_2 M_2\rangle$ . In the following we will assume  $\alpha_1$  and  $\alpha_2$  to be fixed and suppress the dependence of the state vectors on these quantum numbers. The treatment will be further simplified by neglecting the finite lifetime of the final state.

The emitted photons will be described in terms of state vectors  $|\mathbf{n}\omega\lambda\rangle$  in the helicity representation, where  $\mathbf{n}$  is fixed by the direction of observation. We will now derive an expression for the polarization density matrix of the emitted photons. In the first part of the calculation we will use  $\mathbf{n}$  as the quantization axis and relate all angular momentum quantum numbers to this axis. This choice will considerably simplify the second part of the calculations in the following section. At the end of

the calculations we will transform to a coordinate system defined with respect to the excitation process.

Immediately after the excitation the ensemble of excited atoms may be characterized by a density matrix  $\rho(0)$  which evolves according to (2.50) into a density matrix:

$$\rho(t)_{\text{out}} = U(t)\rho(0)U(t)^\dagger \quad (5.1)$$

where the operator  $U(t)$  describes the time evolution under the influence of the interaction with the virtual radiation field. (In this section it is assumed that the atomic states are not perturbed by internal or external fields between excitation and decay.) The matrix  $\rho_{\text{out}}$  describes the entire ensemble of atoms and photon at time  $t$ , that is, the atoms which are still in the excited state, the atoms in the lower levels, and the photons emitted in the time interval  $0 \dots t$ .

The decay process can be described in first-order perturbation theory. In this approximation the operator  $U(t)$  is given by (2.73) and (2.69):

$$\begin{aligned} U(t) &= U(t)_0 \left[ \mathbf{1} - \frac{i}{\hbar} \int_0^t V(\tau) d\tau \right] \\ &= U(t)_0 \left[ \mathbf{1} - \frac{i}{\hbar} \int_0^t U(\tau)_0^\dagger V U(\tau)_0 d\tau \right] \end{aligned} \quad (5.2)$$

where we inserted (2.61). The elements of the operator  $V$ , describing the interaction between atoms and virtual radiation field, will be specified later.  $U(t)_0$  is the free time evolution operator; hence

$$U(t)_0 |J_2 M_2 \omega \mathbf{n} \lambda \rangle = \exp[-(i/\hbar) E_2 t - i \omega t] |J_2 M_2 \omega \mathbf{n} \lambda \rangle \quad (5.3a)$$

$$U(t)_0 |J_1 M_1 \rangle = \exp[-(i/\hbar) E_1 t - \gamma_1 t/2] |J_1 M_1 \rangle \quad (5.3b)$$

where the finite level width of the initial state has been included.  $E_1$  and  $E_2$  denote the energy of the states with angular momentum  $J_1$  and  $J_2$ , respectively, and  $\gamma_1$  is the decay constant.

We are interested in the elements  $\langle \omega \mathbf{n} \lambda' | \rho(t) | \omega \mathbf{n} \lambda \rangle$  of the reduced density matrix  $\rho(t)$  which describe the polarization state of the emitted photons only. The normalization is as in (1.69) so that the diagonal elements  $\langle \omega \mathbf{n} \lambda | \rho(t) | \omega \mathbf{n} \lambda \rangle$  give the intensity of those photons detected in the direction  $\mathbf{n}$  with frequency  $\omega$  and helicity  $\lambda$ . Using (3.5) the matrix elements are given by

$$\langle \omega \mathbf{n} \lambda' | \rho(t) | \omega \mathbf{n} \lambda \rangle = \sum_{J_2 M_2} \langle J_2 M_2 \omega \mathbf{n} \lambda' | \rho(t)_{\text{out}} | J_2 M_2 \omega \mathbf{n} \lambda \rangle \quad (5.4)$$

Substituting (5.1) for  $\rho(t)_{\text{out}}$  and (5.2) for  $U(t)$  gives<sup>1</sup>

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<sup>1</sup>We have to multiply by  $\hbar \omega$  in accordance with the normalization (1.69).

$$\begin{aligned} \langle \omega \mathbf{n} \lambda' | \rho(t) | \omega \mathbf{n} \lambda \rangle &= \frac{\hbar \omega}{\hbar^2} \sum_{\substack{J_2 M_2 \\ J'_1 M'_1 J_1 M_1}} \left\langle J_2 M_2 \omega \mathbf{n} \lambda' \left| \int_0^t U(\tau)_0^\dagger V U_0(\tau) d\tau \right| J'_1 M'_1 \right\rangle \\ &\quad \times \langle J'_1 M'_1 | \rho(0) | J_1 M_1 \rangle \left\langle J_1 M_1 \left| \int_0^t U(\tau)_0^\dagger V U \tau(0) d\tau \right| J_2 M_2 \omega \mathbf{n} \lambda \right\rangle \end{aligned}$$

The terms proportional to the identity matrix cannot contribute to the transitions  $J_1 \rightarrow J_2 \neq J_1$ . By applying (5.3) we obtain

$$\begin{aligned} \langle \omega \mathbf{n} \lambda' | \rho(t) | \omega \mathbf{n} \lambda \rangle &= \frac{\omega}{\hbar} \sum_{\substack{J_2 M_2 \\ J'_1 M'_1 J_1 M_1}} \langle J_2 M_2 \omega \mathbf{n} \lambda' | V | J'_1 M'_1 \rangle \langle J'_1 M'_1 | \rho(0) | J_1 M_1 \rangle \\ &\quad \times \langle J_1 M_1 | V | J_2 M_2 \omega \mathbf{n} \lambda \rangle \left\{ \int_0^t d\tau \exp \left[ i \left( \omega + \omega_{21'} + \frac{i}{2} \gamma_{1'} \right) \tau \right] \right\} \\ &\quad \times \left\{ \int_0^t d\tau \exp \left[ i \left( -\omega - \omega_{21} + \frac{i}{2} \gamma_1 \right) \tau \right] \right\} \end{aligned} \quad (5.5)$$

with  $\omega_{21'} = (1/\hbar)(E_2 - E_1')$ ,  $\omega_{21} = (E_2 - E_1)/\hbar$ , and where  $E_{1'}$ ,  $\gamma_{1'}$  and  $E_1$ ,  $\gamma_1$  denote energy and decay constants of the states  $|J'_1 M'_1\rangle$  and  $|J_1 M_1\rangle$ , respectively.

Taking the nonrelativistic limit the elements of  $V$  are given in the dipole approximation by

$$\langle J_2 M_2 \omega \mathbf{n} \lambda | V | J_1 M_1 \rangle = -i \omega_{21} [(2\pi\hbar/\omega)]^{1/2} e \langle J_2 M_2 | \mathbf{e}_\lambda^* \mathbf{r} | J_1 M_1 \rangle \quad (5.6)$$

(for details, see, for example, [Landau and Lifschitz 1965](#)), where  $\mathbf{e}_\lambda$  denotes the polarization vector (1.59) ( $\lambda = \pm 1$ ) and  $\mathbf{r}$  is the dipole operator. The time integrations in (5.5) can easily be carried out:

$$\begin{aligned} \langle \omega \mathbf{n} \lambda' | \rho(t) | \omega \mathbf{n} \lambda \rangle &= \frac{2\pi e^2 \omega_{21}^2}{\omega \hbar^2} \sum_{\substack{J_2 M_2 \\ J'_1 M'_1 J_1 M_1}} \langle J_2 M_2 | \mathbf{e}_\lambda^* \mathbf{r} | J'_1 M'_1 \rangle \langle J'_1 M'_1 | \rho(0) | J_1 M_1 \rangle \\ &\quad \times \left\langle J_1 M_1 \left| (\mathbf{e}_\lambda^* \mathbf{r})^\dagger \right| J_2 M_2 \right\rangle \left( \frac{\exp[i(\omega + \omega_{21'} + i\gamma_{1'}/2)t] - 1}{i(\omega + \omega_{21'} + i\gamma_{1'}/2)} \right) \\ &\quad \times \left( \frac{\exp[i(\omega - \omega_{21} + i\gamma_1/2)t] - 1}{i(-\omega - \omega_{21} + i\gamma_1/2)} \right) \end{aligned} \quad (5.7)$$

In obtaining the numerical factor multiplying the right-hand side we have set  $\omega_{21} \approx \omega_{21'}$ , since the splitting of the upper levels is much smaller than the energy difference between upper and lower states. Finally, we multiply with the density

of final states  $\omega^2 d\Omega/(2\pi c)^3\hbar$  and integrate both sides of (5.7) over the line profile. Because the main contributions come from the region  $\omega \approx \omega_{21}$  the integral over  $\omega$  can be extended to  $-\infty$  with negligible error and the  $\omega$  integration can then be carried out in the complex  $\omega$  plane by using Cauchy's integral formula. This gives

$$\begin{aligned} \rho(\mathbf{n}, t)_{\lambda'\lambda} &= C(\omega) \sum_{\substack{J_2 M_2 \\ J'_1 M'_1 J_1 M_1}} \langle J_2 M_2 | e_{\lambda'}^* \mathbf{r} | J'_1 M'_1 \rangle \langle J'_1 M'_1 | \rho(0) | J_1 M_1 \rangle \\ &\times \langle J_1 M_1 | (e_{\lambda}^* \mathbf{r})^\dagger | J_2 M_2 \rangle \frac{1 - \exp[-i(E_{1'} - E_1)t/\hbar - (\gamma_1 + \gamma_{1'})t/2]}{i(E_{1'} - E_1)t/\hbar - (\gamma_1 + \gamma_{1'})/2} \end{aligned} \quad (5.8)$$

where

$$C(\omega) = \frac{e^2 \omega^4 d\Omega}{2\pi c^3 \hbar} \quad (5.9)$$

and where  $d\Omega$  is the element of solid angle into which the photons are emitted. In (5.8) the notation  $\rho(\mathbf{n}, t)_{\lambda'\lambda}$  is introduced for the elements of the obtained density matrix. The polarization vectors  $e_{\lambda'}$ , and  $e_{\lambda}$  in (5.9) can be eliminated by noting that in the helicity system the coordinate system is "spanned" by the three unit vectors  $\mathbf{e}_{+1}$ ,  $\mathbf{e}_{-1}$ ,  $\mathbf{n}$ , and that the dipole vector  $\mathbf{r}$  can be expanded in terms of this basis:

$$\mathbf{r} = r_{+1}^* \mathbf{e}_{+1} + r_{-1}^* \mathbf{e}_{-1} + r_0^* \mathbf{n}$$

where  $r_{\pm 1}$  and  $r_0$  are the components of  $\mathbf{r}$  along the directions of  $\mathbf{e}_{\pm 1}$  and  $\mathbf{n}$ , respectively. That is,  $r_{\pm 1}$  and  $r_0$  are therefore the spherical components of the vector  $\mathbf{r}$ . In this system the scalar product of  $\mathbf{r}$  and  $e_{\lambda}$  is given by

$$\mathbf{e}_{\lambda}^* \cdot \mathbf{r} = r_{\lambda}^* = -r_{-\lambda} \quad (5.10)$$

This then finally gives the elements of the polarization density matrix of photons observed in the direction  $\mathbf{n}$ :

$$\begin{aligned} \rho(\mathbf{n}, t)_{\lambda'\lambda} &= C(\omega) \sum_{\substack{J_2 M_2 \\ J'_1 M'_1 J_1 M_1}} \langle J_2 M_2 | r_{-\lambda'} | J'_1 M'_1 \rangle \langle J'_1 M'_1 | \rho(0) | J_1 M_1 \rangle \\ &\times \langle J_1 M_1 | r_{-\lambda}^\dagger | J_2 M_2 \rangle \frac{1 - \exp[-i(E_{1'} - E_1)t/\hbar - (\gamma_1 + \gamma_{1'})t/2]}{i(E_{1'} - E_1)/\hbar + (\gamma_1 + \gamma_{1'})/2} \end{aligned} \quad (5.11)$$

## 5.2 General Theory II: Separation of Dynamical and Geometrical Factors

In order to disentangle the dynamical and geometrical factors in (5.11) and to take angular momentum conservation explicitly into account we can apply the irreducible tensor operator method. First of all  $\rho(0)$  is expanded in terms of state multipoles, characterizing the excited atoms immediately after the excitation defined in the system with  $\mathbf{n}$  as the quantization axis:

$$\rho(0) = \sum_{KqJ'_1J_1} \left\langle T \left( J'_1 J_1 \right)_{Kq}^\dagger \right\rangle T \left( J'_1 J_1 \right)_{Kq} \quad (5.12)$$

Substitution of (5.12) into (5.11) yields

$$\begin{aligned} \rho(\mathbf{n}, t)_{\lambda'\lambda} &= C(\omega) \sum_{KqJ'_1J_1} \text{tr} \left[ r_{-\lambda'} T \left( J'_1 J_1 \right)_{Kq} r_{-\lambda}^\dagger \right] \left\langle T \left( J'_1 J_1 \right)_{Kq}^\dagger \right\rangle \\ &\times \frac{1 - \exp[-i(E_{1'} - E_1)t/\hbar - (\gamma_1 + \gamma_{1'})t/2]}{i(E_{1'} - E_1)/\hbar + (\gamma_{1'} + \gamma_1)/2} \end{aligned} \quad (5.13)$$

where the trace is given by the sum

$$\begin{aligned} \text{tr} \left[ r_{-\lambda'} T \left( J'_1 J_1 \right)_{Kq} r_{-\lambda}^\dagger \right] &= \sum_{J_2 M_2 M'_1 M_1} \left\langle J_2 M_2 \left| r_{-\lambda'} \right| J'_1 M'_1 \right\rangle \\ &\times \left\langle J'_1 M'_1 \left| T \left( J'_1 J_1 \right)_{Kq} \right| J_1 M_1 \right\rangle \left\langle J_1 M_1 \left| r_{-\lambda}^\dagger \right| J_2 M_2 \right\rangle \end{aligned} \quad (5.14)$$

In order to perform the sum in (5.14) we first apply the Wigner–Eckart theorem (4.27), which allows the dynamical factors (reduced matrix elements) and the geometrical elements ( $3j$  symbols) to be separated, and then we use (C.9) (Appendix C.1) in order to express the sum over  $M'_1 M_1 M_2$  in terms of a  $6j$  symbol. Inserting the elements of the tensor operators (4.9) we obtain

$$\begin{aligned} \text{tr} \left[ r_{-\lambda'} T \left( J'_1 J_1 \right)_{Kq} r_{-\lambda}^\dagger \right] &= \sum_{J_2} \left\langle J_2 \left\| \mathbf{r} \right\| J'_1 \right\rangle \left\langle J_2 \left\| \mathbf{r} \right\| J_1 \right\rangle^* (-1)^{J_1 + J_2 + \lambda} (2K + 1)^{1/2} \\ &\times \begin{pmatrix} 1 & 1 & K \\ -\lambda' & \lambda & q \end{pmatrix} \begin{Bmatrix} 1 & 1 & K \\ J_1 & J'_1 & J_2 \end{Bmatrix} \end{aligned} \quad (5.15)$$

While the multipoles  $\left\langle T \left( J'_1 J_1 \right)_{Kq}^\dagger \right\rangle$  are defined with respect to  $\mathbf{n}$  as the quantization axis, the information on the excited states is usually given in terms of tensors  $\left\langle T \left( J'_1 J_1 \right)_{KQ}^\dagger \right\rangle$  which are defined in a coordinate system  $XYZ$  which is more

appropriate to a description of the excitation process (for example, the “collision system” introduced in Sect. 3.5). As the last step in our calculations, we therefore transform the tensors from the helicity to the  $XYZ$  system. If  $\theta$  and  $\varphi$  are the polar angles of  $\mathbf{n}$  in the  $XYZ$  system (see, for example, Fig. 4.1, where the axis  $z$  may now denote the direction of  $\mathbf{n}$ ), then (4.41) gives

$$\left\langle T \left( J'_1 J_1 \right)_{KQ}^\dagger \right\rangle = \sum_q \left\langle T \left( J'_1 J_1 \right)_{Kq}^\dagger \right\rangle D(0\theta\varphi)_{qQ}^{(K)*} \quad (5.16a)$$

with the inverse relation

$$\left\langle T \left( J'_1 J_1 \right)_{Kq}^\dagger \right\rangle = \sum_Q \left\langle T \left( J'_1 J_1 \right)_{KQ}^\dagger \right\rangle D(0\theta\varphi)_{qQ}^{(K)} \quad (5.17)$$

Substitution of (5.15) and (5.17) into (5.13) then finally yields

$$\begin{aligned} \bullet \quad \rho(n, t)_{\lambda'\lambda} &= C(\omega) \sum_{J_2 J'_1 J_1 K Q_q} \left\langle J_2 \parallel \mathbf{r} \parallel J'_1 \right\rangle \left\langle J_2 \parallel \mathbf{r} \parallel J_1 \right\rangle^* (-1)^{J_1+J_2+\lambda} (2K+1)^{1/2} \\ &\times \begin{pmatrix} 1 & 1 & K \\ -\lambda' & \lambda & q \end{pmatrix} \begin{Bmatrix} 1 & 1 & K \\ J_1 & J'_1 & J_2 \end{Bmatrix} D(0\theta\varphi)_{qQ}^{(K)} \left\langle T \left( J'_1 J_1 \right)_{KQ}^\dagger \right\rangle \\ &\times \frac{1 - \exp[-i(E_{1'} - E_1)t/\hbar - (\gamma_{1'} + \gamma_1)t/2]}{i(E_{1'} - E_1)/\hbar + (\gamma_{1'} + \gamma_1)/2} \end{aligned} \quad (5.18)$$

with  $q = \lambda' - \lambda$ . Note that the helicity is invariant with respect to rotation so that  $\lambda'$  and  $\lambda$  have the same values in both coordinate systems.

Equation 5.18 gives the polarization density matrix of photons observed in the direction  $\mathbf{n}$  and emitted in the time interval  $0 \dots t$ . One may also determine the state of those photons which are only emitted at time  $t$  (that is, in a short time interval  $t \dots t + dt$ ). The relevant density matrix is obtained by differentiating (6.13) with respect to the time. Denoting the time derivative of the density matrix by  $\dot{\rho}(\mathbf{n}, t)_{\lambda'\lambda}$  we obtain

$$\begin{aligned} \bullet \quad \dot{\rho}(\mathbf{n}, t)_{\lambda'\lambda} &= C(\omega) \sum_{J'_1 J_1 J_2 K Q_q} \left\langle J_2 \parallel \mathbf{r} \parallel J'_1 \right\rangle \left\langle J_2 \parallel \mathbf{r} \parallel J_1 \right\rangle^* (-1)^{J_1+J_2+\lambda} (2K+1)^{1/2} \\ &\times \begin{pmatrix} 1 & 1 & K \\ -\lambda' & \lambda & q \end{pmatrix} \begin{Bmatrix} 1 & 1 & K \\ J_1 & J'_1 & J_2 \end{Bmatrix} D(0\theta\varphi)_{qQ}^{(K)} \\ &\times \exp \left[ \frac{-i(E_{1'} - E_1)t}{\hbar} - \frac{(\gamma_{1'} + \gamma_1)t}{2} \right] \left\langle T \left( J'_1 J_1 \right)_{KQ}^\dagger \right\rangle \end{aligned} \quad (5.19)$$

The density matrix elements can then be further expressed in terms of the Stokes parameters by means of (1.77). From this expression and from (1.82) all information on the behavior of the radiation in polarization experiments can be obtained.

## 5.3 Discussion of the General Formulas

### 5.3.1 General Structure of the Equations

Equations 5.18 and 5.19 will form the basis of our discussions in the remainder of this and the following chapter. It is therefore useful to discuss their meaning in more detail. We will concentrate here on (5.19) and postpone a discussion of (5.18) until Sect. 5.5, although many of the following remarks apply in both cases.

Equation 5.19 is the polarization density matrix of those photons emitted at time  $t$ . The time evolution of the initially excited atomic states between the excitation and decay is assumed to be undisturbed except by the decay process and is characterized by the time evolution operator

$$U(t)_0 = \exp[-iH_0t/\hbar - \Gamma t/2] \quad (5.20)$$

where the states  $|J_1 M_1\rangle$  are eigenfunctions of  $H_0$  and where  $\Gamma$  denotes the decay matrix:

$$\exp(-\Gamma t/2)|J_1 M_1\rangle = \exp(-\gamma_1 t/2)|J_1 M_1\rangle$$

By inserting (5.20) into (4.118) it may be shown that the corresponding perturbation coefficient is

$$G(J'_1 J_1 j'_1 j_1 t)_{Kk}^{Qq} = \exp[-i\omega_{1'1}t - (\gamma_{1'} + \gamma_1)t/2]\delta_{J'_1 j'_1} \delta_{J_1 j_1} \delta_{Kk} \delta_{Qq} \quad (5.21)$$

for all  $K$  and  $Q$ . The state multipoles describing the excited states at time  $t$  are given by

$$\langle T(J'_1 J_1, t) \rangle_{KQ}^\dagger = \exp[-i\omega_{1'1}t - (\gamma_{1'} + \gamma_1)t/2] \langle T(J'_1 J_1)_{KQ}^\dagger \rangle \quad (5.22)$$

Reading (5.19) from the right to the left and taking (5.21) into account we have the following scheme:

$$\langle \hat{\rho}(\mathbf{n}, t) \rangle_{\lambda' \lambda} = [\dots] \langle T(J'_1 J_1 t) \rangle_{KQ}^\dagger \quad (5.23a)$$

$$= [\dots] \exp[-i\omega_{1'1}t - (\gamma_{1'} + \gamma_1)t/2] \langle T(J'_1 J_1)_{KQ}^\dagger \rangle \quad (5.23b)$$

That is, the state multipoles  $\langle T(J'_1 J_1)_{KQ}^\dagger \rangle$  characterize the atomic states immediately after the excitation and contain all information on the excitation process. The

exponential factor describes the time evolution of the excited states between excitation and decay. The remaining factors in (5.19), indicated by the brackets in (5.23b), are related to the decay process at time  $t$ .

Let us now consider the factors in brackets in (5.23b) in more detail. Here the reduced matrix elements contain all information on the dynamics of the decay process, and the  $3j$  and  $6j$  symbols are geometrical factors depending on the angular momentum quantum numbers. The angular dependence of the emitted radiation is given explicitly by the elements of the rotation matrix. Any element  $D_{qQ}^{(K)}$  is related to the corresponding multipoles with the same  $K$  and  $Q$ . Thus *any state multipole with rank  $K$  and component  $Q$  present gives rise to a characteristic angular dependence of the emitted light*. As a consequence, by determining the elements  $\rho_{\lambda'\lambda}$  as a function of  $\theta$  and  $\varphi$  information can be obtained on the state multipoles  $\langle T (J'_1 J_1)_{KQ}^\dagger \rangle$ . We will discuss this topic in more detail in Chap. 6.

Multipoles with the same  $K$  and  $Q$  but different  $J'_1$  and  $J_1$  are related to the same element  $D_{qQ}^{(K)}$  and thus cannot be determined separately by measuring the angular distribution and polarization of the radiation. However, these multipoles are combined with different exponential factors and can therefore be determined separately by analyzing the time modulation of  $\rho_{\lambda'\lambda}$ . Experiments which use this technique have been performed, for example, in the case of beam–foil-excited hydrogen atoms (see, for example, [Burns and Hancock 1971](#)).

Of particular importance are the consequences of angular momentum conservation in the radiative decay expressed explicitly by the  $3j$  and  $6j$  symbols in (5.18) and (5.19). We note that these symbols vanish for  $K > 2$ . This is a consequence of observation of dipole radiation where the total angular momentum carried away by the photons is  $j = 1$ . In general, if radiation with multipolarity  $j$  is detected then state multipoles with rank  $K \leq 2j$  will contribute to  $\rho_{\lambda'\lambda}$ .

Thus, although all state multipoles satisfying  $|J'_1 - J_1| \leq K \leq J'_1 + J_1$  are required for a complete description of the excited state density matrix,

- the elements  $\rho_{\lambda'\lambda}$  depend only on the tensors with  $K = 0$ ,  $K = 1$ ,  $K = 2$ , and only these can be determined from an observation of dipole radiation.

The determination of the higher tensors with  $K > 2$  requires, for example, observation of the emitted dipole radiation in the presence of external fields mixing tensors of rank  $K \leq 2$  with tensors of rank  $K > 2$  (see, for example, Sect. 6.3). Information on the higher multipoles can also be obtained by scattering electrons from laser-excited atoms (further details on this technique are given in the review by [Hertel and Stoll 1978](#)).

In the special case of  $J_1 = 0$  all atoms land in the same final state, and using (C.11)

$$\left\{ \begin{array}{ccc} 1 & 1 & K \\ J_1 & J'_1 & 0 \end{array} \right\} = \frac{1}{3} \delta_{J'_1 1} \delta_{J_1 0}$$

In general the  $6j$  symbol is smaller than  $1/3$  if  $J_2 \neq 0$ . If  $J_1$  is sharp then all elements  $\rho_{\lambda'\lambda}$  and hence the values of the Stokes parameters and the degree of

polarization  $P$  are reduced by a factor

$$3 \left\{ \begin{matrix} 1 & 1 & K \\ J_1 & J_1 & J_2 \end{matrix} \right\}$$

compared to  $J_0 = 0$ . In fact, if  $J_2 \neq 0$  the atoms land in states with different  $M_2$  which are not detected in the experiment under discussion. As discussed in Sect. 3.3, the detected light is necessarily depolarized in the sense that  $P < 1$ . We can therefore interpret the  $6j$  symbol as a *depolarization factor* which describes the depolarization of the radiation caused by the nonobservation of the final atomic states.

### 5.3.2 *Manifestations of Coherence. Quantum Beats*

Equation 5.19 shows that the angular distribution and polarization of the emitted photons are time modulated because of the presence of time-dependent factors with  $J'_1 \neq J_1$ . These factors give the time evolution of the state multipoles  $\langle T (J'_1 J_1)_{KQ}^\dagger \rangle$  as expressed by (5.31). If the states with different  $J_1$  have been incoherently excited then the density matrix  $\rho(0)$  is diagonal in  $J_1$  and, according to the discussion in Sect. 4.3.1, only state multipoles with  $J'_1 = J_1$  can contribute to (5.19), all terms with  $J'_1 \neq J_1$  vanish and no quantum beats occur. Thus *the observation of quantum beats can be regarded as a manifestation of the coherent excitation of states with different  $J_1$  (different energy)*.

Coherent excitation of states with different energies is only possible if the excitation process satisfies certain conditions. In the case of an isotropic excitation process (Sect. 4.5.2) all multipoles with  $K \neq 0$  vanish. From (5.18) and (5.19) and from the properties of the rotation matrix  $D_{QQ}^{(K)}$  it follows that the photons are emitted isotropically and are unpolarized. The  $6j$  symbols vanish unless  $J'_1 = J_1$ , in which case no quantum beats occur. Thus *anisotropic excitation is an essential requirement for the observation of any beat signal*. Furthermore, consider for example excitation of states from a ground state with sharp energy by photon absorption. Because of energy conservation coherent excitation requires that the exciting light contain a range of frequencies  $\Delta\omega$  which is sufficiently broad to cover the difference  $(1/\hbar)(E_{1'} - E_1) = \omega_{1'1}$  of levels with different energy (Sect. 3.1). Light pulses with a finite width  $\Delta\omega$  can be represented by a coherent superposition of plane waves with different frequency, and *this coherence is transferred to the atoms* and is responsible for the quantum beats (see Sect. 2.3). Alternatively, coherent excitation can be considered a result of the requirement that the excitation time  $\Delta t$  is much shorter than any “characteristic” time of the excited states. Excitation times and energy spread of the exciting particles (electrons, photons) are related by the time–energy uncertainty relation  $\Delta t \sim 1/\Delta\omega$ . The “characteristic” time is the time interval  $\Delta t_c \sim 1/\omega_{1'1}$  with  $\omega_{1'1} = (1/\hbar)(E_{1'} - E_1)$  determining the

largest energy difference of the excited states. From the condition that  $\Delta t \ll \Delta t_c$  it follows once more that the condition for coherent excitation is that the energy uncertainty of the exciting particles must cover the energy difference of several excited states.

Let us now consider the observational effects of coherence between states with the same  $J_1$  but different  $M_1$ . If these states can be considered to be degenerate the coherence does not produce quantum beat effects. If the magnetic substates have been incoherently excited  $\rho(0)$  is diagonal in  $M_1$ . As discussed in Sect. 4.5, the source is then axially symmetric with respect to the  $Z$  axis of the collision system and all tensors with  $Q \neq 0$  vanish. The angular dependence of the elements  $\rho_{\lambda'\lambda}$  is then determined by the elements of the rotation matrix with  $Q = 0$  which are represented by the “small”  $d$  functions:

$$D(0\theta\varphi)_{q0}^{(K)} = d(\theta)_{q0}^{(K)}$$

(with  $q = \lambda' - \lambda$ ). Consequently, the elements  $\rho_{\lambda'\lambda}$  depend only on the polar angle  $\theta$  of  $\mathbf{n}$  but not on the azimuthal angle  $\varphi$ : hence the emitted light is axial symmetric about the  $Z$  axis of the collision system.

If different magnetic substrates have been excited coherently then multipoles with  $Q \neq 0$  will be different from zero and the elements  $\rho_{\lambda'\lambda}$  will depend on the azimuthal angle  $\varphi$ . Thus *coherence between states with the same  $J_1$  but different  $M_1$  manifests itself in a change of the angular dependence of the emitted radiation*.

Consider now the case of an axially symmetric atomic source which is aligned but not oriented. [This can be obtained, for example, by exciting the atoms by electron impact and not observing the scattered electrons (Sect. 4.6.3) or by absorption of unpolarized or linearly polarized photons (Sect. 4.5.3).] Because of the relation

$$\begin{pmatrix} 1 & 1 & K \\ -\lambda' & \lambda & q \end{pmatrix} = (-1)^K \begin{pmatrix} 1 & 1 & K \\ \lambda' & -\lambda & -q \end{pmatrix}$$

it follows that  $\rho_{11} = \rho_{-1-1}$  and thus  $\eta_2 = 0$ . Hence, in this case, the emitted light contains photons in both helicity states with equal intensity, and the degree of circular polarization vanishes.

Finally, let us assume that the geometry of the excitation process contains a plane of symmetry. This applies for the case discussed in Sect. 4.6. For sharp  $J_1$  the elements  $\rho_{\lambda'\lambda}$  depend on four parameters (besides the monopole), one component of the orientation vector and three components of the alignment tensor. This situation occurs also in the case of beam–foil-excited atoms when the foil axis is tilted with respect to the incoming beam axis.

## 5.4 Perturbed Angular Distribution and Polarization

### 5.4.1 General Theory

In this section we will consider the case in which the excited atoms are perturbed by an external or internal field. The theory of perturbed angular distributions has been developed in nuclear physics (see, for example, [Steffen and Alder 1975](#)). Here, we will begin by discussing the basic principles of the theory and in the following section and in Chap. 6 we will give some examples of its use.

In what follows it will always be assumed that the perturbation is weak and of little relevance to excitation and decay processes but is sufficiently strong to change the state of the atoms between excitation and decay (assuming sharply defined excitation and decay times). In this case the theory developed in Sect. 4.7 applies.

If the perturbation can be neglected during the excitation process the excited atomic states at time  $t = 0$  can be characterized in terms of state multipoles  $\langle T (J'_1 J_1)_{KQ}^\dagger \rangle$ . The subsequent time evolution of the multipoles is now governed by a Hamiltonian  $H = H_0 + H'$  (where  $H'$  is the perturbation term), and the evolution operator is  $U = \exp[-(i/\hbar)Ht - \Gamma t/2]$ . Consequently,  $U(t)$  replaces  $U(t)_0$  in the equations of Sect. 5.3. The excited atoms at time  $t$  are characterized by the state multipoles:

$$\langle T (J'_1 J_1 t)_{KQ}^\dagger \rangle = \sum_{\substack{K'Q' \\ j'_1 j_1}} \langle T (j'_1 j_1)_{K'Q'}^\dagger \rangle G (j'_1 j_1 J'_1 J_1, t)_{K'K}^{Q'Q} \quad (5.24)$$

as in the general equation (4.117) where the radiative decay term has now been included. Substitution of (5.24) for  $\langle T (J'_1 J_1)_{KQ}^\dagger \rangle$  into (5.23a)) yields

$$\begin{aligned} \hat{\rho}(\mathbf{n}, t)_{\lambda' \lambda} &= C(\omega) \sum_{\substack{J'_1 J_1 j'_1 j_1 \\ KK' Q' Q}} \text{tr} \left[ r_{-\lambda'} T (J'_1 J_1)_{KQ} r_{-\lambda}^\dagger \right] \\ &\times D(0\theta\phi)_{QQ}^{(K)} G (j'_1 j_1 J'_1 J_1, t)_{K'K}^{Q'Q} \langle T (j'_1 j_1)_{K'Q'}^\dagger \rangle \end{aligned} \quad (5.25)$$

By comparing with (5.23b) it can be seen that the time-dependent exponential factor in (5.23b) is replaced by the general perturbation coefficient describing the time evolution.

Various external and internal perturbations may influence the time evolution, and by observing experimentally the way in which these perturbations affect the angular distribution and polarization of the emitted light it is possible to extract information on various properties of the excited states. We will now illustrate this with some examples.

### 5.4.2 *Quantum Beats Produced by “Symmetry Breaking”*

In Sects. 5.1–5.3 it was assumed that atomic states with different angular momenta  $J_1$  had been coherently excited at time  $t = 0$ . This coherency leads to a time modulation of the exponential decay of the excited states. No quantum beats will occur if the excitation is incoherent.

This conclusion may not be correct if the atomic lifetime is sufficiently long and if the excited states are perturbed by external or internal fields during the time between excitation and decay. These perturbations will disturb the excited states and lead to time modulation of the orientation and alignment parameters and, hence, of the angular distribution and polarization of the emitted light, even if there is no coherence between the initially excited states. In this case *the perturbation subsequent to the excitation forms the basis for the quantum beats*.

A clear discussion of the underlying principles has been given, for example, by [Series and Dodd \(1978\)](#) and [Andrä \(1979\)](#). *The essence of the method is a sudden change in the Hamiltonian describing the excited atoms.* If at times  $t < 0$  the atoms are in eigenstates  $|\varphi_0\rangle$  of  $H_0$  and a sudden change in the Hamiltonian from  $H_0$  to  $H$  is introduced at time  $t = 0$ , then for  $t > 0$  the time evolution is governed by  $H$ . Any eigenstate  $|\varphi_0\rangle$  will evolve into a coherent superposition of eigenstates of  $H$  and this coherence gives rise to quantum beats.

This general principle applies, for example, to situations where a beam of free atoms enters an external field with a sudden onset for the passing beam. Another example is provided by the case described in Sects. 3.5 and 4.6. An atomic ensemble is “instantaneously” excited at  $t = 0$  into eigenstates  $|LMS_1 M_{s1}\rangle$  of a Hamiltonian  $H_0$  with all explicit spin couplings neglected. The subsequent time evolution for  $t > 0$  is then governed by the full Hamiltonian  $H$  of the free atoms including fine-structure (and possibly hyperfine-structure) effects. A similar situation is encountered in beam–foil excitation. Here the atoms are assumed to be excited into uncoupled states  $|LMS_1 M_{S1}\rangle$  during the short time interval in which the atoms pass through the foil. After emerging from the foil the atoms evolve under the influence of the full Hamiltonian and explicit spin-dependent coupling terms must be taken into account.

As an illustration of this let us consider the situation in which an atomic ensemble is assumed to be excited “instantaneously” at time  $t = 0$  with the spins unaffected and evolves for  $t > 0$  under the influence of the fine-structure interaction.

We obtain the elements  $\hat{\rho}(\mathbf{n}, t)_{\lambda'\lambda}$  of the density matrix of the photons, emitted at time  $t$ , by inserting the relevant perturbation coefficient in (5.25). The perturbation coefficient for fine-structure interaction is given by (4.130). Taking into account the radiative decay we substitute

$$U(t) = \exp(-iHt/\hbar - \Gamma t/2)$$

and obtain a perturbation coefficient  $G(L, t)_K \exp(-\gamma t)$ , where  $G(L, t)_K$  is given by (4.130). In doing this it is assumed that all fine-structure states belonging to the

same level ( $LS_1$ ) have the same decay constant  $\gamma$ . We then obtain from (5.25)

$$\begin{aligned} \dot{\rho}(\mathbf{n}, t)_{\lambda'\lambda} &= C(\omega) \sum_{KQ_q} \text{tr} [r_{\lambda'} T(L)_{Kq} r_{\lambda}^{\dagger}] D(0\theta\varphi)_{qQ}^{(K)} G(L, t)_K \\ &\times \exp(-\gamma t) \langle T(L_{KQ}^{\dagger}) \rangle \end{aligned} \quad (5.26a)$$

In particular, for the intensity  $I(\mathbf{n}, t)$  of the light emitted at time  $t$  in the direction  $\mathbf{n}$  is given by

$$\begin{aligned} I(\mathbf{n}, t) &= \dot{\rho}(\mathbf{n}, t)_{11} + \dot{\rho}(\mathbf{n}, t)_{-1-1} \\ &= C(\omega) \sum_{L_2 KQ} |\langle L_2 | \mathbf{r} | L \rangle|^2 (-1)^{L+L_2} C(K) \\ &\times \begin{Bmatrix} 1 & 1 & K \\ L & L & L_2 \end{Bmatrix} Y(\theta\varphi)_{KQ} \frac{\exp(-\gamma t)}{2S_1 + 1} \\ &\times \left[ \sum_{J'_1 J_1} (2J'_1 + 1)(2J_1 + 1) \begin{Bmatrix} L & J'_1 & S_1 \\ J_1 & L & K \end{Bmatrix}^2 \cos \omega_{1'1} t \right] \langle T(L)_{KQ}^{\dagger} \rangle \end{aligned} \quad (5.26b)$$

where  $C(K)$  denotes the numerical factors:

$$C(0) = -2(4\pi/3)^{1/2}, \quad C(1) = 0, \quad C(2) = -(8\pi/15)^{1/2} \quad (5.27)$$

Equation 5.26 shows that direct measurements of fine-structure splittings are possible merely by observing the emitted light as a function of time (see Sect. 2.3).

For  $K = 0$  the  $6j$  symbols within the brackets in (5.26) reduce to the expression

$$\begin{Bmatrix} L & J'_1 & S_1 \\ J_1 & L & 0 \end{Bmatrix} = \frac{(-1)^{S_1+L+J_1}}{[(2L+1)(2J_1+1)]^{1/2}} \delta_{J'_1 J_1} \quad (5.28)$$

and all interference terms with  $J'_1 \neq J_1$  vanish. Thus *orientation and/or alignment of the atomic source is essential for the observation of fine-structure quantum beats*.

Since the fine-structure interaction is isotropic it does not relate multipoles with different  $K$  and  $Q$  as shown by (4.131). Thus the initial symmetry is maintained for all times  $t > 0$ . If, for example, the initially excited states are axially symmetric with respect to some axis the light emission will be axially symmetric with respect to the same axis irrespective of the perturbation.

Similar results hold for the hyperfine interaction. The joint effect of fine and hyperfine interactions can be taken into account by substituting the relevant perturbation coefficient (4.135) for  $G(L_1 t)_K$  in (5.26a).

In the treatment given here we have considered separately the effects due to the coherent excitation of nondegenerate states (Sects. 5.1–5.3) and the effects caused by the fine-structure interaction. In general, both effects will overlap and the corresponding quantum beats will be superposed on each other. Such situations have been analyzed experimentally, for example, by [Burns and Hancock \(1971\)](#) (see also the review of [Macek and Burns 1976](#), and the references therein).

In conclusion, it has been seen that *the observation of quantum beats requires (1) a well-defined excitation time (pulsed excitation with pulses shorter than any characteristic atomic time), and (2) time-resolved detection of the emitted light* together with an observation time resolution  $t_R \gtrsim 1/\omega_{1'1}$ . The lack of appropriate equipment with sufficient time resolution initially limited quantum beat experiments to Zeeman effect studies where the level splittings can be adjusted by the magnetic field to a few megahertz. A wider use of quantum beats has only become possible after the advent of lasers with pulse lengths of nanoseconds and in particular of beam–foil excitation, which allows excitation times of the order of  $10^{-14}$  s.

Experimental details, results, and further discussions of the method may be found in recently published reviews and books. We particularly refer to [Corney \(1977\)](#) and to the various chapters in [Hanle and Kleinpoppen \(1978, 1979\)](#).

## 5.5 Time Integration Over Quantum Beats

### 5.5.1 Steady-State Excitation

Let us now return to (5.18). This expression describes, for example, the following situation. An atomic ensemble has been excited at time  $t = 0$  and the radiation, emitted in the subsequent decay, is observed in the direction  $\mathbf{n}$ . The photon detector may have a resolution time  $t_R$  so that all photons emitted in the time interval  $x 0 \cdots t_R$  are taken into account. The corresponding density matrix elements are then given by (5.18) with the substitution  $t \rightarrow t_R$ .

The periods  $\omega_{1'1}$  and the mean lifetime  $\tau = \gamma^{-1}$  are much shorter than commonly employed resolution times so that the factor  $\exp(-\gamma t_R)$  is effectively zero. Substituting this into (5.18) gives

$$\begin{aligned} \rho(\mathbf{n})_{\lambda'\lambda} = & C(\omega) \sum_{J'_1 J_1 J_2} \langle J_2 \| r \| J'_1 \rangle \langle J_2 \| r \| J_1 \rangle^* (-1)^{J_1 - J_2 + \lambda} \\ & \times \sum_{KQq} (2K + 1)^{1/2} \begin{pmatrix} 1 & 1 & K \\ -\lambda' & \lambda & q \end{pmatrix} \begin{Bmatrix} 1 & 1 & K \\ J'_1 & J_1 & J_2 \end{Bmatrix} \\ & \times D(\mathbf{n})_{qQ}^{(K)} \frac{1}{i\omega_{1'1}} + \gamma \left\langle T \left( J'_1 J_1 \right)_{KQ}^\dagger \right\rangle \end{aligned} \quad (5.29)$$

where we have put  $\gamma_i = \gamma$  for all  $i$  and where  $\rho(\mathbf{n})_{\lambda'\lambda}$  denotes the time-integrated density matrix elements for  $t_R \gg \tau$ .

Equation 5.29 applies in particular to *steady-state excitation* (starting at time  $t = 0$ ), for example, by wave packets of light emitted by a resonance lamp, or by a current of electrons. In this and the following chapter we will use the *pulse approximation*. That is, we will always approximate the incoming flux by a succession of random pulses at random times. This causes the fluctuations to be smoothed out. For a discussion of this point we refer to the article by [Series and Dodd \(1978\)](#) (see also Chap. 8).

Since in the case of steady-state excitation the time at which the emitted photons are observed is no longer well defined with respect to the time at which excitation took place, it is necessary to integrate over all observation times and (5.29) applies. The interaction between the atoms and a sequence of randomly phased pulses is an incoherent process. Each pulse gives rise to a radiation described by (5.29). The total density matrix is then given by  $N_\rho(\mathbf{n})_{\lambda\lambda'}$ , where  $N$  is the number of pulses per second.

It is important to realize that the terms  $\sim \langle T (J'_1 J_1)_{KQ}^\dagger \rangle$ , characterizing the coherence between the initial states with different  $J_1$ , vanish if the levels do not overlap, that is, if  $\omega_{1'1}$  is much larger than the linewidth:  $\omega_{1'1} \gg \gamma$ . In this case

$$\left| \frac{1}{i\omega_{1'1} + \gamma} \right| \ll \frac{1}{\gamma} \quad (5.30)$$

and the dominant contributions to  $\rho_{\lambda'\lambda}$  come from the incoherent terms with  $J'_1 = J_1$ . Alternatively, if the mean lifetime  $\tau$  is much larger than the times  $\omega_{1'1}^{-1}$  many oscillations will take place during the lifetime of the atoms, and will practically cancel each other in all time-dependent expressions. *In this case the initial coherence between the atomic states with different energies has no observational effect.*

We may summarize our results as follows. If a number of states  $|J_1 M_1\rangle$  with different  $J_1$  and energy are coherently excited (which requires a sufficiently short excitation time as discussed in Sect. 5.4) then this coherence leads to quantum beats. (Compare, for example, Fig. 2.1 with Fig. 3.1 and see the discussion in Sect. 3.4.2.) The corresponding interference terms can be directly observed in experiments with sufficiently high time resolution and well-defined excitation time. *If, however, time-integrated quantities are observed (as is always the case in steady-state excitation) the coherence between states with different energy is retained when the energy separation of the excited states is small compared to their width, the coherence being destroyed when the levels are well separated.*

### 5.5.2 Depolarization Effects Caused by Fine and Hyperfine Interactions

Let us now consider the case in which the assumptions of Sect. 5.4.2 apply but where the resolution time is not high enough to observe quantum beats. Equation 5.26a

must then be integrated over a time interval  $0 \cdots t_R$ . Assuming that  $t_R$  is much larger than the mean lifetime of the excited states, we can extend the upper limit to infinity with negligible error. The integral over the perturbation coefficients  $G(Lt)_K \exp(-\gamma t)$  gives

$$\begin{aligned} G(L)_K &\equiv \int_0^\infty dt G(L, t)_K \exp(-\gamma t) \\ &= \frac{1}{2S_1 + 1} \sum_{J'_1 J_1} (2J'_1 + 1) (2J_1 + 1) \left\{ \begin{matrix} L & J'_1 & S_1 \\ J_1 & L & K \end{matrix} \right\}^2 \frac{\gamma}{\gamma^2 + \omega_{1'1}^2} \end{aligned} \quad (5.31)$$

The time-integrated density matrix elements are then given by

$$\rho(\mathbf{n})_{\lambda'\lambda} = C(\omega) \sum_{KQq} \text{tr} \left[ r_{-\lambda'_{<??>}} T(L)_{Kq} r_{-\lambda}^\dagger \right] D(\mathbf{n})_{qQ}^{(K)} G(L)_K \left\langle T(L)_{KQ}^\dagger \right\rangle \quad (5.32)$$

For singlet–singlet transitions we have  $G(L)_K = 1/\gamma$ . For  $S_1 \neq 0$  it can be shown, using the properties of the  $6j$  symbols, that  $G(L)_K < 1/\gamma$  for  $K \neq 0$ . Because of this relation the quantities  $G(L)_K \left\langle T(L)_{KQ}^\dagger \right\rangle$  are smaller than the corresponding parameters  $(1/\gamma) \left\langle T(L)_{KQ}^\dagger \right\rangle$  in the singlet case: *the coupling of the orbital system to the unpolarized spins results in a loss of orientation and alignment*. In addition to this there is a second depolarization effect if  $L_2 \neq 0$  (see the discussion in Sect. 5.3.1).

In a similar way the influence of hyperfine interaction on the emitted radiation may be discussed simply by substituting the relevant perturbation coefficient (4.134) or (4.135) for  $G(L, t)_K$  in (5.26a).

It is instructive to consider the extreme cases in which the linewidth is either much larger or much smaller than the fine-structure splitting  $\omega_{1'1}$ . In the first case we have

$$\frac{\gamma}{\gamma^2 + \omega_{1'1}^2} \approx \frac{1}{\gamma} \quad (5.33)$$

for all terms in the equations for the Stokes parameters. From (5.31) and the orthogonality conditions of the  $6j$  symbols [(C.10)] we obtain for all  $K$

$$\begin{aligned} G(L)_K &= \frac{1}{\gamma} \frac{1}{2S_1 + 1} \sum_{J'_1 J_1} (2J'_1 + 1) \left\{ \begin{matrix} L & J'_1 & S_1 \\ J_1 & L & K \end{matrix} \right\}^2 (2J_1 + 1) \\ &= \frac{1}{\gamma} \frac{1}{(2S_1 + 1)(2L + 1)} \sum_{J'_1} (2J'_1 + 1) \end{aligned}$$

which gives

- $$G(L)_K = 1/\gamma \quad (5.34)$$

which are the same values as in the spinless case.

The result is readily understood since in the case under discussion the mean lifetime of the excited states  $\tau \sim \gamma^{-1}$  is small compared to the precession times  $\omega_{1'1}^{-1}$  associated with the spin-orbit coupling. That is, the atoms emit the photons before the precessional motion can be set up. Fine-structure interaction can then be neglected and the expressions for the Stokes parameters are the same as in the case of spinless atoms.

Consider now the case  $\gamma \ll \omega_{1'1}$  or, alternatively,  $\tau \gg \omega_{1'1}^{-1}$ . Here,

$$\frac{\gamma}{\gamma^2 + \omega_{1'1}^2} \begin{cases} = \frac{1}{\gamma} & \text{for } J'_1 = J_1 \\ \approx \frac{1}{\gamma} \cdot \frac{\gamma^2}{\omega_{1'1}^2} \ll \frac{1}{\gamma} & \text{for } J'_1 \neq J_1 \end{cases} \quad (5.35)$$

Thus, as discussed in Sect. 5.5.1, the main contributions to the Stokes parameters stem from the terms with  $J'_1 = J_1$ , and the interference terms with  $J'_1 \neq J_1$  can be neglected. In this case it follows from (5.31) and (5.35) that

- $$G(L)_K = \frac{1}{\gamma} \frac{1}{2S_1 + 1} \sum_{J_1} (2J_1 + 1)^2 \begin{Bmatrix} L & J_1 & S_1 \\ J_1 & L & K \end{Bmatrix}^2 \quad (5.36)$$

Since  $G(L)_K < 1/\gamma$  for  $K \neq 0$  anisotropy and polarization of the emitted radiation are reduced.

This result can be understood by realizing that in the case under consideration many precessions take place during the atomic lifetime. Since we are interested in quantities averaged over a time interval  $0 \dots t_R$  with  $t_R \gg \tau$  all interference terms practically cancel each other and only the time-independent terms with  $J'_1 = J_1$  will survive (compare this with the discussion in Sect. 4.7.3).

In conclusion, if the fine-structure separation is comparable with the linewidths expression (5.31) has to be used. If the linewidth is much larger than the energy separation  $\omega_{1'1}$  fine-structure effects can be neglected. If  $E_{1'} - E_1 \gg \hbar\gamma \gg E_{J_1 F'_1} - E_{J_1 F_1}$  fine-structure effects must be taken into account but hyperfine interaction can be neglected. The relevant factors  $G(L)_K$  are given by (5.36). If  $\gamma$  is small compared to the hyperfine splitting ( $E_{J_1 F'_1} - E_{J_1 F_1}$ ) then hyperfine interaction must be taken into account. The corresponding expressions for the Stokes parameters are obtained simply by substituting the relevant perturbation coefficient (4.135) for  $G(Lt)_K$  into all the above formulas.

# Chapter 6

## Some Applications

### 6.1 Theory of Electron–Photon Angular Correlations in Atomic Physics

#### 6.1.1 Singlet–Singlet Transitions

The fundamental (5.18), (5.19), and (5.25) can be applied to a variety of experimental situations and in this chapter we will give some instructive examples of their utility. As the first example, we will show how *information on the excitation process* can be obtained from a determination of the Stokes parameters. In particular, we will consider the case of excitation of atoms by electron impact under the conditions described in Sects. 3.5 and 4.6.

All information on the collision process is contained in the relevant reduced density matrix  $\rho(0)$  describing the excited atomic states immediately after the excitation. Its complete determination requires the measurement of all independent state multipoles of rank  $K \leq 2L$  and component  $Q$  satisfying  $-K \leq Q \leq K$ . If the scattered electrons are not observed only tensors with  $Q = 0$  can be nonzero. It is possible to obtain more information on the excitation process if scattered electrons and emitted photons are detected in coincidence. In this case the observation is restricted to light emitted by an atomic subensemble only, namely, those atoms excited by the detected electrons. It was shown in Sect. 4.6 that the atomic subensemble of interest is characterized by a monopole, one component of the orientation vector, three components of the alignment tensor, and all independent tensors with higher rank  $2 < K \leq 2L$ . However, the multipoles with  $K > 2$  cannot be obtained from an observation of dipole radiation unless perturbations are present mixing tensors with different rank (see Sect. 5.3). The electron-photon coincidence experiments to be discussed here allow the determination of four parameters in addition to the differential cross section  $\sigma$ . An experimental determination of these parameters and comparison with theoretical results provides more sensitive tests for theoretical predictions than the more traditional experiments in which only  $\sigma$  is

determined. In this section we will consider the excitation of singlet states from an atomic ground state for which  $S_0 = 0$  and  $L_0 = 0$ . Suppose that light emitted in a transition  $L \rightarrow L_2$  is observed ( $S_2 = 0$ ) and that the resolution time  $t_R$  of the photon detector is much larger than the mean lifetime of the excited atoms. Assuming that no perturbations are present the polarization density matrix of the photons emitted in the time interval  $0 \cdots t_R$  is given by (5.29) with  $L$  replacing  $J_1$  and  $J'_1$ .

Explicit expressions for the Stokes parameters can be derived from the polarization density matrix. The emitted photons are observed in the direction of the unit vector  $\mathbf{n}$  with polar angles  $\theta$  and  $\varphi$  in the collision system. The Stokes parameters are most conveniently discussed in a coordinate system where  $\mathbf{n}$  is the quantization axis. The polarization vector of the emitted light is restricted to the plane perpendicular to the direction of propagation  $\mathbf{n}$ . Two orthogonal unit vectors  $\mathbf{e}_1$  and  $\mathbf{e}_2$  can be chosen to span this plane (see Sect. 1.2).  $\mathbf{e}_1$  is chosen to lie in the plane formed by  $\mathbf{n}$  and the  $Z$  axis and to point in the direction of increasing  $\theta$ .  $\mathbf{e}_2$  is then chosen to be perpendicular to both  $\mathbf{e}_1$  and  $\mathbf{n}$  and to point in the direction of increasing  $\varphi$ . The vector  $\mathbf{e}_1$  then has polar angles  $(\theta + 90^\circ, \varphi)$  in the collision system and the vector  $\mathbf{e}_2$  has the polar angles  $(90^\circ, \varphi + 90^\circ)$ .  $\mathbf{e}_1$  therefore has the same azimuth angle as  $\mathbf{n}$  and  $\mathbf{e}_2$  lies in the  $X$ - $Y$  plane at an angle  $\varphi$  to the  $Y$  axis (see Fig. 6.1). In this “detector” system the Stokes parameter  $\eta_3$  is the degree of linear polarization in the direction  $\mathbf{e}_1$  and  $\eta_1$  the degree of linear polarization at angles  $\pm 45^\circ$  to  $\mathbf{e}_1$ . The Stokes parameters can be calculated from (5.19) (with  $J'_1 = J_1 = L$ ), (1.76), and substituting explicit expressions for the rotation matrix elements. This gives

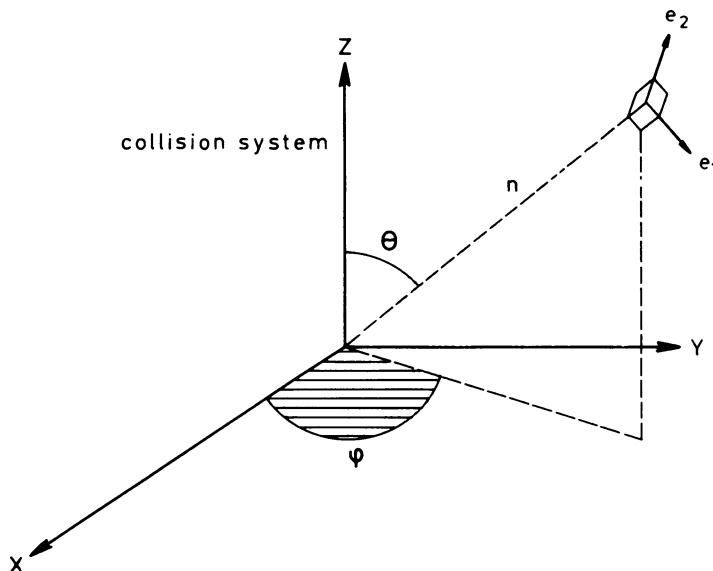


Fig. 6.1 Coordinate systems used in the description of coincidence experiments

$$I = \frac{C(\omega)}{\gamma} |\langle L_2 \parallel \mathbf{r} \parallel L \rangle|^2 (-1)^{L+L_2} \left[ \langle T(L)_{00} \rangle - \begin{Bmatrix} 1 & 1 & 2 \\ L & L & L_2 \end{Bmatrix} \right. \\ \times \left( \langle T(L)_{22}^\dagger \rangle \sin^2 \theta \cos 2\varphi - \langle T(L)_{21}^\dagger \rangle \sin 2\theta \cos \varphi \right. \\ \left. \left. + \frac{\langle T(L)_{20}^\dagger \rangle (3 \cos^2 \theta - 1)}{6^{1/2}} \right) \right] \quad (6.1a)$$

$$I \eta_3 = \frac{C(\omega)}{\gamma} |\langle L_2 \parallel \mathbf{r} \parallel L \rangle|^2 (-1)^{L+L_2} \begin{Bmatrix} 1 & 1 & 2 \\ L & L & L_2 \end{Bmatrix} \\ \times \left[ \langle T(L)_{22}^\dagger \rangle (1 + \cos^2 \theta) \cos^2 \varphi + \langle T(L)_{21}^\dagger \rangle \sin 2\theta \cos \varphi \right. \\ \left. + \left( \frac{3}{2} \right)^{1/2} \langle T(L)_{20}^\dagger \rangle \sin^2 \theta \right] \quad (6.1b)$$

$$I \eta_1 = -\frac{C(\omega)}{\gamma} |\langle L_2 \parallel \mathbf{r} \parallel L \rangle|^2 (-1)^{L+L_2} \begin{Bmatrix} 1 & 1 & 2 \\ L & L & L_2 \end{Bmatrix} \\ \times \left[ \langle T(L)_{22}^\dagger \rangle 2 \cos \theta \sin 2\varphi + \langle T(L)_{21}^\dagger \rangle 2 \sin \theta \sin \varphi \right] \quad (6.1c)$$

$$I \eta_2 = -\frac{C(\omega)}{\gamma} |\langle L_2 \parallel \mathbf{r} \parallel L \rangle|^2 (-1)^{L+L_2} \begin{Bmatrix} 1 & 1 & 1 \\ L & L & L_2 \end{Bmatrix} 2i \langle T(L)_{11}^\dagger \rangle \sin \theta \sin \varphi \quad (6.1d)$$

Note that the tensors  $\langle T(L)_{2Q}^\dagger \rangle$  and  $i \langle T(L)_{11}^\dagger \rangle$  are real quantities (see Sect. 4.6). We have used the approximation 5.5.

The monopole  $\langle T(L)_{00} \rangle$  can be obtained from a measurement of the differential cross section. Equation 6.1 afford then several possibilities for determining the state multipoles with  $K > 0$ . For example,  $I$  can be measured for three different pairs of angles  $\theta, \varphi$  (this gives three equations which allow the extraction of the three independent components of the alignment tensor) and  $I \eta_2$  obtained at one set of angles  $\theta, \varphi$  (which gives the orientation vector). Alternatively, all four Stokes parameters can be measured in the same direction  $\theta, \varphi$ , and by inserting the obtained values into (6.1) four equations are obtained from which the orientation and alignment parameters can be extracted. Using these methods these excitation parameters have been experimentally determined for several atoms and compared with theoretical predictions (for further details see the review by [Blum and Kleinpoppen 1979](#)).

In general, all five multipoles contributing to (6.1) are independent. The four Stokes parameters and the differential cross section  $\sigma$  are therefore also independent quantities. In particular, the angular distribution  $I$  contains information on

the atomic source which cannot be obtained from a determination of the other parameters.

The first experiment of this kind was carried out by [Eminyan et al. \(1974\)](#) for  $^1P$  excitation of helium. In this case ( $L = 1$ ) the excited atoms are completely characterized in terms of three parameters only (see [Sect. 3.5.2](#)). Let us discuss this case in more detail. The Stokes parameters are not independent and only three independent measurements are required for a complete determination of the atomic density matrix, for example  $\sigma$ ,  $I$ , and  $I\eta_2$ . Expressing the multipole parameters in terms of the parameters  $\sigma$ ,  $\lambda$ ,  $\chi$  introduced in [Sect. 3.5.2](#) we obtain from [\(6.1\)](#), with  $L = 1$ ,  $L_2 = 0$ ,

$$I = \frac{C(\omega)}{\gamma} |\langle 0 \parallel \mathbf{r} \parallel 1 \rangle|^2 \frac{\sigma}{3} \left[ \frac{1-\lambda}{2} (1 - \sin^2 \theta \cos 2\varphi + \cos^2 \theta) + \lambda \sin^2 \theta \right. \\ \left. + [\lambda(1-\lambda)]^{1/2} \cos \chi \sin 2\theta \cos \varphi \right] \quad (6.2a)$$

$$I\eta_2 = -\frac{C(\omega)}{\gamma} |\langle 0 \parallel \mathbf{r} \parallel 1 \rangle|^2 \frac{2\sigma}{3} [\lambda(1-\lambda)]^{1/2} \sin \chi \sin \theta \sin \varphi \quad (6.2b)$$

where we inserted explicit values for the  $6j$  symbols. It follows that in this case, a complete determination of the scattering amplitudes is possible. For this reason the case  $L = 1$  and  $S_1 = 0$  is of particular interest.

From [\(6.2b\)](#) it follows that the degree of circular polarization is determined by the phase  $\chi$  and, correspondingly, a measurement of  $I\eta_2$  directly determines  $\chi$ . If the photons are detected in the  $Y$  direction ( $\theta = \varphi = 90^\circ$ ) the degree of circular polarization is given by dividing [\(6.2a\)](#), [\(6.2b\)](#)

$$\eta_2 = -2[\lambda(1-\lambda)]^{1/2} \sin \chi \quad (6.3)$$

By expressing the scattering amplitudes in [\(4.78\)](#) in terms of  $\sigma$ ,  $\lambda$ ,  $\chi$  according to [Sect. 3.5.2](#) it can be shown with the help of [\(4.84a\)](#) that

$$\eta_2 = \langle L_y \rangle \quad (6.4)$$

Thus  $\eta_2$  is a direct measure of the degree of orientation, or, of the net amount of the angular momentum transferred to the atoms during the excitation process.

When the photons are detected in the scattering plane  $\varphi$  is zero and

$$\eta_3 = +1 \quad (6.5)$$

This can be shown by first specializing [\(6.1b\)](#) to the case  $L = 1$ ,  $L_2 = 0$ :

$$I \eta_3 = -\frac{C(\omega)}{\gamma} |\langle 0 \parallel \mathbf{r} \parallel 1 \rangle|^2 \frac{\sigma}{3} \left\{ \frac{1-\lambda}{2} [(-1 - \cos^2 \theta) \cos 2\varphi + \sin^2 \theta] \right. \\ \left. - \lambda \sin^2 \theta - [\lambda(1-\lambda)]^{1/2} \cos \chi \sin 2\theta \cos \varphi \right\} \quad (6.6)$$

Inserting  $\varphi = 0$  and dividing by (6.2a) we obtain the relation (6.5). Thus the photons observed in the scattering plane are completely linearly polarized. The electric vector oscillates along the direction of  $\mathbf{e}_1$ .

As discussed in Sect. 3.5.2 the excited  ${}^1P$  state is a completely coherent superposition of the magnetic substate. From this and the fact that  $L_2 = 0$  it follows that the detected light is emitted in a transition between two pure atomic states. As a result, the light is necessarily completely polarized in the sense that  $P = 1$ . In practice, a measurement of the four standard light polarizations

$$P_1 = \eta_3 \left( \frac{\pi}{2}, \frac{\pi}{2} \right)$$

$$P_2 = \eta_1 \left( \frac{\pi}{2}, \frac{\pi}{2} \right)$$

$$P_3 = -\eta_2 \left( \frac{\pi}{2}, \frac{\pi}{2} \right)$$

$$P_4 = -\eta_3 \left( \frac{\pi}{2}, 0 \right)$$

is sufficient to determine the state multipoles (Andersen et al. 1988). The angles in parentheses refer to  $\Theta$  and  $\varphi$  respectively defined with respect to the collision system.

Experimental results of these four polarizations can be used to characterize the charge cloud of the excited atoms. The alignment angle  $\gamma$  and the height  $h$  are given by

$$\gamma = \frac{1}{2} \arctan \frac{P_2}{P_1}$$

$$h = \frac{(1+P_1)(1-P_4)}{4 - (1-P_1)(1-P_4)}$$

and for the orientation parameter  $L_{\perp} = \langle L_y \rangle$  one obtains

$$L_{\perp} = -P_3$$

For details and for a review of experimental and theoretical studies we refer to Andersen et al. (1988) and Andersen and Bartschat (1996).

The experimental determination of multipoles with rank  $K > 2$  can be achieved by observing cascade processes. For theoretical derivations and for experimental results we refer to Wang et al. (1994) and references cited therein.

### 6.1.2 Influence of Fine and Hyperfine Interactions on the Emitted Radiation

We will now discuss the excitation of atomic levels with orbital angular momentum  $L$  and spin  $S_1 \neq 0$  by electron impact and the coincident detection of scattered electrons and emitted photons. We will assume that the assumptions discussed in Sects. 3.5 and 4.7.2 apply.

Immediately after the excitation the state of the atomic subensemble of interest is characterized by the state multipoles (4.78). These are perturbed by the fine (and possibly hyperfine) interaction which in turn influences the emitted light.

Assuming that only *time-integrated quantities* are observed (with an upper limit  $t_R \gg \tau$ ) the density matrix elements of the emitted radiation are given by (5.32) where now the state multipoles are given by (4.78). Recalling that  $G(L)_K = 1/\gamma$  in the case of spinless atoms the Stokes parameters in the present case of interest can be obtained by substituting  $G(L)_K \langle T(L)_{KQ}^\dagger \rangle$  for  $1/\gamma \langle T(L)_{KQ}^\dagger \rangle$  in (6.1). Thus, for example, the angular distribution becomes, with  $G(L)_0 = 1/\gamma$ ,

$$I = \frac{C(\omega)}{\gamma} |\langle L_2 \parallel \mathbf{r} \parallel L \rangle|^2 \left\{ \frac{2}{3(2L+1)^{1/2}} \langle T(L)_{00}^\dagger \rangle \right. \\ - (-1)^{L+L_2} \gamma G(L)_2 \left\{ \begin{array}{c} 1 \ 1 \ 2 \\ L \ L \ L_2 \end{array} \right\} \\ \times \left[ \langle T(L)_{22}^\dagger \rangle \sin^2 \theta \cos 2\varphi - \langle T(L)_{21}^\dagger \rangle \sin 2\theta \cos \varphi \right. \\ \left. + \frac{\langle T(L)_{20}^\dagger \rangle (3 \cos^2 \theta - 1)}{6^{1/2}} \right] \right\} \quad (6.7)$$

In order to obtain the parameters  $I\eta_3$  and  $I\eta_1$  (6.1b),  $c$  must be multiplied by a common factor  $\gamma G(L)_2$ , and  $I\eta_2$  is obtained by multiplying (6.1d) by  $\gamma G(L)_1$ .

In these expressions the loss of orientation and alignment, caused by the coupling to the unobserved spin system, is described by the factors  $G(L)_1$  and  $G(L)_2$ . Since  $G(L)_K < 1/\gamma$  for  $K \neq 0$  (6.7) shows that the angular distribution becomes more isotropic compared to the spinless case (the angular distribution is “smeared out” as a result of spin-orbit coupling). The values of the other Stokes parameters are reduced from their values for spinless atoms by a factor  $\gamma G(L)_1$  and  $\gamma G(L)_2$ , respectively, which results in a depolarization of the emitted radiation.

The perturbation factors  $G(L)_K$  are given by (5.31) if the fine-structure separation  $\omega_{1'1}$  and linewidth are comparable, by (5.36) if the fine-structure levels do not overlap ( $\gamma \ll \omega_{1'1}$ ), or by (5.34) if  $\gamma \gg \omega_{1'1}$ . In the latter case the fine-structure interaction does not affect the emitted light.

The effect of hyperfine interaction can be treated by the method outlined in Sect. 5.5.2.

## 6.2 Steady-State Excitation

### 6.2.1 *Polarization of Impact Radiation*

The formulas presented in Sect. 6.1 describe the polarization properties of light detected in coincidence with the scattered electrons, that is, those photons which are only emitted by a particular subensemble of atoms. We will now consider the case where the scattered electrons are not observed. It will be assumed that the resolution of the photon detector is sufficient to restrict the observation to photons emitted in a transition between levels with fixed quantum numbers  $LS_1 \rightarrow L_2S_2$ . Since the electrons are not observed, however, all photons emitted in this transition must now be taken into account irrespective of the direction in which the electrons are scattered.

If we now consider excitation by a steady flux of incoming electrons the time at which the photons are emitted is no longer uniquely defined with respect to the excitation time. Thus the time-integrated form of the polarization density matrix must be used.

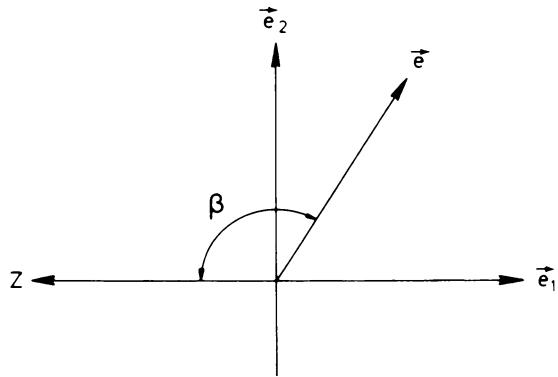
When the scattered electrons are unobserved the atomic system of interest is aligned but not oriented according to the discussions in Sect. 4.6.3. Consequently, the detected radiation depends on only two parameters, the monopole  $\langle T(L)_{00} \rangle$ , which is proportional to the total cross section  $Q$ , and the alignment parameter  $\langle T(L)_{20}^\dagger \rangle$  given by (4.91). Thus the relevant Stokes parameters are readily obtained by putting all multipoles equal to zero in (6.7) and the equations for the other Stokes parameters except  $\langle T(L)_{00} \rangle$  and  $\langle T(L)_{20}^\dagger \rangle$ . The degree of circular polarization and the parameter  $\eta_1$  vanish and the nonzero Stokes parameters are found to be

$$\begin{aligned} I(\mathbf{n}) = & C(\omega) |\langle L_2 \parallel \mathbf{r} \parallel L \rangle|^2 \frac{2}{3(2L+1)^{1/2}} \langle T(L)_{00} \rangle \frac{1}{\gamma} \\ & - C(\omega) |\langle L_2 \parallel \mathbf{r} \parallel L \rangle|^2 (-1)^{L+L_2} \left\{ \begin{array}{ccc} 1 & 1 & 2 \\ L & L & L_2 \end{array} \right\} G(L)_2 1/6^{1/2} \langle T(L)_{20}^\dagger \rangle \\ & \times (3 \cos^2 \theta - 1) \end{aligned} \quad (6.8a)$$

$$\begin{aligned} I\eta_3(\mathbf{n}) = & C(\omega) |\langle L_2 \parallel \mathbf{r} \parallel L \rangle|^2 (-1)^{L+L_2} \left\{ \begin{array}{ccc} 1 & 1 & 2 \\ L & L & L_2 \end{array} \right\} G(L)_2 \left( \frac{3}{2} \right)^{3/2} \\ & \times \langle T(L)_{20}^\dagger \rangle \sin^2 \theta \end{aligned} \quad (6.8b)$$

The monopole can be obtained from a measurement of the total cross section. In order to determine  $\langle T(L)_{20}^\dagger \rangle$  experimentally either the angular distribution  $I$  or the parameter  $I\eta_3$  can be measured. Usually, a combination of both parameters is determined. The emitted radiation is detected at right angles to the incident beam

**Fig. 6.2** See text for explanations



axis. We will take the incoming beam direction as the  $Z$  axis of our coordinate system and the direction of observation  $\mathbf{n}$  as the  $X$  axis. The unit vectors  $\mathbf{e}_1$  and  $\mathbf{e}_2$ , specifying the detector system introduced in Sect. 6.1, are then parallel to  $-Z$  and  $Y$ , respectively.

The radiation detected in the  $X$  direction passes a Nicol prism which has its axis of transmission at an angle  $\beta$  to the incident beam direction (this corresponds to an angle  $180^\circ - \beta$  with respect to the axis  $\mathbf{e}_1$ ). The transmitted light is linearly polarized with polarization vector  $\mathbf{e}$  given by (1.56) with  $180^\circ - \beta$  replacing  $\beta$  (see Fig. 6.2, which should be compared with Fig. 1.4):

$$\mathbf{e} = -\mathbf{e}_1 \cos \beta - \mathbf{e}_2 \sin \beta \quad (6.9)$$

The transmitted intensity is obtained from (1.82) with  $\eta_1 = \eta_2 = 0$ :

$$I_e = (1/2)[I(X) + I\eta_3(X) \cos 2\beta] \quad (6.10)$$

where  $I(X)$  and  $I\eta_3(X)$  are given by (6.8a), b, respectively, with  $\theta = 90^\circ$ ,  $\varphi = 0^\circ$ .

Usually one determines experimentally the *polarization*  $P$ , which is defined as

$$P = \frac{I_{\parallel} - I_{\perp}}{I_{\parallel} + I_{\perp}} \quad (6.11)$$

Here,  $I_{\parallel}$  and  $I_{\perp}$  denote the intensities of the emitted light which has passed through the Nicol prism with its axis of transmission respectively parallel ( $\beta = 0^\circ$ ) and perpendicular ( $\beta = 90^\circ$ ) to the  $Z$  axis. Using (6.10) we obtain

$$P = \frac{I\eta_3(X)}{I(X)} = \eta(X)_3 \quad (6.12)$$

Since  $\eta_1 = \eta_2 = 0$  the magnitude of the parameter (6.11) is equal to the degree of coherence  $P = (\eta_1^2 + \eta_2^2 + \eta_3^2)^{1/2}$  introduced in Sect. 1.2. Specializing (6.8) to  $\mathbf{n}$  parallel to  $X$ , that is, by inserting  $\theta = 90^\circ$ ,  $\varphi = 0$ , we obtain

$$P = \frac{(-1)^{L+L_2} \left\{ \begin{smallmatrix} 1 & 1 & 2 \\ L & L & L_2 \end{smallmatrix} \right\} G(L)_2 \left( \frac{3}{2} \right)^{1/2} \langle T(L)_{20}^\dagger \rangle}{\frac{1}{\gamma} \frac{2}{3(2L+1)^{1/2}} \langle T(L)_{00} \rangle + (-1)^{L+L_2} \left\{ \begin{smallmatrix} 1 & 1 & 2 \\ L & L & L_2 \end{smallmatrix} \right\} G(L)_2 \frac{1}{6^{1/2}} \langle T(L)_{20}^\dagger \rangle} \quad (6.13)$$

Thus combining a measurement of  $P$  with a determination of the total cross section  $Q$  enables the alignment parameter to be extracted from the experimental results.

For singlet-singlet transitions  $G(L)_K = 1/\gamma$  and (6.13) reduces to the expression

$$P = \frac{(-1)^{L+L_2} \left\{ \begin{smallmatrix} 1 & 1 & 2 \\ L & L & L_2 \end{smallmatrix} \right\} \left( \frac{3}{2} \right)^{1/2} \langle T(L)_{20}^\dagger \rangle}{\frac{2}{3(2L+1)^{1/2}} \langle T(L)_{00} \rangle + (-1)^{L+L_2} \left\{ \begin{smallmatrix} 1 & 1 & 2 \\ L & L & L_2 \end{smallmatrix} \right\} \frac{1}{6^{1/2}} \langle T(L)_{20}^\dagger \rangle} \quad (6.14)$$

As an illustration consider the case of radiation emitted in a  ${}^1D \rightarrow {}^1P$  transition. The alignment parameter may be expressed in terms of the total cross sections  $Q(M)$  using (4.91):

$$\begin{aligned} \langle T(2)_{20}^\dagger \rangle &= 5^{1/2} \sum_M (-1)^M \left( \begin{matrix} 2 & 2 & 2 \\ M & -M & 0 \end{matrix} \right) Q(M) \\ &= -(2/7)^{1/2} [2Q(2) - Q(1) - Q(0)] \end{aligned} \quad (6.15a)$$

where the relation (4.88) has been used. Similarly, from (4.89)

$$\langle T(2)_{00} \rangle = (1/5)^{1/2} [2Q(2) + 2Q(1) + Q(0)] \quad (6.15b)$$

Using (6.15) together with the numerical value of the  $6j$  symbols in (6.14) yields

$$P = \frac{3[-2Q(2) + Q(1) + Q(0)]}{6Q(2) + 9Q(1) + 5Q(0)} \quad (6.16)$$

### 6.2.2 Threshold and Pseudothreshold Excitations

As was first discussed by [Percival and Seaton \(1957\)](#) the formulas given above simplify considerably for threshold excitation. Since all spin couplings have been neglected during the collision orbital and spin angular momenta are separately

conserved, which gives in particular

$$M_0 + m_0 = M + m_1$$

where  $M_0$  and  $m_0$  ( $M$  and  $m_1$ ) are the magnetic quantum numbers of the initial (final) atoms and electrons, respectively. The incident electron has no component of its orbital angular momentum along its direction of propagation ( $m_0 = 0$ ). After the excitation at threshold the projectile electron has zero energy and hence zero orbital angular momentum ( $m_1 = 0$ ). It follows that the magnetic quantum number of the atoms cannot change during the collision and, since excitation from the ground state with  $L_0 = 0$  is assumed, only the substate with  $M = 0$  can be excited at threshold.

As a consequence only the cross section  $Q(0)$  is nonzero at threshold and from (4.91):

$$\langle T(L)_{20}^\dagger \rangle = 5^{1/2} (-1)^L \begin{pmatrix} L & L & 2 \\ 0 & 0 & 0 \end{pmatrix} Q(0) \quad (6.17a)$$

Similarly,

$$\langle T(L)_{00} \rangle = Q(0)/(2L + 1)^{1/2} \quad (6.17b)$$

By inserting (6.17) into (6.13) it can be seen that  $Q(0)$  cancels in the resulting expression. *The Threshold polarization  $P_{\text{thr}}$  is therefore a quantity which depends only on the geometry of the excitation process independent of any (calculated or measured) cross section value:*

$$P_{\text{thr}} = \frac{\left(\frac{15}{2}\right)^{1/2} (-1)^{L_2} G(L)_2 \begin{Bmatrix} 1 & 1 & 2 \\ L & L & L_2 \end{Bmatrix} \begin{pmatrix} L & L & 2 \\ 0 & 0 & 0 \end{pmatrix}}{\frac{1}{\gamma} \frac{2}{3(2L + 1)} + \left(\frac{5}{6}\right)^{1/2} (-1)^{L_2} G(L)_2 \begin{Bmatrix} 1 & 1 & 2 \\ L & L & L_2 \end{Bmatrix} \begin{pmatrix} L & L & 2 \\ 0 & 0 & 0 \end{pmatrix}} \quad (6.18)$$

Specializing (6.18) to the case of  $L = 1$ ,  $L_2 = 0$ ,  $S_1 = 0$  gives  $P_{\text{thr}} = 1$ . This is readily understood by noting that the excited atoms are in a pure state  $|L, M = 0\rangle$  immediately after the excitation. The detected photons are thus emitted in a transition between two pure states  $|L, M = 0\rangle \rightarrow |0\rangle$  and hence are necessarily completely polarized. If  $L_2 \neq 0$  the emitted radiation is depolarized since the final atomic states (with  $M_2 = \pm 1, 0$ ) are not detected. The corresponding depolarization effect is described explicitly by the  $6j$  symbol in (6.18). If, in addition,  $S_1 \neq 0$  a further depolarization is observed, caused by the coupling to the undetected spin system, which is described by the factor  $G(L)_2$  in (6.18). In general  $G(L)_2$  is given by (5.31). If the fine-structure levels do not overlap (5.36) applies and the initial coherence between different fine-structure states is destroyed. If hyperfine-structure interaction must also be taken into account then the relevant perturbation factor can be obtained from (4.135). This discussion shows once more the importance of fine (and hyperfine) interaction and the effect of a finite level width, both of which can considerably affect polarization. An interpretation of these results in terms of the vector model is given in the review by [Kleinpoppen \(1969\)](#).

There is considerable interest in the polarization of impact radiation at threshold. Attempts at direct measurement of threshold polarization have been limited because of intensity problems and also because of the effects of cascades and resonances in the energy range just above threshold. It has been pointed out by [King et al. \(1972\)](#) that polarization measurements made for the subensemble of atoms which have been excited by forward-scattered electrons reproduces threshold conditions as far as polarization is concerned and that errors due to cascade and resonance effects are eliminated. In fact, forward-scattered electrons have a zero angular momentum component both before and after the scattering ( $m_0 = m_1 = 0$ ) with respect to the direction of motion as the quantization axis. In this case exciting the atoms from the ground state (with  $L = 0$ ) and neglecting spin-orbit effects during the collision enables only magnetic substates with  $M = 0$  to be excited. The relevant multipoles  $\langle T_{00} \rangle$  and  $\langle T_{20}^\dagger \rangle$  are given by (6.17) with  $Q(0)$  replaced by the differential cross section  $\sigma(0)$  describing excitation of the  $M = 0$  substates by forward-scattered electrons. Forward-scattered electrons and emitted photons are then detected in coincidence and  $P$  measured.  $\sigma(0)$  cancels in the expression for  $P$  and  $P$  is therefore given by (6.18).

This technique has been recently applied in atomic and molecular physics (see, for example, the report by [McConkey \(1980\)](#), and references therein).

As stated above, many results given in the present section can be traced back to the paper by [Percival and Seaton \(1957\)](#). For further developments and a modern formulation of the Percival–Seaton theory we refer to the reviews by [Bartschat \(1996\)](#) and [Bartschat and Csanak \(1996\)](#).

## 6.3 Effect of a Weak Magnetic Field

### 6.3.1 Perturbation Coefficients for Various Geometries Coherence Phenomena

In this section we will consider the effect of a magnetic field on light emission. The field is assumed to be weak, that is, the mean value of the magnetic interaction is assumed to be much smaller than the separation of the relevant zero field levels. With this assumption the theory developed in Sect. 4.7.4 can be used and the effect of the field on the excitation process can be neglected but must be allowed for in the description of the time evolution of the excited states between excitation and decay. In terms of the vector model, disturbance due to the field is described by the precessional motion of the angular momentum vectors around the direction of the field  $\mathbf{H}$  at the Larmor frequency  $\omega_L$  of the excited states.

Assuming that states  $|JM\rangle$  have been excited at  $t = 0$  the polarization density matrix of the emitted photons is obtained by specializing (5.25) to the case under discussion:

$$\begin{aligned} \dot{\rho}(\mathbf{n}, t)_{\lambda'\lambda} &= C(\omega) \sum_{KQq'} \text{tr} \left[ r_{-\lambda'} T(J_1)_{Kq} r_{-\lambda}^\dagger \right] D(0\theta\varphi)_{qq'}^{(K)} G(t)_{KK}^{Qq'} \\ &\times \exp(-\gamma t) \left\langle T(J_1)_{KQ}^\dagger \right\rangle \end{aligned} \quad (6.19)$$

with  $q = \lambda' - \lambda$  and where the trace is given by (5.15). The relevant perturbation coefficient is given by (4.143):

$$G(t)_{KK}^{Qq'} = \sum_{Q'} D(0\beta'\alpha')_{Q'q'}^{(K)} \exp(-i\omega_L Q't) D(0\beta'\alpha')_{Q'Q}^{(K)} \quad (6.20)$$

where  $\beta'$  and  $\alpha'$  denote the polar angles of the field direction  $\mathbf{H}$  in the coordinate system  $XYZ$  defined by the excitation process. We will now derive explicit expressions for the perturbation coefficients for some geometries of interest.

### 6.3.1.1 Field Parallel to $Z$

In this case (4.144) applies:

$$G(t)_{KK}^{Qq'} = \exp(-i\omega_L t Q) \delta_{Qq'} \quad (6.21)$$

and (6.19) reduces to the expression

$$\begin{aligned} \dot{\rho}(\mathbf{n}, t)_{\lambda'\lambda} &= C(\omega) \sum_{KQ} \text{tr} \left[ r_{-\lambda'} T(J_1)_{K\lambda'-\lambda} r_{-\lambda}^\dagger \right] D(0\theta\varphi)_{\lambda'-\lambda,Q}^{(K)} \\ &\times \exp(-i\omega_L Qt - \gamma t) \left\langle T(J_1)_{KQ}^\dagger \right\rangle \end{aligned} \quad (6.22)$$

This equation shows that the angular distribution and polarization of the emitted radiation oscillate as a function of the magnetic field strength. The quantum beats appear when  $Q \neq 0$ , that is, when *different sublevels have been coherently excited*. The magnetic field will have no effect if the excitation process is axially symmetric with respect to  $Z$  (see, for example, the case discussed in Sect. 4.5.3).

### 6.3.1.2 $\mathbf{n}$ Parallel to $X$ , $\mathbf{H}$ Parallel to $Y$

Next we consider the situation in which the emitted light is observed in the  $X$  direction of the collision system and the field is directed along the  $Y$  axis. In this case  $\theta = 90^\circ$ ,  $\varphi = 0$ , and  $\beta' = \alpha' = 90^\circ$  in (6.19) and (6.20).

After some algebraic manipulations we obtain

$$\sum_{q'} D(0, \pi/2, 0)_{\lambda'-\lambda,q'}^{(K)} G(t)_{KK}^{Qq'} = \exp(i\pi Q/2) (-1)^K d(\omega_L t)_{-\lambda'+\lambda,Q}^{(K)} \quad (6.23)$$

Substitution of (6.23) into (6.19) yields

$$\begin{aligned} \dot{\rho}(X, t)_{\lambda' \lambda} = &_C (\omega) \sum_{KQ} \text{tr} \left[ r_{\lambda'} T(J_1)_{K, \lambda' - \lambda} r_{-\lambda}^\dagger \right] \exp(i \pi Q/2) (-1)^K d(\omega_L t)_{-\lambda' + \lambda, Q}^{(K)} \\ & \times \exp(-\gamma t) \langle T(J_1)_{KQ}^\dagger \rangle \end{aligned} \quad (6.24)$$

The time modulation of  $\dot{\rho}_{\lambda' \lambda}$  is given by the factor  $d(\omega_L t)_{-\lambda' + \lambda, Q}^{(K)}$ .

As an example of the application of (6.23) consider an atomic ensemble excited in a process axially symmetric with respect to the  $Z$  axis (for example, excitation by a beam of unpolarized light or in beam-foil excitation with the foil axis parallel to the incident beam axis). The excited ensemble is then characterized in terms of a monopole and an alignment parameter with  $K = 2$ ,  $Q = 0$ . The intensity  $I(x, t)$  observed at time  $t$  in the  $X$  direction is given by

$$\begin{aligned} I(X, t) &= \dot{\rho}(X, t)_{11} + \dot{\rho}(X_1 t)_{-1-1} \\ &= 2C(\omega) \text{tr} \left( r_{-1} r_{-1}^\dagger \right) \exp(-\gamma t) \langle T(J_1)_{00} \rangle / (2J_1 + 1)^{1/2} \\ &+ C(\omega) \text{tr} \left[ r_{-1} T(J_1)_{20} r_{-1}^\dagger \right] (1/2)(1 + 3 \cos 2\omega_L t) \exp(-1) \langle T(J_1)_{20}^\dagger \rangle \end{aligned} \quad (6.25)$$

where explicit expressions for the  $d$  functions together with

$$\text{tr} \left[ r_{-\lambda'} T(J_1)_{Kq} r_{-\lambda}^\dagger \right] = (-1)^K \text{tr} \left[ r_{\lambda'} T(J_1)_{K-q} r_\lambda^\dagger \right]$$

have been used. Equation 6.25 shows that the intensity  $I(X, t)$  exhibits oscillations with twice the Larmor frequency. It is instructive to consider the coherence effect responsible for these quantum beats. Only  $\langle T_{00} \rangle$  and  $\langle T_{20}^\dagger \rangle$  contribute to (6.25) as a result of the *incoherent* excitation of the substates  $|J_1 M_1\rangle$  with different  $M_1$ , where  $M_1$  is defined with respect to  $Z$  as the quantization axis. The interference effects between the eigenstates  $|J_1 M'_1\rangle$  of the Hamiltonian

$$H = H_0 - g\mu_B \mathbf{J} \cdot \mathbf{H}$$

which governs the time evolution between excitation and decay are responsible for the quantum beats (see the discussion in Sect. 5.4.2). Defining  $M'_1$  with respect to  $\mathbf{H}$  as the quantization axis we have

$$\exp \left( -\frac{i}{\hbar} H t \right) |J'_1 M'_1\rangle = \exp \left[ -\frac{i}{\hbar} (E_1 - \hbar\omega_L M'_1) t \right] |J_1 M'_1\rangle$$

Any state  $|J_1 M_1\rangle$  can be written as a linear superposition of states  $|J_1 M'_1\rangle$ :

$$|J_1 M_1\rangle = \sum_{M'_1} a(M'_1 M_1) |J_1 M'_1\rangle$$

(where not all possible values of  $M'_1$  may exist in the new frame). The density matrix  $\rho$  describing the excited atoms is diagonal in  $M$  but in general nondiagonal in  $M'_1$  provided  $\langle T_{20} \rangle$  is different from zero (otherwise  $\rho$  is proportional to the identity matrix which is diagonal in any representation). This coherence between the substates gives rise to interference effects expressed by the  $d$  function in (6.25). This example illustrates once again that an excitation process which is incoherent for one quantization axis may be coherent for a different axis.

In general, if the magnetic field is not parallel to  $Z$ , interference terms will occur, even if different substates  $|J_1 M_1\rangle$  are incoherently excited. In order to observe quantum beats it is sufficient to produce a different population of the states  $|J_1 M_1\rangle$ , that is, a nonvanishing alignment parameter as shown by (6.25).

Equation 6.25 can be applied to a determination of the alignment parameter as well as the gyromagnetic ratio (further details on this can be found in the review by Macek and Burns 1976).

### 6.3.1.3 $\mathbf{n}$ Parallel to $X$ , $\mathbf{H}$ Parallel to $X$

Finally we will consider a geometry in which the direction of observation  $\mathbf{n}$  and the field are parallel and directed along the  $X$  axis. In this case it can be shown that

$$\sum_{q'} D\left(0, \frac{\pi}{2}, 0\right)_{\lambda'-\lambda, q'}^{(K)} G(t)_{KK}^{Qq'} = d\left(-\frac{\pi}{2}\right)_{Q_1 \lambda' - \lambda}^{(K)} \exp[-i\omega_L(\lambda' - \lambda)t] \quad (6.26)$$

Substitution of this expression into (6.19) yields

$$\begin{aligned} \dot{\rho}(x, t)_{\lambda' \lambda} &= C(\omega) \sum_{KQ} \text{tr} \left[ r_{-\lambda'} T(J_1)_{K, \lambda' - \lambda} r_{-\lambda}^\dagger \right] d\left(-\frac{\pi}{2}\right)_{Q, \lambda' - \lambda}^{(K)} \\ &\times \exp[-i\omega_L(\lambda' - \lambda)t - \gamma t] \left\langle T(J_1)_{KQ}^\dagger \right\rangle \end{aligned} \quad (6.27)$$

It should be noted that in this geometry the interference effects are independent of  $Q$  (and therefore independent of whether substates with different  $M_1$  have been coherently excited or not). The quantum beats depend only on  $\lambda' - \lambda$  and only the off-diagonal elements of the polarization density matrix will exhibit time modulations. We will consider (6.27) and its consequences in detail in the following section.

### 6.3.2 Magnetic Depolarization. Theory of the Hanle Effect

In the 1920s the depolarization of resonance fluorescence from atoms subjected to external magnetic fields was discovered by [Hanle \(1924\)](#). During the last 30 years the techniques of magnetic depolarization have been further developed and widely applied to study Zeeman and hyperfine structure of excited and ground states and to determine radiative lifetimes and interatomic relaxation rates. In this section we will derive the basic formulas necessary for the description of such experiments.

Consider an atomic system excited by linearly polarized light. It is convenient to define the “collision” system in the following way. The  $Z$  axis is chosen to be parallel to the polarization vector  $\mathbf{e}$  of the incident light, the  $Y$  axis parallel to the incident beam axis. We will consider a geometry in which the emitted resonance light is observed in the  $X$  direction with the magnetic field parallel to  $X$ .

As discussed in Sect. 4.5.3 absorption of plane-polarized light with  $\mathbf{e}$  parallel to  $Z$  will produce alignment but no orientation in the excited atoms. The atomic system can therefore be completely characterized by the two parameters  $\langle T(J_1)_{00} \rangle$  and  $\langle T(J_1)_{20}^\dagger \rangle$ . The polarization density matrix of the emitted radiation is given by (6.27) for the geometry under discussion. The Stokes parameters can be calculated from (6.27) and (1.76) using the detector system defined in Sect. 6.2.1 (with  $\mathbf{n}$  parallel to  $X$ ,  $\mathbf{e}_1$  parallel to  $-Z$ , and  $\mathbf{e}_2$  parallel to  $Y$ ). Assuming that the excitation time ( $t = 0$ ) is sharply defined we obtain

$$I(x, t) = \frac{2C(\omega)}{(2J_1 + 1)^{1/2}} \text{tr} \left( r_{-1} r_{-1}^\dagger \right) \exp(-\gamma t) \langle T(J_1)_{00} \rangle - C(\omega) \text{tr} \left[ r_{-1} T(J_1)_{20} r_{-1}^\dagger \right] \exp(-\gamma t) \langle T(J_1)_{20}^\dagger \rangle \quad (6.28a)$$

$$I\eta_3(x, t) = -C(\omega) \text{tr} \left[ r_{-1} T(J_1)_{2-2} r_{+1}^\dagger \right] \left( \frac{3}{2} \right)^{1/2} (\cos 2\omega_L t) \times \exp(-\gamma t) \langle T(J_1)_{20}^\dagger \rangle \quad (6.28b)$$

$$I\eta_1(x, t) = -C(\omega) \text{tr} \left[ r_{-1} T(J_1)_{2-2} r_{+1}^\dagger \right] \left( \frac{3}{2} \right)^{1/2} (\sin 2\omega_L t) \times \exp(-\gamma t) \langle T(J_1)_{20}^\dagger \rangle \quad (6.28c)$$

$$I\eta_2(x, t) = 0 \quad (6.28d)$$

The last equation is a consequence of the fact that the initially excited atoms were unoriented and that the magnetic field does not mix multipoles with different rank [see (6.27)]. Note that  $I(X, t)$  does not depend on the field.

The time-integrated Stokes parameters are of particular interest. Integrating (6.28) over a time interval  $0 \dots t_R$  where  $t_R$  is much larger than the mean lifetime

(so that the upper integration limit can be extended to infinity with negligible error) we obtain

$$I(X) = \frac{2C(\omega)}{\gamma(2J_1 + 1)^{1/2}} \text{tr} \left( r_{-1} r_1^\dagger \right) \langle T(J_1)_{00} \rangle - \frac{C(\omega)}{\gamma} \text{tr} \left[ r_{-1} T(J_1)_{20} r_{-1}^\dagger \right] \langle T(J_1)_{20}^\dagger \rangle \quad (6.29a)$$

$$I\eta_3(X) = -\frac{\gamma}{\gamma^2 + 4\omega_L^2} \left( \frac{3}{2} \right)^{1/2} C(\omega) \text{tr} \left[ r_{-1} T(J_1)_{2-2} r_{+1}^\dagger \right] \langle T(J_1)_{20}^\dagger \rangle \quad (6.29b)$$

$$I\eta_1(X) = \frac{2\omega_L}{\gamma^2 + 4\omega_L^2} \left( \frac{3}{2} \right)^{1/2} C(\omega) \text{tr} \left[ r_{-1} T(J_1)_{2-2} r_{+1}^\dagger \right] \langle T(J_1)_{20}^\dagger \rangle \quad (6.29c)$$

If the fluorescence light observed in the  $X$  direction passes through a linear polarizer with the axis of transmission at an angle  $\beta$  to the  $Z$  axis then the polarization vector  $\mathbf{e}$  of the transmitted light is given by (6.9), which is a special case of the general (1.55) with  $\delta = 0$ . The transmitted intensity can be obtained by substituting (6.29) into (1.82) with  $\delta = 0$ :

$$I(X)_e = I(X)/2 - (1/2)(3/2)^{1/2} \text{tr} \left[ \mathbf{r}_{-1} T(J_1)_{2-2} r_{+1}^\dagger \right] \langle T(J_1)_{20} \rangle \times \left( \frac{\gamma}{\gamma^2 - 4\omega_L^2} \cos 2\beta + \frac{2\omega_L}{\gamma^2 + 4\omega_L^2} \sin 2\beta \right) \quad (6.30)$$

It is instructive to discuss an example of the use of (6.30). Consider the case in which the incident linearly polarized light excites atoms in a  ${}^1S$  ground state to a  ${}^1P$  state. Because of the dipole selection rules only the substate with magnetic quantum number  $M = 0$  can be excited and  $\langle M = 0 | \rho | M = 0 \rangle \equiv \rho_{00}$  is the only nonvanishing element of the excited state density matrix. Application of (4.31) gives

$$\langle T_{00} \rangle = \frac{1}{3^{1/2}} \rho_{00}, \quad \langle T_{20} \rangle = -\left( \frac{2}{3} \right)^{1/2} \rho_{00} \quad (6.31)$$

Calculating the traces in (6.29a) and (6.30) and describing the subsequent decay to the atomic ground state by means of (5.15) we obtain

$$\begin{aligned} \text{tr} \left( r_{-1} r_{-1}^\dagger \right) &= (1/3) |\langle 0 | \mathbf{r} | 1 \rangle|^2 \\ \text{tr} \left[ r_{-1} T(1)_{20} r_{-1}^\dagger \right] &= [1/3(6)^{1/2}] |\langle 0 | \mathbf{r} | 1 \rangle|^2 \\ \text{tr} \left[ r_{-1} T(1)_{2-2} r_1^\dagger \right] &= (1/3) |\langle 0 | \mathbf{r} | 1 \rangle|^2 \end{aligned} \quad (6.32)$$

Substitution of (6.31) and (6.32) into the expressions (6.29a) and (6.30) gives

$$I(X) = C(\omega) |\langle 0 \parallel \mathbf{r} \parallel 1 \rangle|^2 \rho_{00}/3 \quad (6.33a)$$

and

$$I(X)_e = \left[ \frac{I(X)}{2} \right] \left[ 1 + \frac{\gamma^2}{\gamma^2 + 4\omega_L^2} \cos 2\beta + \frac{2\omega_L \gamma}{\gamma^2 + 4\omega_L^2} \sin 2\beta \right] \quad (6.33b)$$

It should be noted that *the shape of the observed signal  $I(X)_e$*  described by (6.33) *depends on the orientation of the polarizer in the detection beam*. The shape is called a *Lorentzian shape* for  $\beta = 0$  and a *dispersion shape* for  $\beta = 45^\circ$ . Fig. 6.3a, b show the curves obtained in the special case when (6.33) applies.

Finally we will consider the polarization  $P$  defined by (6.11) as

$$P = \frac{I_{\parallel} - I_{\perp}}{I_{\parallel} + I_{\perp}} \quad (6.34)$$

where  $I_{\parallel}(I_{\perp})$  is the intensity transmitted by the polarizer if its axis of transmission is parallel (perpendicular) to  $Z$ .  $I_{\parallel}$  and  $I_{\perp}$  can be obtained by inserting  $\beta = 0^\circ$  and  $\beta = 90^\circ$  in (1.82), which gives

$$P = \eta_3 \quad (6.35)$$

Substitution of (6.29a), (6.29b) into (6.35) yields

$$P = P_0 \frac{\gamma^2}{\gamma^2 + 4\omega_L^2}$$

where  $P_0$  denotes the polarization detected in the field-free case ( $\omega_L = 0$ ). The factor

$$\frac{\gamma^2}{\gamma^2 + 4\omega_L^2} < 1$$

describes the *depolarization* of the emitted fluorescence light caused by the magnetic field. If  $\mathbf{H}$  is slowly varied the polarization  $P$  of the radiation changes from its maximum possible value at the zero field to steadily decreasing values with increasing field strength (Fig. 6.4). This constitutes the *Hanle effect* or the *magnetic depolarization* of resonance radiation.

The emphasis of our discussions here has been to illustrate how (6.30) and (6.33) are direct consequences of the general theory presented in Chaps. 4 and 5. For an interpretation of the Hanle effect in terms of a semiclassical model, experimental results and applications we refer, for example, to the review by Cohen-Tannoudji and Kastler (1966) and the book by Corney (1977).

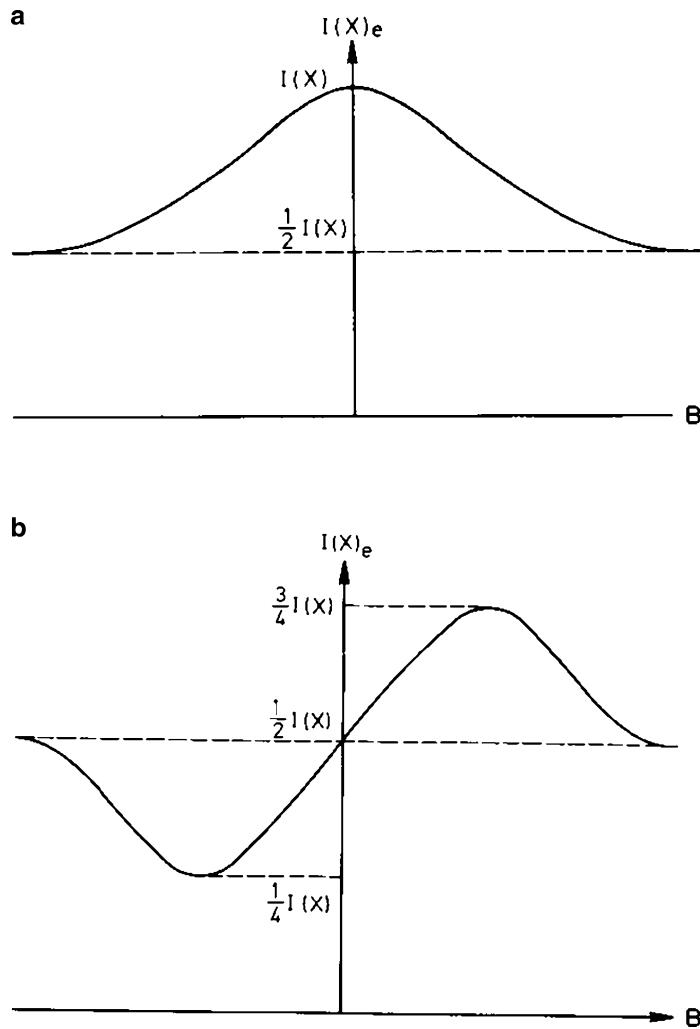
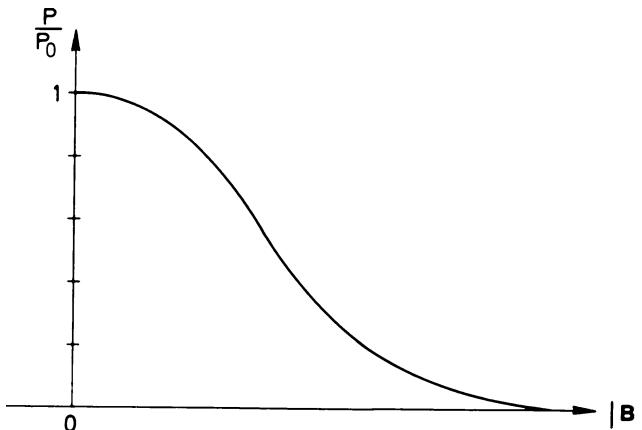


Fig. 6.3 Shape of Hanle curves

### 6.3.3 Physical Interpretation of Zeeman Quantum Beats. Rotation of the Atomic Charge Cloud

In this subsection we give a physical and geometrical interpretation of the results obtained in the previous subsection. We do this by discussing an explicit example. Assume that atoms have been excited at time  $t = 0$  by a short pulse of linearly polarized light in the presence of a magnetic field  $\mathbf{H}$ , which is perpendicular to the



**Fig. 6.4** Depolarization of resonance fluorescence

electric vector  $\mathbf{E}$  of the exciting light. We will choose a coordinate system  $X_N Y_N Z_N$  in such a way that  $X_N$  is parallel to  $\mathbf{E}$ , and  $Z_N$  is parallel to  $\mathbf{H}$ . The magnetic field will be assumed to be sufficiently weak so that its influence on the excitation process can be neglected. Let us therefore first consider the geometry of the atomic charge cloud at  $t = 0$ , that is, immediately after the excitation. Since only the electric field  $\mathbf{E}$  is defined by the geometry of the process it follows that the charge cloud at  $t = 0$  possesses three planes of symmetry: the  $X_N - Y_N$ ,  $X_N - Z_N$ , and  $Y_N - Z_N$  planes (the latter one is a symmetry plane because, due to the rapid oscillation of  $\mathbf{E}$ , the atoms “see” only the axis along  $\mathbf{E}$  but not its direction). This situation would be schematically illustrated by Fig. 4.7 if the alignment angle  $\gamma$  is set to zero.

The symmetry relations (4.83) and (4.96) apply. In particular, for  $L = 1$ , the atomic charge cloud is described by three independent real parameters:  $\langle T_{00} \rangle$ ,  $\langle T_{20}^\dagger \rangle$ , and  $\langle T_{22}^\dagger \rangle = \langle T_{2-2}^\dagger \rangle$ . We will concentrate on this case in the following.

The time evolution of the system is determined by its interaction with the magnetic field. Since  $\mathbf{H}$  is directed parallel to  $Z_N$ , (4.145) applies. This equation [also the more general expression (4.143)] shows that the rank  $K$  of state multipoles remains invariant. It is not possible, for example, to transform alignment into orientation with the help of a magnetic field. (This statement holds as long as the magnetic field is sufficiently weak so that only a linear Zeeman effect is taking place. However, alignment–orientation conversion becomes possible if quadratic effects have to be taken into account. Details may be found in the review by [Auzinsh and Ferber 1995](#).) Furthermore, in the case under discussion,  $Q$  remains also unchanged under the influence of  $\mathbf{H}$ . Consequently,  $\langle T_{00} \rangle$  and  $\langle T_{20}^\dagger \rangle$  are not affected by the field. The time development of the remaining parameters is given by

$$\langle T(t)_{22}^\dagger \rangle = e^{-2i\omega_L t} \langle T_{22}^\dagger \rangle \quad (6.36a)$$

$$\langle T(t)_{2-2}^\dagger \rangle = e^{+2i\omega_L t} \langle T_{22}^\dagger \rangle \quad (6.36b)$$

where  $\langle T_{2Q}^\dagger \rangle$  denotes the multipoles at  $t = 0$  and where we have used the symmetry condition  $\langle T_{22}^\dagger \rangle = \langle T_{2-2}^\dagger \rangle$ . Comparison with (4.104) shows that  $2\omega_L t = -\gamma(22)$ ; that is,  $\omega_L t$  can be interpreted as alignment angle at time  $t$ . We can therefore repeat the steps leading from (4.101) to (4.106) and obtain for the projection of the charge cloud in the  $X_N - Y_N$  plane ( $\Theta = \pi/2$ ) at time  $t$  the expression

$$W\left(\frac{\pi}{2}, \varphi, t\right) = A + B \cos(2\varphi - 2\omega_L t) \quad (6.37)$$

This result shows that the charge distribution retains its shape under the influence of  $\mathbf{H}$ , but rotates in the  $X_N - Y_N$  plane around  $\mathbf{H}$  with the Larmor frequency  $\omega_L$ . However, since the atoms are aligned but not oriented there is no distinction between “head” and “tail” of the charge cloud. Consequently, the positions at time  $t = 0$  and at time  $t = \pi/\omega$ , are physically indistinguishable. Any physical observable quantity will therefore vary in time with twice the Larmor frequency. In particular, if one observes the light emitted by the excited atoms in their subsequent decay, the rotation of the charge cloud results in a modulated response of the detector at twice the Larmor frequency in accordance with (6.22). The quantum beats, described in Sect. 6.3, are a direct manifestation of the precession of the charge cloud around  $\mathbf{H}$ .

Classically, the excitation process can be considered by assuming that an atomic electron receives an impulse at  $t = 0$  which starts it oscillating in the direction of  $\mathbf{E}$ . This corresponds to an oscillating electric dipole which experiences a torque under the magnetic field and precesses around it. As these dipoles rotate and decay, the intensity of the emitted light oscillates with frequency  $2\omega_L$  (see, for example, Series and Dodd 1978).

Finally, we point out that a prerequisite for any rotation of the charge cloud is that a “sense of rotation” is defined by the geometry of the experiment. If an experiment is designed which does not fulfill this condition, no rotation of any kind can be produced. In our present case of interest this essential geometrical condition is satisfied by the transformation properties of the magnetic field.  $\mathbf{H}$  transforms as an axial vector. An axial vector is primarily defined by defining a “sense of rotation.” The rotation sense fixes a plane and an axis normal to the plane. The direction of the vector is chosen by convention only (by applying the usual right-hand rule). In our present case of discussion the essential geometrical element is therefore not the direction of  $\mathbf{H}$  but the corresponding rotation sense in the  $X_N - Y_N$  plane. By interacting with the field the atoms can “see” this sense of rotation and can react to it.

## 6.4 Influence of Electric Fields. Orientation – Alignment Conversion

### 6.4.1 Time Evolution of State Multipoles

In the preceding section we have considered the influence of external magnetic fields on atoms. It has been shown that a weak magnetic field leaves the rank  $K$  of the state multipoles invariant, and the basic symmetry of the ensemble does therefore not change. It has been of significant interest for a long time to examine perturbations able to break the symmetry of a given atomic ensemble and to transform, for example, alignment into orientation. Such a method is of particular interest for producing orientation out of alignment in beams of diatomic molecules.

One possibility to achieve this is by application of external electric fields via second-order Stark effect. The basis for this approach was formulated by [Lombardi \(1969\)](#) and has been developed over the years by several research groups. We refer to the reviews by [Andrä \(1979\)](#) and [Auzinsh and Ferber \(1993, 1995\)](#) for the history of the subject and for a discussion of experimental and theoretical work.

In the present section we describe the method of symmetry breaking by external electric fields. In order to point out the essential features of the method as clearly as possible we concentrate on simple cases. Consider an ensemble of excited atoms in singlet states with orbital angular momentum  $L = 1$ , characterized by state multipoles  $\langle T_{KQ}^\dagger \rangle$ . At time  $t = 0$  an external electric field is switched on and perturbs the excited atoms so that the ensemble at times  $t > 0$  is described by multipoles  $\langle T(t)_{KQ}^\dagger \rangle$ . We will first investigate the time evolution of the multipoles via the second-order Stark effect. Let us assume that the  $X$ - $Z$  plane is a symmetry plane of the unperturbed atoms (so that the results of Sect. 4.6.2 apply) and that the electric field  $\mathbf{E}$  is directed parallel to the  $Z$  axis.

It has been shown that the second-order Stark effect can be described by an “effective” Hamiltonian

$$H = H_0 - \frac{1}{2}E^2 A - E^2 B \left( L_Z^2 - \frac{1}{3}L^2 \right) \quad (6.38)$$

where  $A$  and  $B$  are essentially reduced matrix elements and  $L_Z^2$  and  $L^2$  denote angular momentum operators ([Sobelmann 1979](#)). We rewrite (6.38),

$$H = a + bL_Z^2 \quad (6.39)$$

with

$$a = H_0 - \frac{1}{2}AE^2 + \frac{1}{3}E^2BL^2$$

and

$$b = E^2 B$$

and write the corresponding time evolution operator as

$$U(t) = e^{-(i/\hbar)(a+bL_Z^2)t} \quad (6.40)$$

The time evolution of angular momentum eigenstates is then given by

$$|LM, t\rangle = U(t)|LM\rangle = e^{-(1/\hbar)(a+bM^2)t}|LM\rangle \quad (6.41)$$

where  $|LM\rangle$  denotes the state immediately before switching on the electric field. The time evolution of the tensor operators can then easily be obtained. We use the definition (4.3) and set  $J = J' = L = 1$ . Substitution of explicit values of the Clebsch–Gordan coefficients yields in particular

$$T_{11} = -\left(\frac{1}{2}\right)^{1/2} [|11\rangle\langle 10| + |10\rangle\langle 1-1|] \quad (6.42a)$$

$$T_{21} = -\left(\frac{1}{2}\right)^{1/2} [|-11\rangle\langle 10| + |10\rangle\langle 1-1|] \quad (6.42b)$$

for the unperturbed atoms. At time  $t$  we obtain, by using (6.40) and (6.41),

$$\begin{aligned} U(t)T_{11}U(t)^\dagger &= -\left(\frac{1}{2}\right)^{1/2} [e^{-(i/\hbar)bt}|11\rangle\langle 10| + |10\rangle\langle 1-1|e^{(i/\hbar)bt}] \\ &= -\left(\frac{1}{2}\right)^{1/2} \left[ (|11\rangle\langle 10| + |10\rangle\langle 1-1|) \cos \frac{bt}{\hbar} \right. \\ &\quad \left. + i(-|11\rangle\langle 10| + |10\rangle\langle 1-1|) \sin \frac{bt}{\hbar} \right] \\ &= T_{11} \cos \frac{bt}{\hbar} - iT_{21} \sin \frac{bt}{\hbar} \end{aligned} \quad (6.43a)$$

Taking expectation values and remembering  $\langle T_{KQ}^\dagger \rangle = \langle T_{KQ} \rangle^*$ , we obtain

$$\langle T(t)_{11}^\dagger \rangle = \langle T_{11}^\dagger \rangle \cos \frac{bt}{\hbar} + i \langle T_{21}^\dagger \rangle \sin \frac{bt}{\hbar} \quad (6.43b)$$

In a completely similar way we obtain

$$\langle T(t)_{21}^\dagger \rangle = \langle T_{21}^\dagger \rangle \cos \frac{bt}{\hbar} + i \langle T_{11}^\dagger \rangle \sin \frac{bt}{\hbar} \quad (6.43c)$$

and that  $\langle T_{20}^\dagger \rangle$  and  $\langle T_{22}^\dagger \rangle$  are unaffected by the field.

With  $\mathbf{E}$  parallel to  $Z$  the  $X$ – $Z$  plane is still a symmetry plane of the system. According to (4.83) the alignment components are real and the orientation imaginary:

$$\langle T_{11}^\dagger \rangle = \frac{i}{2} \langle L_y \rangle \quad (6.44)$$

where we have applied (4.84a).  $\langle L_y \rangle$  is the mean value of the angular momentum of the atomic ensemble. Combining (6.43) and (6.44) we obtain

- $\langle L(t)_y \rangle = \langle L_y \rangle \cos \frac{bt}{\hbar} + 2 \langle T_{21}^\dagger \rangle \sin \frac{bt}{\hbar} \quad (6.45a)$

- $\langle T(t)_{21}^\dagger \rangle = \langle T_{21}^\dagger \rangle \cos \frac{bt}{\hbar} - \frac{1}{2} \langle L_y \rangle \sin \frac{bt}{\hbar} \quad (6.45b)$

$\langle T_{21}^\dagger \rangle$  can be expressed in Cartesian components by using (4.85).

Equations 6.45 show that the alignment component  $\langle T_{21}^\dagger \rangle$  is reversibly transformed into orientation  $\langle L_y \rangle$  by the influence of the electric field, whereas  $\langle T_{20}^\dagger \rangle$  and  $\langle T_{22}^\dagger \rangle$  remain unaffected.  $\langle T_{21}^\dagger \rangle$  characterizes the spatial direction of the atomic charge cloud within the  $X$ – $Z$  plane according to (4.103a). In order to obtain more insight into the relationship between  $\langle J_y \rangle$  and the orientation of the charge cloud we will consider some examples.

#### 6.4.2 Variation of Shape and Spatial Direction of Atomic Charge Clouds

Assume that atoms have been excited from the ground state ( $L = 0$ ) to states with  $L = +1$  by a short pulse of circularly polarized light at time  $t = 0$  in the presence of a static electric field  $\mathbf{E}$ .

The field is assumed to be sufficiently weak so that it can be neglected during the excitation. The  $Y$  axis of our coordinate system will be chosen parallel to the incident light beam, and the  $Z$  axis parallel to  $\mathbf{E}$ . We will consider atomic excitation from the ground state ( $L = 0$ ) to states with  $L = 1$ .

If the light has positive helicity then only one atomic state  $|1, 1\rangle_y$  can be excited, where the subscript “ $y$ ” indicates that the  $Y$  axis has been chosen as quantization axis. We obtain from (4.31) that, with respect to  $Y$  as quantization axis, the following two multipoles are different from zero:

$$\langle L_y \rangle = 1 \quad (6.46a)$$

$$\langle T_{20}^\dagger \rangle_y = \left( \frac{1}{6} \right)^{1/2} \quad (6.46b)$$

We obtain the alignment components  $\langle T_{2Q}^\dagger \rangle$  with respect to  $Z$  as quantization axis by using (4.41). The  $Y$  axis has polar angle  $\Theta = \pi/2$  and azimuth angle  $\varphi = \pi/2$ , and the third Euler angle can be set to zero.

We obtain, by applying relation (C12) and by inserting explicit values for the  $d$  functions,

$$\langle T_{20}^\dagger \rangle = \langle T_{20}^\dagger \rangle_y D \left( 0 \frac{\pi}{2} \frac{\pi}{2} \right)_{00}^{(2)*} = -\frac{1}{2} \left( \frac{1}{6} \right)^{1/2} \quad (6.47a)$$

$$\langle T_{21}^\dagger \rangle = \langle T_{20}^\dagger \rangle_y D \left( 0 \frac{\pi}{2} \frac{\pi}{2} \right)_{01}^{(2)*} = 0 \quad (6.47b)$$

$$\langle T_{22}^\dagger \rangle = \langle T_{20}^\dagger \rangle_y D \left( 0 \frac{\pi}{2} \frac{\pi}{2} \right)_{02}^{(2)*} = -\frac{1}{4} \quad (6.47c)$$

Since under the assumed conditions the  $X - Z$  plane is a symmetry plane, these components are real parameters according to (4.82).

After the excitation the atomic states will be perturbed by the field  $\mathbf{E}$ , and the corresponding time evolution of the multipoles is given by (6.45):

- $\langle L(T)_y \rangle = \langle L_y \rangle \cos \frac{bt}{\hbar} = \cos \frac{bt}{\hbar} \quad (6.48a)$

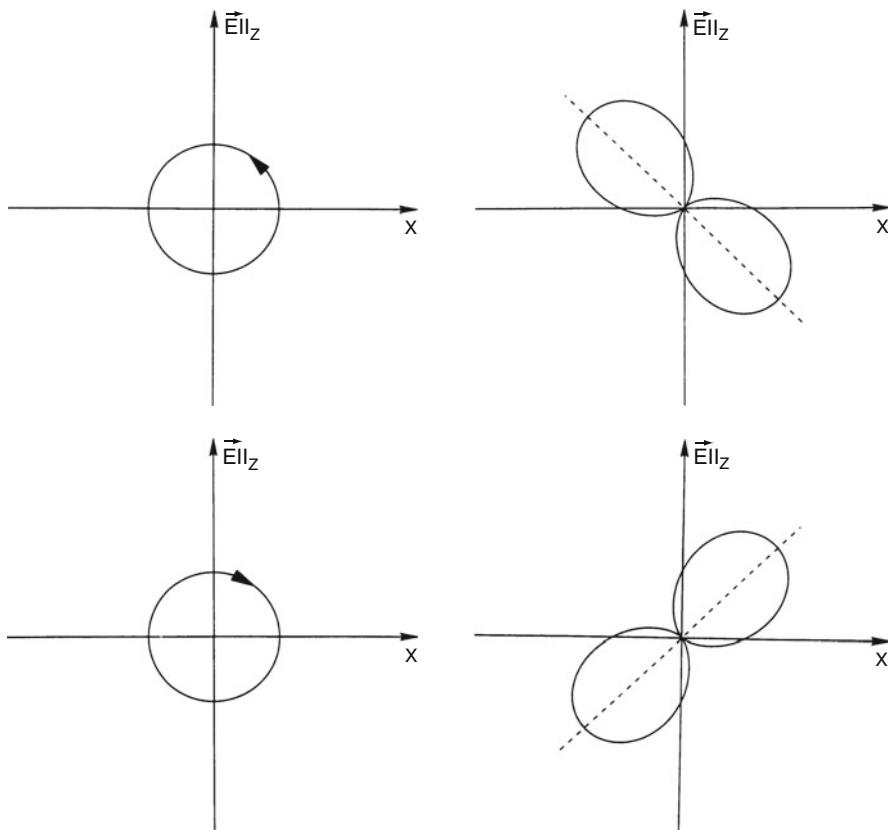
- $\langle T(t)_{21}^\dagger \rangle = -\frac{1}{2} \sin \frac{bt}{\hbar} \quad (6.48b)$

where the initial conditions (6.47b) and (6.46a) have been taken into account. It follows that an orientation component perpendicular to  $\mathbf{E}$  is transformed into the alignment component  $\langle T_{21}^\dagger \rangle$ . The time evolution of the charge cloud follows by inserting the results (6.47a), (6.47c), and (6.48b) into (4.102). Considering again the cut through the  $X - Z$  plane (corresponding to  $\varphi = 0$ ) we obtain

- $$\begin{aligned} W(\Theta, 0, t) &= \frac{3}{8\pi} \left[ 1 + 2 \langle T(t)_{21}^\dagger \rangle \sin 2\Theta \right] \\ &= \frac{3}{8\pi} \left[ 1 - \sin \frac{bt}{\hbar} \sin 2\Theta \right] \end{aligned} \quad (6.49)$$

where  $\Theta$  is the angle between the radius vector and  $Z$ , and  $W(\Theta, 0)$  is the length of the corresponding radius vector.

Equation 6.49 allows us to follow the time variation of the shape of the charge distribution. At time  $t = 0$  the shape in the  $X - Z$  plane is a circle with radius  $W = 3/8\pi$ . Under the influence of the electric field the charge cloud is gradually deformed. Its shape at four different times is depicted by Fig. 6.5. The orientation has its maximum value  $\langle L_y \rangle = +1$  at  $t = 0$  and  $\langle L_y \rangle = -1$  at  $t = \pi\hbar/b$ . The sign



**Fig. 6.5** Variation of the shape and direction of a charge cloud with time (a)  $t = 0$ , (b)  $t = \pi\hbar/2b$ , (c)  $t = \pi\hbar/b$ , (d)  $t = 3\pi\hbar/b$ . The arrow in figs, (a) and (c) indicate the sign of  $\langle L_y \rangle$ . The electric field is parallel to  $Z$ .

is indicated by the arrows in Fig. 6.5a, c. The orientation vanishes if the alignment  $\langle T_{21}^\dagger \rangle$  is maximal, that is, at times  $t = \pi\hbar/2b$  and  $t = 3\pi\hbar/2b$ .

Several features are apparent from Fig. 6.5. The alignment angle  $\gamma$  is either  $45^\circ$  or  $135^\circ$  [this follows also from (4.103a) if the values (6.47) for  $\langle T_{22}^\dagger \rangle$  and  $\langle T_{20}^\dagger \rangle$  are inserted], and these are the only directions along which the charge cloud can be deformed by the electric field. A rapid change of  $\gamma$  occurs near the maximum and the minimum values of  $\langle L_y \rangle$ .

It is interesting that the same type of behavior of the alignment angle has been observed in electron–atom collisions: A rapid change of  $\gamma$  is always connected with a maximum value of  $|\langle L_y \rangle|$  (Andersen et al. 1988). Our discussion suggests that the observed correlation between  $\gamma$  and  $\langle L_y \rangle$  is caused by a long-range effect: The excited atoms “see” the electric field of the outgoing projectile, and in this field orientation and alignment are transformed into each other.

### 6.4.3 Creation of Orientation Out of Alignment

Let us now consider the conversion of alignment into orientation. Assume that the orientation  $\langle \mathbf{L} \rangle$  vanishes at  $t = 0$  and that the alignment is different from zero. Let us suppose that the  $X - Z$  plane is a mirror plane of the corresponding charge cloud and that  $\mathbf{E}$  is parallel to  $Z$ . The alignment angle  $\gamma$  may have an arbitrary value (Fig. 4.7). Under the influence of the field an orientation is produced perpendicular to  $\mathbf{E}$  and perpendicular to the alignment axis of the charge cloud (that is, the longest principal axis in the  $X - Z$  plane). We find from (6.45):

- $$\langle L_y(t) \rangle = 2 \left\langle T_{21}^\dagger \right\rangle \sin \frac{bt}{\hbar} \quad (6.50a)$$

- $$\left\langle T(t)_{21}^\dagger \right\rangle = 2 \left\langle T_{21}^\dagger \right\rangle \cos \frac{bt}{\hbar} \quad (6.50b)$$

where  $\left\langle T_{21}^\dagger \right\rangle$  is the value of  $t = 0$ . However, a prerequisite for the transformation of alignment into orientation is that  $\left\langle T_{21}^\dagger \right\rangle$  be different from zero. This requires that the charge cloud be neither parallel to  $\mathbf{E}$  ( $\gamma = \pi/2$ ) nor parallel to the  $X$  axis ( $\gamma = 0$ ), as follows from an inspection of (4.103a)). The most effective geometry would be to apply an electric field at  $\Theta = 45^\circ$  to the alignment axis.

### 6.4.4 Comparison Between Electric and Magnetic Field Influences

Comparing the results of the present subsection with those of Sect. 6.3, we see that there is a striking difference between the influence of weak electric and magnetic fields on excited atoms. The former converts alignment into orientation and vice versa; under the influence of the latter atomic charge clouds are set into rotation. This difference can be traced to the fact that the effective Hamiltonian (6.38) depends on  $L_Z^2$ , whereas the Hamiltonian (4.140) depends on  $L_Z$ . If we repeat the calculations leading to (6.45), with the Hamiltonian (4.140) we obtain that the rank  $K$  of the multipoles remains invariant, and we rediscover the results of Sect. 6.3.3. The different behavior of excited atoms in electric and magnetic fields follows therefore from the fact that a magnetic field completely removes the degeneracy between different Zeeman levels, whereas states with  $M$  and  $-M$  remain degenerate in electric fields. This result can further be traced to the different transformation properties of  $\mathbf{E}$  and  $\mathbf{H}$ : the former transforms as a polar vector, and the latter as an axial vector (see, for example, Chapter XV in [Messiah 1965](#)).

# Chapter 7

## The Role of Orientation and Alignment in Molecular Processes

### 7.1 Introduction

In typical spectroscopic or collision experiments molecules rotate freely and isotropic averaging of the process considerably reduces the amount of information on the interactions. In recent years several methods have therefore been developed to produce anisotropic distributions of molecular angular momenta: for example, focusing by external electric fields, optical pumping by polarized laser excitation, or rotational cooling in supersonic expansions (see, for example, the reviews by [Herschbach 1992](#); [Friedrich et al. 1991](#); [Scoles 1988](#)).

A considerable amount of molecular orientation and alignment can also be created in collisions of molecules with surfaces or by scattering electrons or atoms from molecules. Here, a well-defined plane (surface or scattering plane respectively) exists against which all angular momentum directions can be measured. These processes are therefore anisotropic by their very nature, which manifests itself in an anisotropic distribution of angular momentum vectors.

These developments allow us to carry out experiments with a nonuniform distribution of angular momenta and molecular axes in the probed species, either in the initial or the final states. By studying the dependence of molecular processes on the initial orientation and alignment, or by determining rotational polarization in the final states, a wealth of information can be obtained about the symmetry of the excited states as well as on the dynamics of the reactions. The use of these techniques has become a central feature of much contemporary work in laser studies, photofragmentation, chemical reactions, and in general in the “dynamical stereochemistry” field.

It is the purpose of the present chapter to develop the techniques necessary to characterize angular momentum and axes distributions, and illustrate the results with examples of experimental interest. We will first discuss linear rotors, and then generalize the results to symmetric top molecules. Knowledge of the essential parts of Chaps. 2 and 3 and in particular of Sects. 4.3 and 4.5 will be assumed.

## 7.2 Rotational Polarization. Semiclassical Interpretation of State Multipoles: Distribution Functions of Angular Momentum Vectors

In this section we will derive the semiclassical limits of some of the quantum mechanical formulas of Sect. 4.3. This will in particular lead to a visual interpretation of state multipoles. We will concentrate on *axially symmetric systems* throughout this section.

We will consider linear rotors (e.g., diatomic molecules in their electronic ground state) because their rotational states depend on two quantum numbers  $J$  and  $M$  only. We will consider an ensemble of rotating molecules with sharp value  $J$  of the magnitude of the angular momentum but it will be assumed that different molecules may be in states with different  $M$ . Semiclassically, this corresponds to a distribution of  $\mathbf{J}$  vectors as shown for example in Figs. 4.2 and 4.3, and the corresponding state multipoles  $\langle T(\mathbf{J})_{K0}^\dagger \rangle$  are a measure of the spatial anisotropy of the  $\mathbf{J}$  vectors. Quantum mechanically, the state multipoles are a measure of the unequal population of the available  $M$  states and their coherence properties [see (4.76)].

In this section we will consider the semiclassical treatment in more detail in order to visualize the concept of state multipoles. In molecular physics one deals frequently with states with large angular momenta (with  $J$  values of the order 10–100) so that the semiclassical approach should often be applicable.

We will start with the quantum mechanical formulations of Sects. 4.1 and 4.2 and derive their semiclassical limits in the high  $J$  approximation. Throughout this and the following sections we will normalize the density matrix  $\rho$  according to

$$\text{tr } \rho = 1 \quad (7.1a)$$

which corresponds to

$$\langle T(\mathbf{J})_{00} \rangle = \frac{1}{(2J+1)^{1/2}} \quad (7.1b)$$

Let us consider *axially symmetric* ensembles. We recall that  $\rho$  is diagonal in  $M$  and that the diagonal element  $\langle M | \rho | M \rangle$  is equal to the probability  $W(M)$  of finding a molecule in the state  $|JM\rangle$ . Equation 4.34 gives

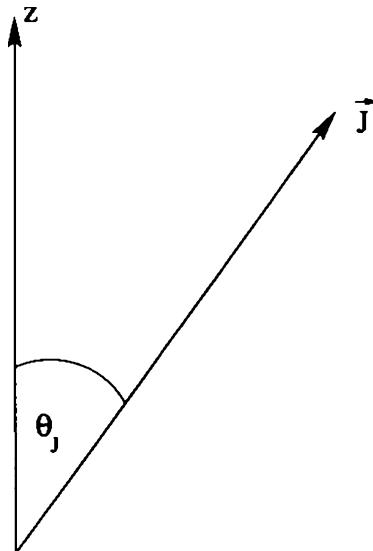
$$W(M) = \sum_K (-1)^{J-M} \langle JM, J-M | K0 \rangle \langle T(\mathbf{J})_{K0}^\dagger \rangle \quad (7.2)$$

where the state multipoles are real parameters according to Sect. 4.3.2.

In the semiclassical vector model  $\mathbf{J}$  has length  $\sqrt{J(J+1)}$  and a constant projection  $M$  on  $Z$  (see Fig. 7.1). The angle  $\theta_J$  between  $J$  and  $Z$  is given by the relation

$$\cos \theta_J = \frac{M}{\sqrt{J(J+1)}} \approx \frac{M}{J} \quad (7.3a)$$

**Fig. 7.1** Semiclassical vector model



in the high- $J$  limit.  $W(M)$  can therefore be interpreted as probability  $W(\theta_J)$  of finding a molecule with  $\mathbf{J}$  at an angle  $\theta_J$  with respect to  $Z$ .

In order to make the relation between state multipoles and semiclassical pictures more explicit we approximate the Clebsch–Gordan coefficient in (7.2) by a Legendre polynomial. The relevant expression is valid for high  $J$  and is given in [Edmonds \(1957\)](#):

- $(JM, J - M | K0) \approx \left( \frac{2K + 1}{2J + 1} \right)^{1/2} (-1)^{J+M} P_K(\cos \theta_J)$  (7.3b)

where  $\cos \theta_J$  is given by (7.3a). In particular, we obtain from (7.3a), (7.3b)

- $(J0, J0 | K0) \approx \left( \frac{2K + 1}{2J + 1} \right)^{1/2} (-1)^J P_K(0)$  (7.3c)

Substitution of (7.3b) into (7.2) yields

$$W(M) = \left( \frac{1}{2J + 1} \right)^{1/2} \sum_K (2K + 1)^{1/2} \left\langle T(J)_{K0}^\dagger \right\rangle P_K(\cos \theta_J) \quad (7.4)$$

In the high- $J$  limit the distribution of  $\mathbf{J}$  vectors can be considered to be a continuum. In this limit we put  $W(M) = W(\theta_J)$  and recall that the normalization factor  $2J + 1$  should be replaced by  $4\pi$ . (This is because, in passing from quantum mechanics to the classical limit, the number of possible spatial orientations of  $\mathbf{J}$ , equaling  $2J + 1$ , must be replaced by the full solid angle  $4\pi$ .)

Hence,  $\langle T(J)_{00} \rangle = (2J + 1)^{-1/2}$  will be replaced by  $\langle T(J)_{00} \rangle = (4\pi)^{-1/2}$ , and  $\sum_M W(M) = 1$  corresponds to

$$\int_0^{2\pi} d\varphi_J \int_0^\pi d\theta_J \sin \theta_J W(\theta_J) = 1 \quad (7.5)$$

Here,  $W(\theta_J) \sin \theta_J d\theta_J d\varphi_J$  is the probability of finding the angular momentum  $\mathbf{J}$  of a molecule within the range  $\theta_J \dots \theta_J + d\theta_J, \varphi_J \dots \varphi_J + d\varphi_J$ . We therefore obtain from (7.4)

- $W(\theta_J) = \sum_K \left( \frac{2K + 1}{4\pi} \right)^{1/2} \langle T(J)_{K0}^\dagger \rangle P_K(\cos \theta_J) \quad (7.6)$

which satisfies condition (7.5). We define the mean value  $\langle P_K(\cos \theta_J) \rangle$  of the Legendre polynomial  $P_K$ , taken over the distribution of  $\mathbf{J}$  vectors, by the relation

$$\langle P_K(\cos \theta_J) \rangle = \int_0^{2\pi} d\varphi_J \int_0^\pi d\theta_J \sin \theta_J W(\theta_J) P_K(\cos \theta_J) \quad (7.7)$$

Inserting (7.6) into (7.7) and using

$$\int_0^{2\pi} d\varphi_J \int_0^\pi d\theta_J \sin \theta_J P_K(\cos \theta_J) P_{K'}(\cos \theta_J) = \frac{4\pi}{2K + 1} \delta_{KK'} \quad (7.8a)$$

we obtain

$$\langle P_K(\cos \theta_J) \rangle = \left( \frac{4\pi}{2K + 1} \right)^{1/2} \langle T(J)_{K0}^\dagger \rangle$$

and in particular  $\langle P_0(\cos \theta_J) \rangle = 1$ .

Hence, we have

- $\langle T(J)_{K0}^\dagger \rangle = \left( \frac{2K + 1}{4\pi} \right)^{1/2} \langle P_K(\cos \theta_J) \rangle \quad (7.9)$

and

- $W(\theta_J) = \frac{1}{4\pi} \sum_K (2K + 1) \langle P_K(\cos \theta_J) \rangle P_K(\cos \theta_J) \quad (7.10)$

Equation 7.10 shows that the state multipoles  $\langle T_{K0} \rangle$  are proportional to the corresponding Legendre polynomials, averaged over the given distribution of  $\mathbf{J}$  vectors. In particular, we obtain for the orientation vector

$$\langle T(J)_{10}^\dagger \rangle = \left( \frac{3}{4\pi} \right)^{1/2} \langle \cos \theta_J \rangle \quad (7.11)$$

which is zero if the average of  $\cos \theta_J$  vanishes. This is the case if either an equal number of  $\mathbf{J}$  vectors are pointing in the  $+z$  and  $-z$  directions as in Fig. 4.2, or if all angular momenta are perpendicular to  $z$ . We have  $\langle \cos \theta_J \rangle = 1$  if all  $\mathbf{J}$  vectors are parallel to  $z$  (corresponding to  $M = J$ ), and  $\langle \cos \theta_J \rangle = -1$  if all angular momenta are pointing in the negative  $z$  direction.

Similarly, the alignment parameter is proportional to the average of the second Legendre polynomial

$$\langle T(J)_{20}^\dagger \rangle = (5/4\pi)^{1/2} \left\langle \frac{1}{2}(3 \cos^2 \theta_J - 1) \right\rangle \quad (7.12)$$

The mean value of  $P_2(\cos \theta_J)$  is  $-\frac{1}{2}$  if all  $\mathbf{J}$  vectors are perpendicular to  $z$ , and  $+1$  if all angular momenta are parallel to  $z$  (corresponding to  $\theta_J = \pi/2$  and  $\theta_J = 0$  respectively).

These expressions give explicit relations between state multipoles and distributions of angular momentum vectors. The equations show how spatial correlations between  $\mathbf{J}$  and a single reference vector ( $z$  direction) can be expressed in terms of multipole parameters. The azimuthal angle  $\varphi_J$  of  $\mathbf{J}$  is uniformly distributed, and the polar angle  $\theta_J$  measures the directional correlation. The system is oriented if at least one state multipole with  $K$  odd is nonvanishing. The mean value of the corresponding Legendre polynomial contains then factors  $\sim (\cos \theta_J)^K$ , and the distribution shows a “head-versus-tail” distinction (Fig. 4.3).

If all multipoles with  $K$  odd vanish then the system cannot distinguish between the  $+z$  and  $-z$  directions. In this case there exists a preferred axis but no preferred direction. The system is then aligned but not oriented (Fig. 4.2).

Equation 7.10 expresses the probability density function of an axially symmetric  $\mathbf{J}$  distribution in terms of expectation values of the  $P_K$ , or alternatively in terms of state multipoles. Let us consider an explicit example of an aligned system where only  $\langle T(J)_{20}^\dagger \rangle$  is nonvanishing. Equation 7.10 reduces then to the expression

$$W(\theta_J) = \frac{1}{4\pi} \left[ 1 + \frac{b}{2}(3 \cos^2 \theta_J - 1) \right] \quad (7.13a)$$

where the “alignment parameter”  $b$  has been defined by

$$b = \sqrt{20\pi} \langle T(J)_{20}^\dagger \rangle = 5 \langle P_2(\cos \theta_J) \rangle \quad (7.14)$$

The limiting values of  $b$  follow from the condition that the probability density  $W(\theta_J)$  must be nonnegative for all values of  $\theta_J$ . This gives the condition

$$-1 \leq b \leq 2 \quad (7.15)$$

$b = 2$  corresponds to a pure  $\cos^2 \theta_J$  distribution of angular momentum vectors, and  $b = -1$  gives rise to a pure  $\sin^2 \theta_J$  distribution.

In this section we have considered the semiclassical limit of some quantum mechanical formulas for axially symmetric systems only. Classical probability

functions for  $\mathbf{J}$  distributions in more general cases will not be considered here. For a detailed discussion with various applications we refer to the book by [Auzinsh and Ferber \(1995\)](#).

## 7.3 Axis Distributions of Linear Rotors

### 7.3.1 Basic Relations. States with Sharp $J$ and $M$

In the preceding section we have discussed molecular ensembles with an anisotropic distribution of angular momenta characterized in terms of states multipoles  $\langle T(J)_{KQ}^\dagger \rangle$ . Often, however, the distribution of the axes of rotating molecules is of primary interest. Consider, for example, inelastic or reactive scattering events. The collision time is often much shorter than the rotation time of the molecules. The incoming projectiles “see” therefore the instantaneous axis distribution of the molecules, and the “elementary” scattering event is a collision between a projectile and a molecule with fixed axis  $\mathbf{n}$ . In theoretical problems one has therefore first to calculate the cross section for the elementary collision, and then one has to take the average over the axes distribution. If the molecular target system has been prepared in states with an anisotropic  $\mathbf{J}$  distribution one has therefore to determine the corresponding axis distribution.

There is of course a close kinship imposed on the  $\mathbf{J}$  and  $\mathbf{n}$  distributions. Classically, the angular momentum of a rotating diatomic molecule is perpendicular to its internuclear axis  $\mathbf{n}$  (assuming that the molecule is in its electronic ground state). In quantum mechanics the relation between  $\mathbf{J}$  and  $\mathbf{N}$  is more complex particularly for small  $J$ . In this and the following subsection we will discuss this relation in some detail, concentrating on ensembles with sharp magnitudes  $J$  of the angular momentum. In Sect. 7.4 we will then consider ensembles without definite  $J$ . There exist important differences between those two cases and for this reason we will treat them separately.

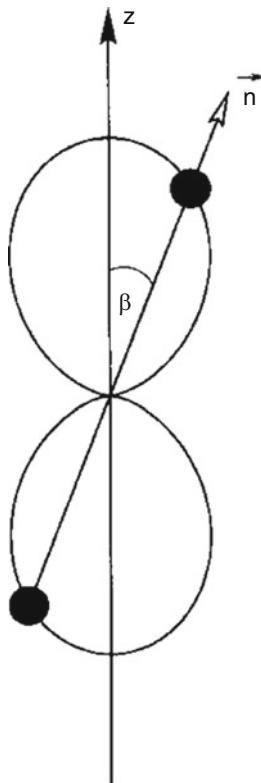
We will start by considering rigid rotor states  $|JM\rangle$  with sharp  $J$  and sharp  $M$ . The corresponding eigenfunction in coordinate representation are given by the corresponding spherical harmonic  $Y(\beta\alpha)_{JM}$ , where  $\beta$  and  $\alpha$  denote polar and azimuth angle of the molecular axis  $\mathbf{n}$  respectively with regard to a given coordinate system. From the usual probability interpretation of quantum mechanical wave functions it follows that the probability of finding a molecular axis pointing in the solid angle  $d\Omega = \sin\beta d\beta d\alpha$ , when the molecule is in the state  $|JM\rangle$ , is given by  $W(\beta\alpha) \sin d\beta d\alpha$  with

$$W(\beta\alpha) = |Y(\beta\alpha)_{JM}|^2 \quad (7.16)$$

We normalize according to

$$\int_0^{2\pi} d\alpha \int_0^\pi d\beta \sin\beta W(\beta\alpha) = 1 \quad (7.17)$$

**Fig. 7.2** Probability density for the axes distribution of linear rotors in states with  $J = 1, M = 0$



Hence, the axis distributions of linear rotors in states with sharp  $J$  and sharp  $M$  is given by (7.16), which is independent of the azimuth angle  $\alpha$ . For example, for  $J = 1$  and  $M = 0$ , we have

$$|Y(\beta\alpha)_{10}|^2 = \frac{3}{4\pi} \cos^2 \beta \quad (7.18)$$

This distribution is illustrated by the polar diagram in Fig. 7.2 where the arrow represents one possible direction of  $\mathbf{n}$ , and where the length of the arrow is proportional to the probability density  $|Y_{10}|^2$  of finding an axis under an angle  $\beta$  to  $z$ .

If  $J$  is increased then the axis distribution resembles more and more the classical case where any axis is confined to a plane perpendicular to  $\mathbf{J}$ . This can be shown by taking the semiclassical approximation of the spherical harmonics (see [Zare 1988](#), Chap. 1).

### 7.3.2 General Equations. Examples and Experimental Studies

We will now generalize our results and consider an ensemble of linear rotors with sharp  $J$  but different molecules may have different values of  $M$ . The ensemble will be characterized by the set of state multipoles  $\langle T(J)_{KQ}^\dagger \rangle$  with  $K \leq 2J$ . We will derive an expression for the probability density  $W(\beta\alpha)$ , describing the corresponding instantaneous axis distribution, and express it in terms of the state multipoles. The final result will then relate any anisotropy in the  $\mathbf{J}$  distribution to the corresponding anisotropy in the spatial distribution of axes.

Let  $\rho$  be the density operator describing the ensemble.  $\rho$  can be written in the form (4.29):

$$\rho = \sum_{M'M} \langle JM' | \rho | JM \rangle |JM' \rangle \langle JM | \quad (7.19)$$

We recall that, in abstract notation, the spherical harmonics are given by the scalar product

$$\langle \beta\alpha | JM \rangle = Y(\beta\alpha)_{JM} \quad (7.20)$$

where  $|\beta, \alpha\rangle$  represents a state with fixed axis  $\mathbf{n}$  pointing in the direction with polar angle  $\beta$  and azimuth  $\alpha$  with respect to a space-fixed coordinate system. Furthermore, we recall from Sect. 2.2 that the diagonal elements of  $\rho$  are probabilities [assuming the normalization (7.1)]; that is, the diagonal element  $\langle \beta\alpha | \rho | \beta\alpha \rangle$  is equal to the probability density of finding a molecule with internuclear axis  $\mathbf{n}$  pointing in the  $\beta, \alpha$  direction. Hence,

$$\langle \beta\alpha | \rho | \beta\alpha \rangle = W(\beta\alpha) \quad (7.21)$$

By “sandwiching” (7.19) between states  $|\beta\alpha\rangle$  and  $\langle \beta\alpha|$  we obtain

$$\begin{aligned} W(\beta\alpha) &= \sum_{M'M} \langle JM' | \rho | JM \rangle \langle \beta\alpha | JM' \rangle \langle JM | \beta\alpha \rangle \\ &= \sum_{M'M} \langle JM' | \rho | JM \rangle Y(\beta\alpha)_{JM'} Y(\beta\alpha)_{JM}^* \end{aligned} \quad (7.22)$$

where we used (7.20) and the corresponding equation for the complex conjugate expression. Application of the addition theorem of the spherical harmonics (C.22) yields

$$\begin{aligned} W(\beta\alpha) &= \frac{(-1)^J}{(4\pi)^{1/2}} \sum_{kq} \left[ \sum_{M'M} \langle JM' | \rho | JM \rangle (-1)^{J-M'} (2k+1)^{1/2} \begin{pmatrix} J & J & k \\ M' & -M & -q \end{pmatrix} \right] \\ &\quad \times (2J+1) \begin{pmatrix} J & J & k \\ 0 & 0 & 0 \end{pmatrix} Y(\beta\alpha)_{kq} \end{aligned}$$

Finally we insert (4.34) and express the density matrix elements in terms of the state multipoles  $\langle T(J)_{KQ}^\dagger \rangle$  which specify the angular momentum distribution

$$\langle JM' | \rho | JM \rangle = \sum_{KQ} (-1)^{J-M'} (2K+1)^{1/2} \begin{pmatrix} J & J & K \\ M' & -M & -Q \end{pmatrix} \langle T(J)_{KQ}^\dagger \rangle$$

and perform the sum over  $M, M'$  by applying (C.4b) and obtain finally (Dellen et al. 1994)

$$\bullet \quad W(\beta\alpha) = \frac{(-1)^J}{(4\pi)^{1/2}} \sum_{KQ} \langle T(J)_{KQ}^\dagger \rangle (2J+1) \begin{pmatrix} J & J & K \\ 0 & 0 & 0 \end{pmatrix} Y(\beta\alpha)_{KQ} \quad (7.23)$$

Equation 7.23 gives the relation between a given distribution of  $\mathbf{J}$  vectors (characterized by the set  $\langle T(J)_{KQ}^\dagger \rangle$ ) and the corresponding instantaneous axis distribution  $W(\beta\alpha)$ . It should be noted that the  $3j$  symbol in (7.23) vanishes for  $K$  odd because of the symmetry condition (C5c). Hence, *only multipoles with K even contribute to the probability density W(βα)*. We will discuss this result in detail in Sect. 7.4.2.

Let us consider some examples. An isotropic  $\mathbf{J}$  distribution ( $K = 0$ ) corresponds to an isotropic axis distribution  $W(\beta\alpha) = \text{constant}$ . The next simple case is an aligned distribution where, besides the monopole, only  $\langle T(J)_{20}^\dagger \rangle$  contributes. The corresponding axes distribution is obtained from (7.23) by inserting the explicit expressions for the  $3j$  symbols and the addition theorem (C.22) of the spherical harmonics. We obtain

$$W(\beta) = \frac{1}{4\pi} \left[ 1 + \frac{a}{2} (3 \cos^2 \beta - 1) \right] \quad (7.24)$$

where the “alignment parameter”  $a$  has been defined by

$$a = - \left( \frac{5J(J+1)(2J+1)}{(2J+3)(2J-1)} \right)^{1/2} \langle T(J)_{20}^\dagger \rangle \quad (7.25)$$

Let us consider the high- $J$  limit where the distribution of  $\mathbf{J}$  vectors can be considered to be continuous. Remembering that  $2J+1$  must be replaced by the full solid angle  $4\pi$  we obtain

$$a = -\frac{1}{2} \sqrt{20\pi} \langle T(J)_{20}^\dagger \rangle = -\frac{b}{2} \quad (7.26)$$

where  $b$  is the alignment parameter for the corresponding  $\mathbf{J}$  distribution given by (7.14).

The relation (7.26) allows us to compare the instantaneous axis distribution (7.24) with the corresponding distribution (7.13a) of the  $\mathbf{J}$  vectors. Both equations depend on the same multipole  $\langle T(J)_{20}^\dagger \rangle$ . Any alignment in the  $\mathbf{J}$  distribution is

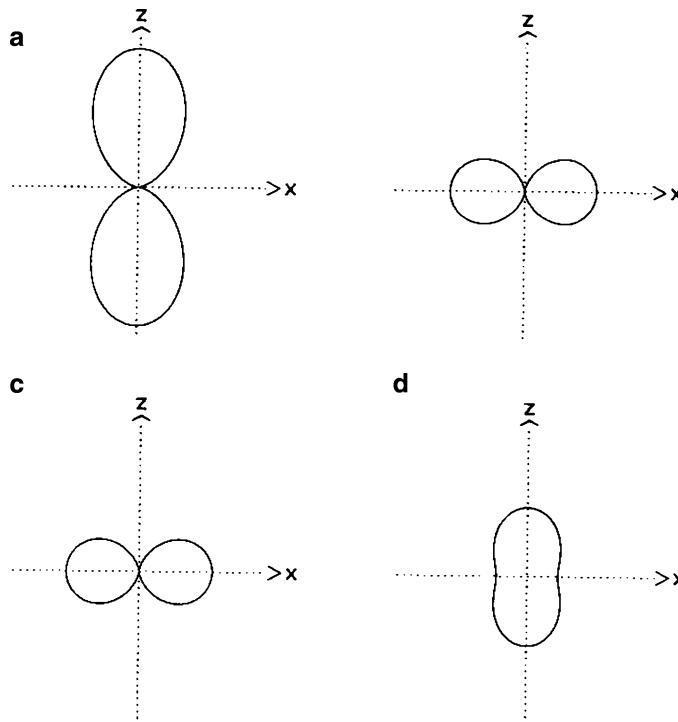
attenuated in the axes distribution, any alignment in the axes distribution produces an amplified alignment for the  $\mathbf{J}$  vectors.

Requiring  $0 \leq W(\beta) \leq 1$  for all  $\beta$  we obtain from (7.24) that the parameter  $a$  can in principle vary between the limits  $a = -1$  and  $a = 2$ . However, we have to take into account that the molecules are rotating, and that conditions (7.25) and (7.15) impose further restrictions on  $a$ . In the high- $J$  limit we obtain from relation (7.26) that  $a = -1$  for  $b = 2$  and  $a = 0.5$  for  $b = -1$ , hence

$$-1 \leq a \leq 0.5 \quad (7.27)$$

(It can be shown that the limit  $a = 2$  is only possible for  $J = 1$ .)

The negative sign in (7.26) reflects the fact that for high  $J$  the angular momentum  $\mathbf{J}$  is perpendicular to the axis  $\mathbf{n}$ . Compare, for example, (7.24) with the corresponding probability density  $W(\theta_J)$  specified by (7.13a). For  $b = 2$  we have  $a \cos^2 \theta_J$  distribution of angular momenta and  $a \sin^2 \beta$  distribution of axes



**Fig. 7.3** Schematic representation for the alignment of linear rotors in the high- $J$  limit: (a)  $\mathbf{J}$  distribution for  $b = 2$ ; (b) the corresponding axes distribution ( $a = -1$ ); (c)  $\mathbf{J}$  distribution for  $b = -1$ ; (d) corresponding axes distributions ( $a = 0.5$ ). All distributions are axially symmetric around  $Z$

(corresponding to  $a = -1$ ). The value  $b = -1$  gives  $W(\theta_J) \sim \sin^2 \theta_J$  and  $W(\beta) \sim 1 + \cos^2 \beta$ . These two cases are shown in Fig. 7.3.

Let us apply these results to molecular beams propagating along the  $z$  direction, and let us assume that the probability  $W(\theta_J)$  and  $W(\beta)$  are specified by (7.13a) and (7.24) respectively with  $b = 2$ ,  $a = -1$ . The axes are then rotating predominantly in the plane perpendicular to the flight direction (“propeller type”). For  $b = -1$  we have  $a = 0.5$  and the axes are aligned mainly in the direction of propagation. The rotation of the axes resembles that of a cartwheel (Aquilanti et al. 1991).

Considerable alignment has been found after scattering molecules off surfaces (both of the “propeller” and the “cartwheel” types). For example, in collisions between  $\text{N}_2$  and  $\text{Ag}(111)$  surfaces Sitz et al. (1987) found the  $\text{N}_2$  alignment to be more pronounced with increasing rotational excitation, approaching the limiting value of  $b = -1$  which corresponds to  $\mathbf{J}$  vectors perpendicular to  $z$  (with  $z$  being the normal to the surface). In the same experiments substantial values of the orientation parameter  $\langle T(J)_{10} \rangle$  and of the multipole  $\langle T(J)_{40} \rangle$  have also been found.

In supersonic expansions of alkali dimers values of  $b \approx -0.2$  to  $-0.4$  have been measured, indicating that  $\mathbf{J}$  is predominantly aligned perpendicular to  $z$  (beam direction). The rotation of the axes should then be predominantly of the “cartwheel” type. These results can qualitatively be explained in terms of a simple picture for the collisional mechanism in bulk media. Molecules rotating in a plane perpendicular to the flight direction present a target of larger cross section for collisions with other particles than molecules rotating in planes that contain the beam axis. Due to the differing cross sections molecules of the first category are therefore reoriented with higher probability than molecules with  $\mathbf{J}$  perpendicular to the beam axis. This results in a  $b < 0$  ( $a > 0$ ) alignment in the transmitted beam. For a detailed review we refer to Friedrich et al. (1991).

## 7.4 Order Parameters: General Description of Axis Orientation and Alignment

### 7.4.1 General Theory for Linear Molecules and Examples

In the preceding section we have discussed the axes distribution of rotating linear molecules with sharp  $J$ . However, there are different physical situations. Often one deals with molecular beams where different molecules may have different angular momenta  $J$ . There are other cases where the molecules are in coherent superposition states with respect to  $J$ . Furthermore, molecules might have been prepared in states with “axes fixed in space,” as is the case for molecules adsorbed at surfaces, or in stretched polymers. In these cases the anisotropic environment establishes a unique direction or directions in space, and the molecular axes distribution will exhibit orientation, or alignment, or both.

The formalism developed in the preceding subsection does not apply to these cases. We will therefore derive a more general description which will contain our previous results as a special case. Our results will also further illuminate the relation between  $\mathbf{J}$  and  $\mathbf{n}$  vectors. We will concentrate on diatomic molecules in their electronic ground state and discuss polyatomic molecules in Sect. 7.6.4.

In order to cover all the different situations mentioned above we will proceed as follows. The ensemble of diatomic molecules will be characterized in terms of a function  $W(\beta\alpha)$ . As before,  $W(\beta\alpha)$  will be the probability density of finding a molecule with an axis  $\mathbf{n}$  oriented within a range between  $\alpha$  and  $\alpha + d\alpha$  and  $\beta + d\beta$  with respect to a space-fixed coordinate system.  $\beta$  is the polar angle and  $\alpha$  the azimuth of  $\mathbf{n}$ . We will normalize according to condition (7.17).  $W(\beta\alpha)$  may characterize a fixed-axes distribution (for example, molecules at surfaces) or it may describe the instantaneous  $\mathbf{n}$  distribution of rotating molecules.

Since the spherical harmonics form a complete set any function of  $\beta$  and  $\alpha$  can be expanded in terms of these functions. Hence, we can always write

$$\bullet \quad W(\beta\alpha) = \sum_{KQ} \langle Y_{KQ}^* \rangle Y(\beta\alpha)_{KQ} \quad (7.28)$$

with  $-K \leq Q \leq K$ . In general no upper limit of  $K$  can be given.

The expansion coefficients  $\langle Y_{KQ}^* \rangle \equiv \langle Y(\beta\alpha)_{KQ}^* \rangle$  are often called “order parameters” and have been used extensively for studying various anisotropic systems, e.g., in polymers (Michl and Thulstrup 1986, and refs. therein). They are obtained from the distribution function by the relation

$$\bullet \quad \langle Y_{KQ}^* \rangle = \int_0^{2\pi} d\alpha \int_0^\pi d\beta \sin \beta W(\beta\alpha) Y(\beta\alpha)_{KQ}^* \quad (7.29)$$

which is obtained by multiplying (7.28) by  $Y(\beta\alpha)_{K'Q'}^*$ , integrating both sides over all angles, and using the orthogonality property (C23) of the spherical harmonics. We normalize according to (7.17), which gives

$$\langle Y_{00} \rangle = \frac{1}{\sqrt{4\pi}} \quad (7.30)$$

for the monopole.

From (7.29) we can read off the basic properties of the order parameters by using the symmetry properties (C21) of the spherical harmonics:

1. Order parameters with  $Q = 0$  are real.
2.  $\langle Y_{KQ}^* \rangle = \langle Y_{KQ} \rangle^*$  [where  $\langle Y_{KQ} \rangle$  is defined by (7.29) with  $Y_{KQ}$  substituted for  $Y_{KQ}^*$ ].
3.  $\langle Y_{K-Q}^* \rangle = (-1)^Q \langle Y_{KQ} \rangle$ .

Equation 7.29 shows explicitly that the order parameters  $\langle Y_{KQ}^* \rangle$  are the mean values of the corresponding functions  $Y(\beta\alpha)_{KQ}$ . For example, for  $K = 1$ , we obtain

$$\langle Y_{10} \rangle = \left( \frac{3}{4\pi} \right)^{1/2} \langle \cos \beta \rangle \quad (7.31a)$$

where the mean value  $\langle \cos \beta \rangle$  provides us with an effective average orientation angle  $\beta$  between the molecular axes and  $z$ .

As a simple example consider the distribution

$$\begin{aligned} W(\beta\alpha) &= \langle Y_{00} \rangle Y_{00} + \langle Y_{10} \rangle Y(\beta)_{10} \\ &= \frac{1}{4\pi} \left[ 1 + \sqrt{12\pi} \langle Y_{10} \rangle \cos \beta \right] \end{aligned} \quad (7.31b)$$

which is independent of  $\alpha$  and where  $\langle Y_{10} \rangle$  can vary within limits determined by the condition  $0 \leq W(\beta) \leq 1$ . If  $\langle Y_{10} \rangle > 0$  is positive then more molecules have axes pointing in the  $z$  direction than pointing in the opposite direction, and vice versa for negative  $\langle Y_{10} \rangle$ . Hence, the distribution shows a “head-versus-tail” distinction.

Another simple case is described by the expression

$$\begin{aligned} W(\beta\alpha) &= \langle Y_{00} \rangle Y_{00} + \langle Y_{20} \rangle Y(\beta)_{20} \\ &= \frac{1}{4\pi} \left[ 1 + (20\pi)^{1/2} \langle Y_{20} \rangle \frac{1}{2} (3 \cos^2 \beta - 1) \right] \end{aligned} \quad (7.32)$$

The distribution (7.32) is axially symmetric without head-versus-tail distinction; that is, an equal number of molecules is pointing in the  $z$  and  $-z$  directions. If  $\langle Y_{20} \rangle$  is positive then more molecular axes are aligned parallel to  $z$  than perpendicular to  $z$ , and the opposite result holds for negative  $\langle Y_{20} \rangle$  (“end-on” and “broadside” alignment respectively).

In general, we will call an axis distribution *aligned* if at least one order parameter with  $K$  even (and  $K \neq 0$ ) contributes to the expansion (7.28), and *oriented* if at least one order parameter with  $K$  odd is nonvanishing. The system will be called *polarized*, or simply *anisotropic*, if at least one order parameter with  $K \neq 0$  contributes to (7.28). Simple examples of an oriented and an aligned distribution are given by (7.31b) and (7.32) respectively.

The parameters  $\langle Y_{KQ}^* \rangle$  play the same role in characterizing axes distributions as the state multipole  $\langle T(J)_{KQ}^\dagger \rangle$  in characterizing  $\mathbf{J}$  distributions. In fact, from the tensor properties of the spherical harmonics (Zare 1988) it follows that *the order parameter  $\langle Y_{KQ} \rangle$  transforms as tensors of rank  $K$  and component  $Q$ ; that is, (4.41) applies*.

The use of the order parameters is particularly convenient for characterizing the symmetry properties of an axes distribution. We list the main results:

1. If the axes are randomly distributed in space then all order parameters with  $K \neq 0$  vanish.

2. Assume that the distribution is axially symmetric with respect to the  $z$  axis. This means that  $W(\beta\alpha)$  must be independent of  $\alpha$ . The directional correlation between  $\mathbf{n}$  and  $z$  is then specified by the polar angle  $\beta$ . Consequently, only those spherical harmonics can contribute to (7.28) which are independent of  $\alpha$ ; that is, only terms with  $Q = 0$ . In this case the probability density can be expressed in terms of Legendre polynomials  $P_K(\cos \beta)$ . We write

$$W(\beta\alpha) = \frac{1}{2\pi} W(\beta)$$

normalizing according to

$$\int_0^\pi d\beta \sin \beta W(\beta) = 1 \quad (7.33a)$$

and obtain

$$\begin{aligned} \bullet \quad W(\beta) &= 2\pi \sum_K \langle Y_{K0} \rangle Y(\beta)_{K0} \\ &= \frac{1}{2} \sum_K (2K + 1) \langle P_K(\cos \beta) \rangle P_K(\cos \beta) \end{aligned} \quad (7.33b)$$

Here  $P_K(\cos \beta)$  are Legendre polynomials with the mean values

$$\langle P_K(\cos \beta) \rangle = \left( \frac{4\pi}{2K + 1} \right)^{1/2} \langle Y_{K0} \rangle \quad (7.33c)$$

In particular,  $\langle P_0 \rangle = 1$ ,  $\langle P_1 \rangle = \langle \cos \beta \rangle$  (which is the average orientation angle between  $z$  and the molecular axes), and  $\langle P_2 \rangle = \langle \frac{1}{2}(3\cos^2 \beta - 1) \rangle$ . If only  $K$  values with  $K \leq 2$  contribute to (7.33b) then maximal end-on alignment yields  $\langle P_2(\cos \beta) \rangle = 1$ , and maximal broad side alignment corresponds to  $\langle P_2(\cos \beta) \rangle = -\frac{1}{2}$ . For the case of perfect orientation along  $z$   $\langle P_K(\cos \beta) \rangle = 1$  for all  $K$  in general.

3. Finally, consider an axially symmetric system which is invariant against reversal of the  $z$  axes:  $z \rightarrow -z$ . The corresponding distribution function must then satisfy the symmetry condition  $W(\beta) = W(\pi - \beta)$ . Since  $Y(\pi - \beta)_{K0} = (-1)^K Y(\beta)_{K0}$  it follows that all parameters  $\langle Y_{K0} \rangle$  with  $K$  odd must vanish in (7.33b).

Such a situation occurs, for example, after absorption of linearly polarized light where the electric vector defines an axis but no direction (because of its rapid oscillation), or if the molecules themselves have a nonpolar shape. Examples are given in Sect. 7.5.

### 7.4.2 Relation Between Angular Momenta and Axis Distributions for Linear Rotors. “Pendulum States”

Equations 7.28–7.33a apply to a variety of cases. They describe an instantaneous axes distribution of rotating linear molecules, and they can be used to analyze molecular ensembles with axes fixed in space. In particular, the results of Sect. 7.3.2 are contained in our present equations as special cases. We will show this in some detail in order to further illuminate the relation between  $\mathbf{n}$  and  $\mathbf{J}$  distributions for rotating molecules. Assuming that all molecules have the same  $J$  value then (7.23) applies. Comparison of (7.23) and (7.28) yields the relation

- $$\langle Y_{KQ}^* \rangle = \frac{(-1)^J}{(4\pi)^{1/2}} (2J+1) \begin{pmatrix} J & J & K \\ 0 & 0 & 0 \end{pmatrix} \langle T(J)_{KQ}^\dagger \rangle \quad (7.34)$$

Relation (7.34) shows that the order parameters characterizing the  $\mathbf{n}$  distribution are proportional to the corresponding state multipoles which describe the  $\mathbf{J}$  distribution. Hence, the  $K$  summation in (7.28) runs from  $K = 0$  to  $K = 2J$  if the molecules have sharp  $J$ .

Equation 7.34 takes on a very simple form in the semiclassical limit particularly for axially symmetric systems. Substituting (7.3c), (7.9), and (7.33c) into (7.34) and remembering that in the continuum limit we have to replace  $2J+1$  by  $4\pi$ , we obtain

- $$\langle P_K(\cos \beta) \rangle = P_K(0) \langle P_K(\cos \theta_J) \rangle \quad (7.35a)$$

This equation relates the directional correlation between  $\mathbf{J}$  and  $z$  [expressed by  $\langle P_K(\cos \theta_J) \rangle$ ] to the correlation between  $\mathbf{n}$  and  $z$  [expressed by  $\langle P_K(\cos \beta) \rangle$ ]. In particular, for  $K = 2$ , we obtain  $\langle P_2(\cos \beta) \rangle = -\frac{1}{2} \langle P_2(\cos \theta_J) \rangle$ , which should be compared with (7.26).

It should be noted that the  $3j$  symbol in (7.34) [and  $P(0)_K$  in (7.35a)] vanishes for  $K$  odd. It follows that *the axes distribution of linear rotors cannot be oriented, even if the corresponding J distribution exhibits orientation*. This can be explained in terms of a classical picture. Since  $\mathbf{n}$  is perpendicular to  $\mathbf{J}$ , and because of the rotation of  $\mathbf{n}$  around  $\mathbf{J}$ , any orientation of the axes averages out. In particular, the mean value of the electric dipole moment of rotating polar linear molecules is zero.

The situation is different for symmetric-top molecules, as will be discussed in Sect. 7.6.2. However even for linear rotors there are exceptions. Experiments have demonstrated the feasibility of orienting the axes of rotationally cooled molecules, for example in electric fields, if the molecules are trapped in “pendular states,” confined to librate over a limited angular range about the field direction (see [Loesch and Remscheid 1990](#); [Friedrich et al. 1991](#) for a review). These pendulum-like states are “directed states” corresponding to linear superpositions of rotor states  $|JM\rangle$  with different  $J$  ([Kais and Levine 1987](#)).

In order to discuss directed states in our formalism we generalize (7.34). Coherent superposition states are described by state multipoles  $\langle T(J'J)_{KQ}^\dagger \rangle$  defined in (4.31). Repeating the steps leading to (7.34) we obtain relations of the following form:

$$\bullet \quad \langle Y_{KQ}^* \rangle = \sum_{J'J} \frac{(-1)^{J'}}{(4\pi)^{1/2}} [(2J+1)(2J'+1)]^{1/2} \begin{pmatrix} J' & J & K \\ 0 & 0 & 0 \end{pmatrix} \langle T(J'J)_{KQ}^\dagger \rangle \quad (7.35b)$$

Inspection of the symmetry condition (C5c) yields the result that the  $3j$  symbol is different from zero even for  $K$  odd if  $J' + J$  is odd. Hence, *axes orientation of molecules in “pendulum states” is possible if at least one multipole  $\langle T(J'J)_{KQ}^\dagger \rangle$  with  $K$  odd and  $J' + J$  odd is nonvanishing.*

This result has important consequences for attempts to orient molecules in electric fields  $\mathbf{E}$ . For linear rotors the symmetry arguments of Sect. 4.68 apply and no orientation of  $\mathbf{J}$  can be achieved. In particular,  $\langle T(J)_{10}^\dagger \rangle \sim \langle J_z \rangle = 0$ . This result can also be understood in the following way. Assume that the initial molecular ensemble is isotropic. The electric field  $\mathbf{E}$  transforms as a polar vector. The total system must therefore remain invariant under reflections in any plane containing  $\mathbf{E}$ . Since the axial vector component, such as  $\langle J_z \rangle$ , would change sign under this operation, it must vanish.

However, the electric field mixes states with different  $J$  (see, for example, [Loesch and Remscheid 1990](#); [Friedrich and Herschbach 1991](#)) and the molecular states in the field can be written as linear superpositions of states with different  $J$ . The corresponding set of state multipoles is given by all relevant parameters  $\langle T(J'J)_{KQ}^\dagger \rangle$ , where now multipoles with  $J' \neq J$  occur in addition to those with sharp  $J$ . The parameters  $\langle T(J'J)_{KQ}^\dagger \rangle$ , with  $J' + J$  odd transform as *polar* vectors. [This follows because rotor states  $|JM\rangle$  have parity  $(-1)^J$ , which implies parity  $(-1)^{J'+J}$  for the tensor operators (4.3).] Production of polar vectors like  $\langle T(J'J)_{10}^\dagger \rangle$  by electric fields is not forbidden. Hence, because of (7.35b), the axes distribution of the molecules can exhibit orientation.

## 7.5 Angular Momenta and Axis Distributions of Rotors after Photoabsorption. Quantum Mechanical and Classical Theory

### 7.5.1 Absorption of Linearly Polarized Light

In order to illustrate the general results given in the preceding sections we will consider an explicit example. An isotropic ensemble of diatomic molecules will be excited by optical pumping with linearly polarized laser light. The direction of the electric vector  $\mathbf{E}$  of the light will be chosen as the  $z$  axis of the laboratory system.

Let us assume that the laser is tuned to a particular transition, for example from the vibrational ground state  $v_0 = 0$  and rotational state  $J_0$  to a state with  $v_0 = 1$  and angular momentum  $J$ . We will calculate the state multipoles and the axes distribution of the excited molecules.

The density matrix of the initial isotropic molecular ensemble is given by an expression similar to (2.24):

$$\rho_{in} = \frac{1}{2J_0 + 1} \sum_{M_0} |J_0 M_0\rangle \langle J_0 M_0| \quad (7.36)$$

where we have suppressed the dependence on the vibrational quantum numbers for brevity. The final density matrix  $\rho_{out}$  follows then from the general equation (E.5). The transition operator for interacting with the  $z$  direction polarized light is (in dipole approximation) given by  $T \sim d_z$  where  $d_z$  is the dipole operator, and it follows that

$$\rho_{out} = A(\omega) d_z \rho_{in} d_z \quad (7.37)$$

where  $A(\omega)$  is a numerical factor. By inserting (7.36) into (7.37) and taking matrix elements we obtain

$$\langle J' M' | \rho_{out} | J M \rangle = \frac{A(\omega)}{2J_0 + 1} \sum_{M_0} \langle J' M' | d_z | J_0 M_0 \rangle \langle J M | d_z | J_0 M_0 \rangle^* \quad (7.38)$$

$d_z$  transforms as tensor of rank 1 and component zero. Applying the Wigner-Eckhard theorem (C.19) we obtain

$$\langle J' M' | \rho_{out} | J M \rangle = \delta_{M' M} \frac{A(\omega)}{2J_0 + 1} \langle J \| d \| J_0 \rangle^2 \sum_{M_0} \begin{pmatrix} J & 1 & J_0 \\ -M & 0 & M_0 \end{pmatrix}^2 \quad (7.39)$$

The trace is given by

$$tr \rho_{out} = \frac{A(\omega)}{3(2J_0 + 1)} \langle J \| d \| J_0 \rangle^2 \quad (7.40)$$

where we have applied (C.4b).

We will now calculate the relevant state multipoles which (semiclassically) describe the distribution of the angular momentum vectors. In order to ensure the normalization (7.1) we define a normalized matrix

$$\rho = \frac{\rho_{out}}{tr \rho_{out}} \quad (7.41)$$

and obtain normalized multipoles from the definition (4.31)

$$\left\langle T(J) \right\rangle_{KQ}^\dagger = \sum_M (-1)^{J-M} (2K+1)^{1/2} \begin{pmatrix} J & J & K \\ M & -M & 0 \end{pmatrix} \langle J M | \rho | J M \rangle \quad (7.42a)$$

The tensors with  $Q \neq 0$  vanish since  $\rho_{\text{in}}$  and  $\rho_{\text{out}}$  are diagonal. Substitution of (7.39), 7.40, and (7.41) yields

$$\langle T(J)_{KQ}^\dagger \rangle = 3(2K+1)^{1/2} \sum_{M M_0} (-1)^{J-M} \begin{pmatrix} J & J & K \\ M & -M & 0 \end{pmatrix} \begin{pmatrix} J & 1 & J_0 \\ -M & 0 & M_0 \end{pmatrix}^2$$

and application of relation (C9) yields finally

- $\langle T(J)_{KQ}^\dagger \rangle = 3(2K+1)^{1/2} (-1)^{J-J_0} \begin{pmatrix} 1 & 1 & K \\ 0 & 0 & 0 \end{pmatrix} \begin{Bmatrix} 1 & 1 & K \\ J & J & J_0 \end{Bmatrix}$  (7.43)

From the symmetry properties (C5) of the  $3j$  symbol it follows that only multipoles with  $K = 0$  and  $K = 2$  contribute. Hence, only alignment can be produced by absorption of linearly polarized light, and the alignment parameter is given by the expression

- $\langle T(J)_{20} \rangle = (6)^{1/2} (-1)^{J-J_0} \begin{Bmatrix} 1 & 1 & 2 \\ J & J & J_0 \end{Bmatrix}$  (7.44)

Inserting the numerical value of the  $6j$  symbol into (7.44) we obtain for  $P$ -and  $R$ -type transitions for  $J_0 \gg 1$ , corresponding to  $J = J_0 - 1$  and  $J = J_0 + 1$  respectively,

$$\langle T_{20} \rangle = - \left( \frac{1}{20\pi} \right)^{1/2} \quad (7.45a)$$

where the continuum limit has been taken. Application of (7.9) yields

$$\langle P_2(\cos \theta_J) \rangle = -\frac{1}{5}$$

and (7.10) reduces then to the expression

$$W(\theta_J) = \frac{3}{8\pi} \sin^2 \theta_J \quad (7.45b)$$

This result shows that, in the classical limit, molecules with  $\mathbf{J}_0$  perpendicular to the electric vector  $\mathbf{E}$  will be preferentially excited.

The corresponding order parameters, describing the angular distribution of the axes of the excited molecules, follow from the general (7.34). The only nontrivial nonvanishing parameter is the alignment parameter

- $\langle Y_{20} \rangle = \left( \frac{6}{4\pi} \right)^{1/2} (-1)^{J_0} (2J+1) \begin{pmatrix} J & J & 2 \\ 0 & 0 & 0 \end{pmatrix} \begin{Bmatrix} 1 & 1 & 2 \\ J & J & J_0 \end{Bmatrix}$  (7.46)

and the corresponding axis distribution is axially symmetric with respect to  $z$ :

- $$W(\beta\alpha) = \langle Y_{00} \rangle Y_{00} + \langle Y_{20} \rangle Y(\beta)_{20} \\ = \frac{1}{4\pi} \left[ 1 + \frac{a}{2} (3 \cos^2 \beta - 1) \right] \quad (7.47)$$

with

$$a = \sqrt{20\pi} \langle Y_{20} \rangle \quad (7.48a)$$

Equation 7.47 characterizes the angular distribution of axes when a rigid rotor (e.g., a diatomic molecule in a  $\Sigma$  state) absorbs plane polarized light. By substituting explicit expressions for  $3j$  and  $6j$  symbols in (7.46) the values of the alignment parameter can be obtained for the  $P$  and  $R$  branches (Zare 1982).

Equation 7.47 can be recast in the form

$$W(\beta\alpha) = \frac{1}{4\pi} [a' \cos^2 \beta + b' \sin^2 \beta] \quad (7.49)$$

with

$$a' = 1 + a, \quad b' = 1 - \frac{a}{2}$$

If the initial molecules are not rotating ( $J_0 = 0, J = 1$ ) we obtain, with the help of (7.46),  $a = 2$  and  $W(\beta\alpha) = (3/4\pi) \cos^2 \beta$ . The axes distribution peaks along the  $\mathbf{E}$  vector of the light; that is, molecules with axes parallel to  $\mathbf{E}$  are preferentially excited. If the molecules are rotating ( $J_0 \neq 0$ ), then the  $\sin^2 \beta$  term contributes to  $W(\beta)$ . In the classical limit  $J_0 \gg 1$  we find from (7.46) that  $a = \frac{1}{2}$  and

$$W(\beta\alpha) = \frac{3}{16\pi} [1 + \cos^2 \beta] \quad (7.50)$$

### 7.5.2 Absorption of Circularly Polarized and Unpolarized Light

We will now consider absorption of circularly polarized light, or of radiation with definite helicity  $\lambda = +1$  or  $\lambda = -1$ . As discussed in Sect. 1.54,  $\lambda = +1$  ( $\lambda = -1$ ) refers to photons with spin parallel (antiparallel) to the direction of propagation. In the optical convention states with positive (negative) helicity correspond to left-handed (right-handed) circularly polarized light. The corresponding polarization vector  $\mathbf{e}$  is given by (1.59), and the transition operator for absorption is  $T \sim \mathbf{e}_\lambda \cdot \mathbf{d}^* = d_\lambda$  [see (5.10) for the corresponding expression  $T \sim \mathbf{e}_\lambda^* \cdot \mathbf{d}$  for emission processes]. In this subsection we will choose the propagation direction of the light as the  $z$  axis.

We again assume an isotropic initial ensemble specified by (7.36). The density matrix  $\rho_{\text{out}}$  describing the excited molecules is given by

$$\rho_{\text{out}} = A(\omega) d_\lambda \rho_{\text{in}} d_\lambda^*$$

for absorption of light with sharp helicity  $\lambda$ .

Repeating essentially the same steps as in Sect. 7.5.1 we obtain for the nonvanishing normalized state multipoles characterizing the excited ensemble:

- $\left\langle T(J)_{KQ}^\dagger \right\rangle_c = 3(2K+1)^{1/2}(-1)^{J+J_0+1} \begin{Bmatrix} 1 & 1 & K \\ -\lambda & \lambda & 0 \end{Bmatrix} \begin{Bmatrix} 1 & 1 & K \\ J & J & J_0 \end{Bmatrix}$  (7.51)

where the index  $c$  refers to excitation by circularly polarized light. From the properties of the  $3j$  and  $6j$  symbols it follows that only multipoles with  $K = 0$ ,  $K = 1$ , and  $K = 2$  contribute. Note that orientation can be achieved in contrast to excitation by linearly polarized light. This is in accordance with the general symmetry considerations exploited in Sect. 4.68.

Comparing the values of the  $3j$  symbols, occurring in (7.43) and (7.51), we obtain for the alignment parameter

$$\left\langle T(J)_{20}^\dagger \right\rangle_c = -\frac{1}{2} \left\langle T(J)_{20}^\dagger \right\rangle \quad (7.52)$$

where  $\left\langle T(J)_{20}^\dagger \right\rangle$  is given by (7.44). Note that the quantization axes are different in both cases.

Substitution of the value of the  $3j$  symbol into (7.51) yields for the orientation parameter for  $\lambda = +1$ :

$$\left\langle T(J)_{10}^\dagger \right\rangle_c = \frac{3}{2^{1/2}} (-1)^{J-J_0} \begin{Bmatrix} 1 & 1 & 1 \\ J & J & J_0 \end{Bmatrix} \quad (7.53)$$

and for  $\lambda = -1$  we obtain (7.53) with the opposite sign.

For  $J_0 \gg 1$ , and taking the limit of a continuous distribution of angular momentum vectors, we obtain from (7.53):

$$\left\langle T(J)_{10}^\dagger \right\rangle_c = -\frac{1}{2} \left( \frac{3}{4\pi} \right)^{1/2} \quad (7.54a)$$

for a  $P$  transition ( $J = J_0 - 1$ ) and

$$\left\langle T(J)_{10}^\dagger \right\rangle_c = +\frac{1}{2} \left( \frac{3}{4\pi} \right)^{1/2} \quad (7.54b)$$

for an  $R$  transition ( $J = J_0 + 1$ ). The signs are inverted for excitation by light with negative helicity.

The results (7.54) show that, in the classical limit, molecules with angular momentum parallel to the propagation direction of the light will be preferentially excited in an  $R$  transition. In a  $P$  transition the orientation is negative; that is, molecules with  $\mathbf{J}$  antiparallel to the propagation direction will be predominantly excited. In order to interpret these results consider an  $R$  transition. With  $\lambda = +1$  and  $J_0$  parallel to  $z$ , the sense of rotation of the electric vector and that of the molecule coincide. The angular momentum  $\lambda$  is transferred to the molecule, and its angular momentum must increase. For  $\mathbf{J}_0$  antiparallel to  $z$ , the field vector and molecule rotate in opposite directions, and absorption of light of positive helicity would decrease the molecular angular momentum. Classically, an  $R$  transition of molecules with angular momentum antiparallel to  $Z$  therefore cannot take place if  $\lambda = +1$ . Hence, molecules with  $\mathbf{J}$  parallel to  $z$  will be predominantly excited and  $\langle T(J)_{10} \rangle$  is positive as shown by (7.54b). Similarly, the result for a  $P$  transition can be interpreted as can the results for  $\lambda = -1$ .

Let us further pursue the classical discussion and calculate the  $\mathbf{J}$  distribution. Equations 7.9, (7.54), (7.52), and (7.45a) yield

$$\langle P_1(\cos \theta_J) \rangle_c = \pm \frac{1}{2}$$

where the upper (lower) sign holds for  $R(P)$  transition, and

$$\langle P_2(\cos \theta_J) \rangle_c = \frac{1}{10}$$

for both transitions. Substitution into (7.10) yields the distribution function of the angular momentum vectors of the excited molecules:

$$W(\theta_J) = \frac{3}{6\pi} (1 \pm \cos \theta_J)^2 \quad (7.55)$$

Hence,  $W(\theta_J)$  vanishes for  $\theta_J = \pi$  for an  $R$  transition which is in accordance with the semiclassical interpretation given above. The signs are inverted for  $\lambda = -1$ . Let us now consider the axis distribution of the excited molecules. From (7.34) we obtain  $\langle Y_{10} \rangle_c = 0$ , and from (7.52)

$$\langle Y_{20} \rangle_c = -\frac{1}{2} \langle Y_{20} \rangle$$

where  $\langle Y_{20} \rangle$  is given by (7.46). Hence, although the  $\mathbf{J}$  distribution exhibits orientation, the axis distribution is only aligned as discussed in Sect. 7.4.2. The corresponding probability density is given by the relation

$$W(\beta\alpha) = \frac{1}{4\pi} \left[ 1 - \frac{a}{4} (3 \cos^2 \beta - 1) \right] \quad (7.56)$$

where  $a$  is defined in (7.48a).

The results for unpolarized light are obtained by averaging the results for  $\lambda = +1$  and  $\lambda = -1$ . The orientation vector cancels and only the alignment survives. The relevant parameters can be calculated from the general expression (7.51) for  $P$  and  $R$  transitions and from (7.46).

For a more detailed development of the classical theory we refer to the book by [Auzinsh and Ferber \(1995\)](#).

## 7.6 Distribution Functions for Nonlinear Molecules and for Diatomics with Electronic Angular Momentum

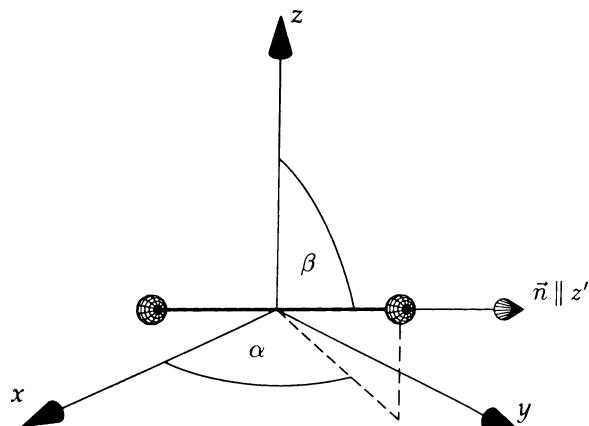
### 7.6.1 Molecular Orientation Euler Angles

We will now generalize the results of the preceding sections to nonlinear molecules. At first we will concentrate on symmetric tops, that is, on molecules having at least a threefold rotation axis. Two of the moments of inertia are equal and different from the third. Examples include  $\text{NH}_3$  and  $\text{CH}_3\text{Cl}$ .

As before we will denote the space-fixed coordinate system (laboratory system) by  $xyz$ , and we choose a right-handed rectangular coordinate system  $x'y'z'$  to be connected rigidly with the molecular framework.  $Z'$  will always be assumed to coincide with the principal symmetry axis of the molecule.

The mutual orientation of the  $x'y'z'$  axes with respect to the laboratory system will be specified by the three Euler angles  $\alpha$ ,  $\beta$ ,  $\gamma$  introduced in Sect. 4.2. Here,  $\beta$  and  $\alpha$  fix the spatial orientation of  $z'$ :  $\beta$  is the angle between  $z$  and  $z'$ , and  $\alpha$  the azimuth angle of  $z'$  with respect to the space-fixed system (see Fig. 7.4). The third Euler angle  $\gamma$  specifies a rotation of the  $x' - y'$  plane around  $z'$ .

In order to bring a molecule into an orientation described by  $\alpha\beta\gamma$ , one first aligns it so that the  $x'y'z'$  axes coincide pairwise with  $xyz$ . One then performs three



**Fig. 7.4** Orientation of a diatomic molecule in the space-fixed system  $x, y, z$ . The  $x'$  axis of the molecular system is perpendicular to  $z'$  and lies within the  $z - z'$  plane corresponding to  $\gamma = 0$

successive rotations of the molecule. The first rotation is by angle  $\alpha$  around  $z'$  (which at this point still coincides with  $z$ ). The second rotation is by angle  $\beta$  around  $y'$ . These two operations bring  $z'$  into a position with polar angle  $\beta$  and azimuth  $\alpha$ , the position of  $x'$  is specified by  $\beta + \pi/2$  and azimuth  $\phi$  ( $x'$  lies in the  $z - z'$  plane), and  $y'$  has polar angle  $\pi/2$  and azimuth  $\phi + \pi/2$ . The  $x' - y'$  plane is finally rotated by angle  $\gamma$  around  $z'$ .  $\gamma$  is therefore the angle by which  $x'$  is rotated out of the  $z - z'$  plane. In the special case of diatomic molecules the angle  $\gamma$  can be chosen arbitrarily because of the axial symmetry of the molecule. Commonly,  $\gamma$  is chosen to be zero, and we will adopt this convention but this must be made consistent for both the electronic and rotational parts of the wave function. It should be noted that  $\gamma = 0$  implies that the molecular  $x'$  axis always lies in the  $z - z'$  plane as described above. For example, for  $\beta = \pi/2$  the  $x'$  axis lies along the negative  $z$  axis of the space-fixed system. The spatial orientation of electronic orbitals must be defined in accordance with this choice (see Sect. 7.7).

### 7.6.2 Angular Momentum and Axis Distributions of Symmetric Tops

In the present section we will study symmetric-top molecules with sharp angular momentum  $J$ .  $M$  is the projection of  $J$  on the space-fixed  $z$  axis, and the projection of  $J$  on the principal molecular symmetry axis  $z'$  will be denoted by  $\Omega$ . The corresponding state vectors will be denoted by  $|\Omega JM\rangle$ . In coordinate representation the rotational wave function is proportional to the corresponding rotation matrix element:

$$\psi_{\Omega JM} = \left( \frac{2J+1}{8\pi^2} \right)^{1/2} D(\gamma\beta\alpha)_{\Omega M}^{(J)} \quad (7.57)$$

The physical interpretation of this wave function follows from its quantum mechanical probability interpretation and is similar to (7.16): The probability of finding a molecule with  $x'y'z'$  axes fixed by the angles  $\alpha\beta\gamma$ , when the molecule is in a state  $|\Omega JM\rangle$ , is given by

$$W(\gamma\beta\alpha) = \frac{2J+1}{8\pi^2} \left| D(\gamma\beta\alpha)_{\Omega M}^{(J)} \right|^2 d\gamma \sin \beta d\beta d\alpha \quad (7.58a)$$

The probability (7.58a) is in this case independent of  $\alpha$  and  $\gamma$  as follows from the explicit representation (C.12). The wave function (7.57) reduces to the corresponding spherical harmonic if  $\Omega = 0$  as follows from (C.16b).

We will now generalize to molecular ensembles with sharp  $J$  and sharp  $\Omega$  but different molecules may have different  $M$  values or be in arbitrary coherence states. We define state multipoles similar to (4.31), assuming the normalization (7.1):

$$\left\langle T(J)_{K\Omega}^{\dagger} \right\rangle = \sum_{M'M} (-1)^{J-M'} (2K+1)^{1/2} \begin{pmatrix} J & J & K \\ M' & -M & -\Omega \end{pmatrix} \langle \Omega JM' | \rho | \Omega JM \rangle \quad (7.59)$$

where  $\rho$  is the corresponding density matrix, and where we have suppressed the dependence of the state multipoles on the fixed value of  $\Omega$ .

We will denote by  $W(\gamma\beta\alpha)$   $d\gamma \sin \beta d\beta d\alpha$  the probability of finding a molecule with  $x'y'z'$  axes in the region of orientations  $\alpha \cdots \alpha + d\alpha$ ,  $\beta \cdots \beta + d\beta$ ,  $\gamma \cdots \gamma + d\gamma$  with respect to the  $xyz$  system as explained in the preceding subsection. An integral over all possible values of  $\alpha$ ,  $\beta$ ,  $\gamma$  must be equal to 1; that is,

$$\int_0^{2\pi} d\gamma \int_0^\pi d\beta \sin \beta \int_0^{2\pi} d\alpha W(\gamma\beta\alpha) = 1 \quad (7.60)$$

The distribution function  $W(\gamma\beta\alpha)$  can be related to the state multipoles (7.59), characterizing the angular momentum distribution, by applying essentially the same procedure as in Sect. 7.3. We start with the expression for the density operator

$$\rho = \sum_{M'M} \langle \Omega JM' | \rho | \Omega JM \rangle | \Omega JM' \rangle \langle \Omega JM | \quad (7.61)$$

and write the  $D$  matrices as scalar products:

$$\langle \gamma\beta\alpha | \Omega JM \rangle = \left( \frac{2J+1}{8\pi^2} \right)^{1/2} D(\gamma\beta\alpha)_{\Omega M}^{(J)} \quad (7.62a)$$

Here,  $|\gamma\beta\alpha\rangle$  is a “directed state” with fixed molecular axes specified by the three Euler angles. “Sandwiching” (7.61) between states  $\langle \gamma\beta\alpha |$  and  $|\gamma\beta\alpha\rangle$  and substituting (7.62a) we obtain

$$\begin{aligned} W(\gamma\beta\alpha) &= \langle \gamma\beta\alpha | \rho | \gamma\beta\alpha \rangle \\ &= \frac{2J+1}{8\pi^2} \sum_{MM'} \langle \Omega JM' | \rho | \Omega JM \rangle D(\gamma\beta\alpha)_{\Omega M'}^{(J)} D(\gamma\beta\alpha)_{\Omega M}^{(J)*} \end{aligned} \quad (7.62b)$$

where we used that the diagonal element  $\langle \gamma\beta\alpha | \rho | \gamma\beta\alpha \rangle$  is equal to the corresponding probability density  $W(\gamma\beta\alpha)$  for the specified value of  $\Omega$ .

For the special case of an incoherent superposition of rotational states ( $M' = M$ ) we abbreviate  $\langle \Omega JM | \rho | \Omega JM \rangle$  by  $W(M)$  and obtain

$$W(\gamma\beta\alpha) = \sum_M W(M) \left( \frac{2J+1}{8\pi} \left| D_{\Omega M}^{(J)} \right|^2 \right)$$

This relation has a simple interpretation. The expression within parentheses represents the axes probability density for molecules with sharp values of  $J$ ,  $M$ ,  $\Omega$ . Multiplying this function by the probability  $W(M)$  of finding a molecule with quantum number  $M$  in the ensemble and summing over all  $M$ , we obtain  $W(\gamma\beta\alpha)$ .

We return now to the general (7.62b) and apply essentially the same steps as in deriving (7.23). Using (C.14), substituting (C.17) into (7.62b), and applying (C.16) and the definition (7.59), we obtain for the axes distribution

- $$W(\beta\alpha) = \frac{2J+1}{(4\pi)^{1/2}} \sum_{KQ} (-1)^{J-\Omega} \begin{pmatrix} J & J & K \\ \Omega & -\Omega & 0 \end{pmatrix} \langle T(J)_{KQ}^\dagger \rangle Y(\beta\alpha)_{KQ} \quad (7.63)$$

Since  $W(\beta\alpha)$  turned out to be independent of  $\gamma$ , an integral over  $\gamma$  is already included in (7.63).  $W(\beta\alpha)$  is then normalized according to condition (7.17).

As an example consider an ensemble of molecules in a single state  $|\Omega JM\rangle$ . The density matrix elements in (7.61) are then equal to one for the given state, and to zero for all other cases. Equation 7.59 reduces to the expression

$$\langle T(J)_{K0}^\dagger \rangle = (-1)^{J-M} (2K+1)^{1/2} \begin{pmatrix} J & J & K \\ M & -M & 0 \end{pmatrix}$$

Substitution of this equation into (7.63) gives the corresponding axes distribution:

- $$W(\beta\alpha) = \frac{2J+1}{4\pi} \sum_K (-1)^{M-\Omega} (2K+1) \begin{pmatrix} J & J & K \\ M & -M & 0 \end{pmatrix} \begin{pmatrix} J & J & K \\ \Omega & -\Omega & 0 \end{pmatrix} P(\cos\beta)_K \quad (7.64a)$$

which is independent of  $\alpha$ . Alternatively, (7.64a) can be derived by using the fact that the axes distribution for a single state is given by the absolute square of  $(2J + 1/8\pi^2)^{1/2} D(\gamma\beta\alpha)_{\Omega M}^{(J)}$ , and by expanding this expression into Legendre polynomials  $P(\cos\beta)_K$  one obtains (7.64a) (Zare 1988).

### 7.6.3 Theory of Oriented Symmetric-Top Molecules. Semiclassical Interpretation

Equation 7.63 relates the probability density function  $W(\beta\alpha)$ , describing the axes distribution, to the state multipoles  $\langle T(J)_{KQ}^\dagger \rangle$ , characterizing the corresponding angular momentum distribution. Alternatively, order parameters may be introduced. Since the axis distribution is independent of  $\gamma$  according to (7.63) we can apply the expansion (7.28) and the following results. Comparing (7.28) and (7.63) we obtain the relation

- $$\langle Y_{KQ}^* \rangle = (-1)^{J-\Omega} (4\pi)^{-1/2} (2J+1) \begin{pmatrix} J & J & K \\ \Omega & -\Omega & 0 \end{pmatrix} \langle T(J)_{KQ}^\dagger \rangle \quad (7.64b)$$

which should be compared with (7.34) for linear rotors ( $\Omega = 0$ ). The essential difference between (7.64b) and (7.34) is that the  $3j$  symbol in relation (7.64b) does not vanish for  $K$  odd. Hence, for symmetric tops, order parameters with  $K$  odd will be different from zero if the corresponding state multipole is nonvanishing. *The axes distribution will therefore be oriented if the angular momentum distribution exhibits orientation.*

It is instructive to consider the semiclassical approximation of (7.64b) for axially symmetric systems in order to clarify the different behavior of linear rotors and symmetric tops. We substitute (7.9) for the state multipoles and use the semiclassical approximation for the  $3j$  symbols which follows from (7.3b). Expressing finally  $\langle Y_{K0} \rangle$  by the mean values of the corresponding Legendre polynomials [(7.33c)] we obtain

- $\langle P_K(\cos \beta) \rangle = P_K(\cos \Theta_\Omega) \langle P_K(\cos \Theta_J) \rangle \quad (7.64c)$

with  $\cos \Theta_\Omega = \Omega/J$  in the high- $J$  limit.  $\Theta_\Omega$  can be interpreted as angle between  $\mathbf{J}$  and the axis  $\mathbf{n}$ , whereas  $\Theta_J$  represents the angle between  $\mathbf{J}$  and  $z$ , and  $\beta$  between  $\mathbf{n}$  and  $z$ . In particular, for  $K = 1$  we obtain

$$\langle \cos \beta \rangle = \cos \Theta_\Omega \langle \cos \Theta_J \rangle \quad (7.64d)$$

If the  $\mathbf{J}$  vectors show a head-versus-tail distinction so that  $\langle \cos \Theta_J \rangle$  is different from zero, then the axes distribution will exhibit orientation, too. *This orientation is not averaged out by the rotation of  $\mathbf{n}$  around  $\mathbf{J}$  since  $\Theta_\Omega \neq 90^\circ$ .* In particular, for polar symmetric-top molecules, ensembles with a nonvanishing mean electric dipole moment can be produced.

These results are in sharp contrast to those obtained in Sect. 7.4.2 for linear rotors. In the latter case  $\mathbf{n}$  and  $\mathbf{J}$  are mutually perpendicular, corresponding to  $\cos \Theta_\Omega = 0$ , and (7.64b) reduces to (7.35b). Any orientation of  $\mathbf{n}$  is then averaged out by the rotation of  $\mathbf{n}$  around  $\mathbf{J}$ , even if  $\mathbf{J}$  is oriented.

Of particular practical importance is the mean value  $\langle \cos \beta \rangle$  of  $\cos \beta$  for an oriented system. Since  $\langle Y_{10} \rangle = (3/4\pi)^{1/2} \langle \cos \beta \rangle$  we obtain from (7.64b)

$$\langle \cos \beta \rangle = \left( \frac{1}{3} \right)^{1/2} (-1)^{J-\Omega} \begin{pmatrix} J & J & 1 \\ \Omega & -\Omega & 0 \end{pmatrix} \langle T(J)_{10}^\dagger \rangle (2J+1)$$

and substitution of the explicit value of the  $3j$  symbol yields

- $\langle \cos \beta \rangle = \left( \frac{2J+1}{3J(J+1)} \right)^{1/2} \Omega \langle T(J)_{10}^\dagger \rangle \quad (7.65)$

Equation 7.65 shows explicitly that two conditions are required in order to produce a nonvanishing mean value of  $\cos \beta$ : (i)  $\Omega \neq 0$ ; (ii) the orientation

parameter  $\langle T(J)_{10}^\dagger \rangle$ , characterizing the angular momentum distribution, must be different from zero. (These conditions relax for pendulum states as discussed in Sect. 7.4.2.)

In the special case that all molecules are in states with the same  $M$  value  $M = M_0$  we put  $W(M) = \delta_{MM_0}$  and obtain from (4.31)

$$\langle T(J)_{10}^\dagger \rangle = \left( \frac{3}{(2J+1)(J+1)J} \right)^{1/2} M_0$$

Inserting this result into (7.65) we obtain

- $\langle \cos \beta \rangle = \frac{\Omega M_0}{J(J+1)}$  (7.66)

This factor plays an essential role in the rotational state selection of polar symmetric tops as achieved by the electric focusing technique. In the high- $J$  limit (7.66) is approximated by (7.64c).

#### 7.6.4 Order Parameters for Nonlinear Molecules

The results of the preceding subsections apply to rotating molecules in states with sharp  $J$ . We will now generalize our treatment to molecular ensembles without sharp  $J$ . Particular examples are molecules adsorbed at surfaces, or anisotropic ensembles produced in stretched polymers, nematic liquid crystals, and lipid bilayers. Other cases include beams with molecules in states with different  $J$ .

The anisotropy of the axes distribution of the sample will be characterized in terms of the probability density  $W(\gamma\beta\alpha)$  (which for rotating molecules would represent the instantaneous distribution). This function can always be expanded in terms of the complete set of rotation matrix elements (see, for example, Michl and Thulstrup 1986),

- $W(\gamma\beta\alpha) = - \sum_{KQQ'} \frac{2K+1}{8\pi^2} \langle D_{Q'Q}^{(K)*} \rangle D(\gamma\beta\alpha)_{Q'Q}^{(K)}$  (7.67)

normalized according to (7.60). The expansion coefficients (“order parameters”) are defined by the relation

- $\langle D_{Q'Q}^{(K)*} \rangle = \int_0^{2\pi} d\gamma \int_0^\pi d\beta \sin \beta \int_0^{2\pi} d\alpha W(\gamma\beta\alpha) D(\gamma\beta\alpha)_{Q'Q}^{(K)*}$  (7.68)

Similar to Sect. 7.4 we call a distribution *oriented* if at least one term with  $K$  odd contributes to (7.67), and *aligned* if at least one order parameter with  $K$  even is nonvanishing.

The normalization condition (7.60) yields

$$\langle D_{00}^{(0)} \rangle = 1$$

It follows from the definition (7.68) that any order parameter represents the mean value of the corresponding  $D$  function. For example, if only terms with  $K \leq 2$  and  $Q = 0$  contribute,

$$\langle D_{00}^{(1)} \rangle = \langle \cos \beta \rangle \quad (7.69a)$$

provides us with an average degree of orientation and

$$\langle D_{00}^{(2)} \rangle = \left\langle \frac{1}{2} (3 \cos^2 \beta - 1) \right\rangle \quad (7.69b)$$

characterizes the alignment.

By applying the symmetry properties (C14) of the rotation matrices we can read off the corresponding relations for the order parameters from the definition (7.68):

1.  $\langle D_{Q'Q}^{(K)*} \rangle = \langle D_{Q'Q}^{(K)} \rangle^*$ .
2. Order parameters with  $Q = Q' = 0$  are real.
3.  $\langle D_{-Q'-Q}^{(K)*} \rangle = (-1)^{Q'-Q} \langle D_{Q'Q}^{(K)} \rangle$ .

Equation 7.67 expresses the continuous function  $W(\gamma\beta\alpha)$  in terms of an infinite set of discrete order parameters. Such an expansion has advantages if only a limited number of parameters contribute. In addition, symmetry properties of the sample are often conveniently characterized in terms of order parameters. We list some general results.

1. If the molecular axes are randomly oriented then all order parameters vanish except for  $K = 0$ .
2. If the sample is axially symmetric with respect to the space-fixed  $z$  axis then all values of  $\alpha$  are equally probable. Hence,  $W(\gamma\beta\alpha)$  is independent of  $\alpha$ . This is possible only if terms with  $Q = 0$  contribute to (7.67) that is, all order parameters with  $Q \neq 0$  must vanish. We obtain

$$W(\gamma\beta\alpha) = \sum_{KQ'} \frac{2K+1}{8\pi^2} \langle D_{Q'0}^{(K)*} \rangle D(\gamma\beta\alpha)_{Q'0}^{(K)} \quad (7.70a)$$

Application of relation (C16a) yields

$$W(\beta\gamma) = \sum_{KQ'} \langle Y_{KQ'}^* \rangle Y(\beta\gamma)_{KQ'} \quad (7.70b)$$

after an integration over  $\alpha$  has been performed.

3. The dependence of  $W(\gamma\beta\alpha)$  on  $\gamma$  reflects either the internal symmetries of the molecules or the symmetry of the total sample with respect to rotations around  $z'$  or to reflections through planes containing  $z'$ . Let us consider some examples. It may happen that all angles of rotation around the molecular  $z'$  axis are equally probable. This is of course always the case if the shape of each molecule is axially symmetric with respect to  $z'$ . More generally, for arbitrary shapes, the molecular  $x'$  and  $y'$  axes may be equally distributed around  $z'$ . In all these cases the probability density must be independent of  $\gamma$ ; that is, only terms with  $Q' = 0$  can contribute to (7.67), and all order parameters with  $Q' \neq 0$  must vanish. Applying (C.16b) and integrating over  $\gamma$  we obtain, similar to (7.70),

$$W(\beta\alpha) = \sum_{KQ} \langle Y_{KQ}^* \rangle Y(\beta\alpha)_{KQ} \quad (7.71)$$

and all results of Sect. 7.3 apply.

If, in addition, the sample is axially symmetric with respect to the space-fixed  $z$  axis, then (7.71) reduces to (7.33b).

4. Consider now molecules where the  $y' - z'$  plane is a symmetry plane of each molecule. This requires  $W(\gamma\beta\alpha) = W(\gamma, \pi - \beta, \alpha)$ . Of great practical importance is the case where the molecule has two mutually perpendicular symmetry planes, for example the  $y' - z'$  and  $x' - z'$  planes. It then follows that  $W(\gamma\beta\alpha) = W(\pi + \gamma, \beta, \alpha)$ , which requires that only order parameters with  $Q'$  even can contribute to (7.67). Order parameters with  $Q'$  odd would vanish.

## 7.7 Electronic Orbital Orientation and Alignment

### 7.7.1 Basic Concepts. Space-Fixed Molecules: Excited State Coherence

So far we have considered ensembles where all molecules have the same value of  $J$  and the same value of  $\Omega$ . Our results can be immediately generalized to ensembles in incoherent superposition states with regard to  $\Omega$ , for example. In that case we multiply (7.63) by the relevant statistical weights and sum over all relevant values of  $\Omega$ .

However, there are more general situations where the molecules have been prepared in coherent superposition states with regard to  $\Omega$ . All processes between the molecular ensemble and some reagents depend then on possible anisotropies in the angular momentum and axes distributions and additionally on shape and spatial orientation of the electronic orbitals. We therefore have to consider how to characterize possible anisotropies of the electronic orbitals. In order to explain the basic ideas in a simple way we will consider nonrotating diatomic molecules with

axes  $\mathbf{n}$  fixed in space (for example, molecules adsorbed at surfaces). It will further be assumed that all axes of the sample are pointing in the same direction  $\mathbf{n}$  and that the molecules are spinless.

The molecular states will be characterized by state vectors  $|\Lambda v \mathbf{n}\rangle$  where  $\Lambda$  and  $v$  denote the electronic and the vibrational quantum numbers, respectively. In the following we will suppress the dependence on  $v$ , and since all molecular axes are assumed to be fixed and pointing in the same direction we will denote the molecular state simply by  $|\Lambda\rangle$ .

Reflections in the molecular  $x' - z'$  and  $y' - z'$  planes are symmetry operations. Denoting the corresponding reflection operators by  $\sigma_{x'z'}$  and  $\sigma_{y'z'}$ , respectively, and choosing the phase relations of [Zare \(1988\)](#), we have the relations

$$\sigma_{x'z'}|\Lambda\rangle = (-1)^{\Lambda+s}|- \Lambda\rangle \quad (7.72a)$$

$$\sigma_{y'z'}|\Lambda\rangle = (-1)^s|- \Lambda\rangle \quad (7.72b)$$

with  $s = 1$  for a  $\Sigma^-$ -state, and  $s = 0$  for all other cases.

It is important to remember that the two states  $|\Lambda\rangle$  and  $|- \Lambda\rangle$  are degenerate to first order.

The different signs indicate opposite directions for the rotation of the electronic charge cloud around  $\mathbf{n}$ . The shape of the charge cloud is axially symmetric around the internuclear axis if the molecules are in states with sharp  $\Lambda$ .

Because of their near degeneracy the two states  $|\Lambda\rangle$  and  $|- \Lambda\rangle$  will in general be coherently excited in collisions with electrons or atoms or other molecules. The coherent superposition state will in general not be axially symmetric, and we are faced with the problem of describing shape and spatial orientation of the electronic orbitals. We will develop the necessary description following [Wöste et al. \(1994\)](#).

Assume that the molecules are initially in a  $|\Sigma^+\rangle$ -state and that they will be excited in collisions with structureless projectiles. The excited molecules will in general be found in coherent superpositions of the basis states  $|\Lambda\rangle$  and  $|- \Lambda\rangle$ :

$$|\varphi\rangle = f(\Lambda)|\Lambda\rangle + f(-\Lambda)|- \Lambda\rangle \quad (7.73)$$

where we assume that the axis direction does not change during the collision.  $f(\Lambda) = f(\Lambda \mathbf{n})$  denotes the relevant scattering amplitude normalized according to the condition

$$\sigma = |f(\Lambda)|^2 + |f(-\Lambda)|^2 \quad (7.74a)$$

where  $\sigma$  is the differential cross section.

In order to characterize the state (7.73) one has to determine three independent parameters, for example the magnitudes  $|f(\Lambda)|$  and  $|f(-\Lambda)|$  and the relative phase  $\chi$ . Alternatively one might use the differential cross section  $\sigma$ , the expectation value of the electronic angular momentum operator  $L_{z'}$ , which is given by

- $\sigma(L_{z'}) = |\Lambda| [|f(\Lambda)|^2 - |f(-\Lambda)|^2]$  (7.74b)

(where we used  $L_{z'}|\Lambda\rangle = \Lambda|\Lambda\rangle$  with  $\hbar = 1$ ), and the expectation value of the reflection operator  $\sigma_{x'z'}$ . Using (7.72a) with  $s = 0$  this expectation value is given by the relation

- $$\begin{aligned}\sigma\langle\sigma_{x'z'}\rangle &= (-1)^\Lambda[f(\Lambda)^*f(-\Lambda) + f(-\Lambda)^*f(\Lambda)] \\ &= 2(-1)^\Lambda|f(\Lambda)||f(-\Lambda)|\cos\chi\end{aligned}\quad (7.74c)$$

with  $f(\Lambda) = |f(\Lambda)|$  and  $f(-\Lambda) = |f(-\Lambda)|e^{i\chi}$  and where the asterisk denotes the complex conjugate amplitude.

The three parameters (7.74a)–(7.74c) fix the magnitudes of the amplitudes and  $\cos\chi$ . It is convenient to have another parameter which depends on  $\sin\chi$  (which fixes the sign of the phase). We choose the expectation value of  $\sigma_{x'z'} L_{z'}$ :

- $$\sigma\langle\sigma_{x'z'} L_{z'}\rangle = i|\Lambda|(-1)^\Lambda 2|f(\Lambda)||f(-\Lambda)|\sin\chi\quad (7.74d)$$

Only the imaginary part  $\text{Im}\langle\sigma_{x'z'}, L_{z'}\rangle$ , which is real, is of direct physical interest.

The expectation value  $\langle L_{z'}\rangle$  characterizes the difference in the population numbers of the two states  $|\Lambda\rangle$  and  $|-\Lambda\rangle$  with opposite rotations around the internuclear axis and will be called the *electronic orientation para-0 meter* similar to atomic physics (see Chap. 4). No net rotation occurs if  $\langle L_{z'}\rangle = 0$ .

Furthermore it can be shown that the absolute square of the wave function (7.73) can be written in the form (Wöste et al. 1994)

- $$|\psi|^2 = \sigma|\varphi_{|\Lambda|}|^2 \left[ 1 + \langle\sigma_{x'z'}\rangle \cos 2|\Lambda|\phi - \frac{1}{|\Lambda|} \text{Im}\langle\sigma_{x'z'} L_{z'}\rangle \sin 2|\Lambda|\phi \right] \quad (7.75)$$

where  $\phi$  is the azimuth angle measured from the molecular  $x'$  axis and where  $|\varphi_{|\Lambda|}|^2$  is independent of  $\phi$ . Equation 7.75 shows how the shapes of the electronic orbitals change as we rotate around the internuclear axis. This change is determined by  $\langle\sigma_{x'z'}\rangle$  and  $\langle\sigma_{x'z'} L_{z'}\rangle$ . If both parameters vanish then the shape is axially symmetric with respect to  $\mathbf{n}$ . Similar to atomic physics, where the shape and spatial orientation of the charge cloud are determined by the alignment parameters (see Chap. 4) we will call  $\langle\sigma_{x'z'}\rangle$  and  $\langle\sigma_{x'z'} L_{z'}\rangle$  *electronic alignment parameters*.

Let us consider some examples. In order to depict the directional properties of the electronic charge density it is often convenient to use linear combinations  $|\Lambda\pm-\Lambda\rangle$  as basis states instead of using  $|\Lambda\rangle$  and  $|-\Lambda\rangle$ . In particular, for  $\Pi$  states ( $|\Lambda| = 1$ ) we have the two  $\Lambda$ -doublet states

$$|\Pi_{x'}\rangle = -\frac{1}{\sqrt{2}}[|\Lambda = 1\rangle = |\Lambda = -1\rangle] \quad (7.76a)$$

$$|\Pi_{y'}\rangle = -\frac{i}{\sqrt{2}}[|\Lambda = 1\rangle + |\Lambda = -1\rangle] \quad (7.76b)$$

This construction is similar to the atomic case. For angular momentum  $l = 1$  and  $m_l = \pm 1$  the familiar states  $|\Psi_{x'}\rangle$  and  $|\Psi_{y'}\rangle$  can be formed which correspond to  $|\Pi_{x'}\rangle$  and  $|\Pi_{y'}\rangle$  respectively. The two orbitals (7.76) have a fixed spatial orientation.  $|\Pi_{x'}\rangle$  is directed along the  $x'$  axis, and  $|\Pi_{y'}\rangle$  along the  $y'$  axis.

If the molecules are in a pure  $|\Pi_{x'}\rangle$  state we obtain from (7.74) and (7.76) that  $\langle \sigma_{x'z'} \rangle = 1$ ,  $\langle \sigma_{x'z'} L_{z'} \rangle = \langle L_{z'} \rangle = 0$ , and from (7.75) that

$$|\varphi(\Pi_{x'})|^2 \sim \cos^2 \phi$$

Similarly, for a pure  $\Pi_{y'}$  state we have  $\langle \sigma_{x'z'} \rangle = -1$ ,  $\langle \sigma_{x'z'} L_{z'} \rangle = \langle L_{z'} \rangle = 0$ , and

$$|\varphi(\Pi_{y'})|^2 \sim \sin^2 \phi$$

A II orbital, obtained by rotating  $|\Pi_{x'}\rangle$  around  $\mathbf{n}$  about an angle  $\epsilon$  without changing its shape, is expressed by

$$|\Pi\rangle = |\Pi_{x'}\rangle \cos \epsilon + |\Pi_{y'}\rangle \sin \epsilon \quad (7.77a)$$

using the two states (7.76) as basis. We obtain  $\langle L_{z'} \rangle = 0$ ,  $\langle \sigma_{x'z'} \rangle = \cos 2\epsilon$ , and  $\text{Im}\langle \sigma_{x'z'} L_{z'} \rangle = \sin 2\epsilon$ . This example shows again that the two alignment parameters characterize the spatial orientation of the orbitals. The most general (normalized) state with  $|\Lambda| = 1$  can be written in the form

$$|\Pi\rangle = |\Pi_{x'}\rangle \cos \epsilon + |\Pi_{y'}\rangle \sin \epsilon e^{i\delta}$$

In this case we obtain

$$\begin{aligned} \langle L_{z'} \rangle &= \sin 2\epsilon \sin \delta \\ \langle \sigma_{x'z'} \rangle &= \cos 2\epsilon \\ \text{Im}\langle \sigma_{x'z'} L_{z'} \rangle &= \sin 2\epsilon \cos \delta \end{aligned}$$

Furthermore, (7.74c) can be rewritten in the form

- $$\langle \sigma_{x'z'} \rangle = \frac{|f(\Pi_{x'})|^2 - |f(\Pi_{y'})|^2}{\sigma} \quad (7.78)$$

where  $f(\Pi_{x'})$  and  $f(\Pi_{y'})$  are the scattering amplitudes for excitation of a  $\Pi_{x'}$  and  $\Pi_{y'}$  state respectively.  $\langle \sigma_{x'z'} \rangle$  determines therefore the preferential  $\Lambda$ -doublet population with respect to the two states (7.76). Its importance for the interpretation of chemical reactions has been shown by several authors (see, e.g., [Andresen and Rothe 1985](#), and references therein). We note, however, that also knowledge of  $\langle L_{z'} \rangle$  and  $\langle \sigma_{x'z'} L_{z'} \rangle$  is required for a more complete description of molecular reactions.

Angular distribution and polarization of the radiation, emitted by the excited molecules in their subsequent decay, depend on the parameters (7.74). It can be

shown by direct computation that the degree of circular polarization of the emitted light is proportional to the orientation  $\langle L_{z'} \rangle$ , and angular distribution and the degree of linear polarization (Stokes parameters  $\eta_1$ ,  $\eta_3$ ) depend on the alignment parameters  $\langle \sigma_{x'z'} \rangle$  and  $\langle \sigma_{x'z'} L_{z'} \rangle$ .

The results of the present section provide an entry into the stereodynamics of collisions, that is, the dependence of scattering processes on the direction of the molecular axis  $\mathbf{n}$  and on the shape and orientation of the electronic orbitals. The relevant information is contained in the parameters (7.74). The interpretation of these parameters is similar to the discussion of atomic collision processes. Consider, for example, electronic excitation of molecules (singlet states) by electrons and assume that the molecular axis is perpendicular to the scattering plane. Semiclassically,  $\langle L_{z'} \rangle$  characterizes the net rotation of the electronic charge cloud around the molecular axis after the excitation from a  $\Sigma$  state. Following our discussion in Sect. 4.6.1 we can interpret  $\langle L_{z'} \rangle$  as the mean angular momentum which has been transferred during the collision from the projectile to the electronic charge cloud.

From numerical or experimental results of  $\langle \sigma_{x'z'} \rangle$  and  $\langle \sigma_{x'z'} L_{z'} \rangle$  one can calculate  $|\phi|^2$  according to (7.75). The plots of  $|\phi|^2$  can then be compared to the atomic charge clouds discussed in Sect. 4.6.5. In particular, the concept of “alignment angle” can be taken over and related to the relative phase  $\chi$  [or, equivalently, to the angle  $\epsilon$  if the basis (7.76) is used].

It can be shown that  $\langle L_{z'} \rangle$  vanishes in first-order Born approximation (due to  $\chi = 0$ ). For II excitation the excited orbital is then represented by (7.77a). The scattering amplitudes depend only on the momentum transfer vector  $\mathbf{q}$ , and not separately on initial and final momenta of the projectiles. Consequently, the  $\mathbf{n} - \mathbf{q}$  plane is a symmetry plane of the total system, and the electronic orbital must lie parallel to  $\mathbf{q}$ . The angle  $\epsilon$  is then the angle between  $\mathbf{q}$  and the molecular  $x'$  axis. If the scattering angle is varied,  $\mathbf{q}$  varies, and the electronic orbital follows the direction of  $\mathbf{q}$  without changing its shape.

We note that the discussion becomes more complex for other orientations of  $\mathbf{n}$  relative to the collision plane. Our brief discussion is meant to indicate the interrelation between the parameters (7.74) and the collision dynamics, and may serve as a basis for more detailed subsequent discussions. Numerical results of the observables (7.74) have been obtained by Wöste et al. (1994) for  $\text{O}_2$  excitation by electron impact, and we refer to that paper for special examples. Other aspects of the problem will be discussed in several of the following sections.

### 7.7.2 Rotating Molecules. States with Definite Parity: Spatial Orientation and Selective Population

We will now consider electronic orientation and alignment for freely rotating molecules, focusing again on diatomics in singlet states. A clear measure of the anisotropy of the electronic orbital distribution will be given by the relevant mean

values of operators like  $\sigma_{x'z'}$ ,  $L_{z'}$ , and  $\sigma_{x'z'}$ ,  $L_{z'}$ , introduced in the previous subsection. Before we consider the general case we will start with a special example. Consider the linear combinations

- $|\Lambda JM\epsilon\rangle = \left(\frac{1}{2}\right)^{1/2} (|\Lambda\rangle|\Lambda JM\rangle + \epsilon|-\Lambda\rangle|-\Lambda JM\rangle) \quad (7.79)$

Here, the “parity index”  $\epsilon = \pm 1$ ,  $\Lambda = |\Lambda|$ , and  $|\Lambda\rangle$  and  $|\Lambda JM\rangle$  denote the electronic and rotational parts of the wave function respectively. (For brevity we will suppress the dependence on the vibrational quantum number, assuming that all molecules are in the same vibrational state.)

The states (7.79) have total parity  $(-1)^J$  for  $\epsilon = +1$ , and  $(-1)^{J+1}$  for  $\epsilon = -1$  (Zare 1988).

The two  $\Lambda$ -doublet states (7.79) with  $\epsilon = \pm 1$  are degenerate to first order. However, preferential population of one member of the  $\Lambda$ -doublet pair has been observed in chemical reactions, inelastic collisions, and photofragmentation (see, e.g., the reviews by Zewail and Bernstein 1992; Delgado-Barrio 1993; Simons 1987). In order to obtain an explanation for the observed propensity rules we must examine what distinguishes one  $\Lambda$ -doublet state from the other. The relevant theoretical basis has been developed by Green and Zare (1975), Alexander and Dagdigan (1984), and Andresen and Rothe (1985). We will follow here a slightly different procedure concentrating on  $^1\Pi$  states.

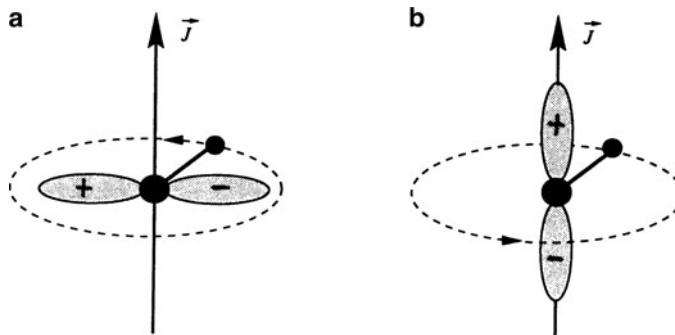
We start by substituting the explicit coordinate representation  $(2J + 1/4\pi)^{1/2} D(0\beta\alpha)_{\Lambda M}^{(J)}$  for the rotational state  $|\Lambda JM\rangle$  in (7.79) [see (7.57)], remembering that we always put  $\gamma = 0$  for diatomic molecules (Fig. 7.4). We obtain for states with  $M = 0$

$$|\Lambda J 0\epsilon\rangle = \left(\frac{2J+1}{8\pi}\right)^{1/2} [|\Lambda\rangle + \epsilon(-1)^{\Lambda}|-\Lambda\rangle] d(\beta)_{\Lambda 0}^{(J)} \quad (7.80)$$

where we have applied relations (C12) and (C13), and where  $|\Lambda| = 1$ . The essential point is that the electronic superposition state in the bracket represents a directed orbital, namely either  $\Pi_{x'}$  for  $\epsilon = +1$ , or  $i\Pi_{y'}$  for  $\epsilon = -1$ , as follows from an inspection of (7.76).

For rotating molecules the orientation of the electronic orbitals relative to the plane of rotation is of particular interest. Let us take the high- $J$  limit ( $J \gg \Lambda$ ) of (7.80) where  $\mathbf{J}$  can be considered to be perpendicular to the internuclear axis  $\mathbf{n}$ .  $\mathbf{J}$  lies in the space-fixed  $x - y$  plane (since  $M = 0$ ) and in the molecular  $x' - y'$  plane; that is,  $\mathbf{J}$  is parallel to the molecular  $y'$  axis (since  $\gamma = 0$ ). Hence, the molecular  $x' - z'$  plane coincides with the rotation plane of the molecule. It follows that the  $\Pi_{x'}$  orbital lies in the rotation plane (Fig. 7.5a), whereas the  $\Pi_{y'}$  orbital is oriented perpendicular to this plane (Fig. 7.5b). Both orbitals are rotating around  $\mathbf{J}$  without changing their shape. Note that the  $\Pi_{x'}$  orbital has the larger moment of inertia.

The charge density, illustrated in Fig. 7.5, is proportional to the absolute square of the wave functions of the  $\Pi_{x'}$  and  $\Pi_{y'}$  orbitals. The wave functions themselves have opposite signs in the two half-lobes, indicated by the positive and negative signs in



**Fig. 7.5** Spatial orientation of electronic orbital lobes relative to  $\mathbf{J}$  for the two  $\Lambda$ -doublet states: (a)  $\epsilon = +1$ , (b)  $\epsilon = -1$

Fig. 7.5. One reads off from the figures that the wave function with  $\epsilon = +1$  ( $\epsilon = -1$ ) is symmetric (antisymmetric) with respect to reflection in the plane of rotation.

Similarly for states with  $M = J$ , the angular momentum is parallel to the  $z$  axis for high  $J$  and  $\mathbf{n}$  rotates therefore in the  $x - y$  plane. We obtain from (7.79) that

$$|\Lambda JJ\epsilon\rangle = \left(\frac{2J+1}{8\pi}\right)^{1/2} \left[ |\Lambda\rangle d\left(\frac{\pi}{2}\right)_{\Lambda J}^{(J)} + \epsilon| -\Lambda\rangle d\left(\frac{\pi}{2}\right)_{-\Lambda J}^{(J)} \right] e^{iJ\alpha} \quad (7.81a)$$

The small  $d$  functions have the symmetry property

$$d\left(\frac{\pi}{2}\right)_{\Lambda M}^{(J)} = (-1)^{J-M} d\left(\frac{\pi}{2}\right)_{-\Lambda M}^{(J)}$$

for the special case  $\beta = \pi/2$ . This allows us to identify in (7.81a) the electronic orbital:

$$|\Lambda JJ\epsilon\rangle = \left(\frac{2J+1}{8\pi}\right)^{1/2} [|\Lambda\rangle + \epsilon| - \Lambda\rangle] d\left(\frac{\pi}{2}\right)_{\Lambda J}^{(J)} e^{iJ\alpha} \quad (7.82)$$

Comparison with (7.76) yields that the electronic orbital in the bracket is directed along the molecular  $x'$  axis if  $\epsilon = -1$ , and along the  $y'$  axis if  $\epsilon = +1$ . Since  $z'$  is perpendicular to  $z$ , and  $\gamma = 0$  the internuclear  $x'$  axis is antiparallel to  $z$  (Fig. 7.4). The  $\Pi_{x'}$  orbital is therefore oriented perpendicular to the rotation plane and is antisymmetric with respect to reflection in this plane (see Fig. 7.5b), whereas the  $\Pi_{y'}$  orbital lies in the rotation plane and is symmetric under reflection (Fig. 7.5a).

Our discussion shows that the spatial orientation of the two  $\Lambda$ -doublet components (7.79) is strikingly different. The relevant distinction between the two states is neither their very small energy splitting nor their total parity; it is this difference of the direction of the orbitals relative to the molecular rotation plane. The various observed propensity rules have often been traced to these different geometrical

properties, and the results have been used to clarify the stereodynamics of chemical reactions (Andresen and Rothe 1985).

So far we have discussed the states (7.79) with definite values of  $\epsilon$ ,  $J$ ,  $M$ . Let us now consider more general cases and assume that a given molecular ensemble is in an arbitrary superposition of molecular states, described by its density matrix  $\rho$ . Using  $|\Lambda\rangle|\Lambda JM\rangle$  as basis states  $\rho$  can always be written in the form

$$\rho = \sum_{\substack{\Lambda' \Lambda \\ M' M}} \langle \Lambda' JM' | \rho | \Lambda JM \rangle | \Lambda' \rangle \langle \Lambda' JM' | \langle \Lambda JM | \langle \Lambda | \quad (7.83)$$

where we have abbreviated  $|\Lambda\rangle|\Lambda JM\rangle$  by  $|\Lambda JM\rangle$  in the density matrix elements, and where we have assumed a sharp  $J$  value for simplicity. In order to characterize the electronic orientation and alignment we have to average the parameters (7.74) over the rotational states. We will briefly indicate the procedure.

Taking  $\langle \sigma_{x'z'} \rangle$  as an example we obtain from (2.18) and (7.83):

$$\begin{aligned} \langle \sigma_{x'z'} \rangle &= \text{tr } \rho \sigma_{x'z'} \\ &= \sum_{\substack{\Lambda' \Lambda \\ M' M}} \langle \Lambda' JM' | \rho | \Lambda JM \rangle \langle \Lambda | \sigma_{x'z'} | \Lambda' \rangle \langle \Lambda JM | \Lambda' JM' \rangle \end{aligned} \quad (7.84)$$

taking into account that  $\sigma_{x'z'}$  acts on the electronic states  $|\Lambda\rangle$  only and not on the rotational states  $|\Lambda JM\rangle$ . Application of (7.72a) yields  $\langle \Lambda | \sigma_{x'z'} | \Lambda' \rangle = (-1)^A \delta_{\Lambda-\Lambda'}$ . The overlap integral between the rotational states is given by the expression

$$\begin{aligned} \langle \Lambda JM | \Lambda' JM' \rangle &= \frac{2J+1}{4\pi} \int_0^{2\pi} d\alpha \int_0^\pi d\beta \sin \beta D(0\beta\alpha)_{\Lambda' M'}^{(J)} D(0\beta\alpha)_{\Lambda M}^{(J)*} \\ &= S(JM)_{\Lambda' \Lambda} \delta_{MM'} \end{aligned}$$

with the definition

$$S(JM)_{\Lambda' \Lambda} = \frac{2J+1}{4\pi} \int_0^{2\pi} d\alpha \int_0^\pi d\beta \sin \beta D(0\beta\alpha)_{\Lambda' M}^{(J)} D(0\beta\alpha)_{\Lambda M}^{(J)*}$$

(Green and Zare 1975; Alexander and Dagdigian 1984).

Substitution of these results into (7.84) yields

$$\bullet \quad \langle \sigma_{x'z'} \rangle = \sum_{\Lambda M} \langle -\Lambda JM | \rho | \Lambda JM \rangle (-1)^A S(JM)_{-\Lambda \Lambda} \quad (7.85)$$

Similar expressions follow for  $\langle L_z' \rangle$  and  $\langle \sigma_{x'z'}, L_z' \rangle$ . In general, the results can be used as a measure of the anisotropy of the electron distribution.

Let us specialize to the case where all molecules are in one of the  $\Lambda$ -doublet states (7.79) with fixed  $\epsilon$  and fixed  $M$ . The density matrix is then given by  $\rho =$

$|\Lambda JM\epsilon\rangle\langle\Lambda JM\epsilon|$ . After recognizing  $S_{-\Lambda\Lambda} = S_{\Lambda-\Lambda}$  we obtain from (7.85) that

$$\langle\sigma_{x'z'}\rangle = (-1)^\Lambda \epsilon S(JM)_{\Lambda-\Lambda} \quad (7.86)$$

The two parameters  $\langle L_{z'}\rangle$  and  $\langle\sigma_{x'z'}L_{z'}\rangle$  vanish in this case.

In the high- $J$  limit  $S_{\Lambda-\Lambda}$  approaches unity for  $M = J$ , and  $S_{\Lambda-\Lambda} = -1$  for  $M = 0$ . For  $|\Lambda| = 1$  and  $M = 0$  it follows that the corresponding level is symmetric (antisymmetric) under reflection in the plane of rotation if  $\epsilon = +1$  ( $\epsilon = -1$ ) as discussed above (Alexander and Dagdigian 1984).

As another example consider homonuclear molecules obeying Hunds-case-*b* coupling, which have been excited by electron impact. From an inspection of the relevant selection rules it follows that only one member of the  $\Lambda$ -doublet pair (7.79) can be excited depending on the quantum numbers of the initial and final states (Nordbeck et al. 1993). All molecules are therefore in states with the same definite parity, and  $\langle L_{z'}\rangle$  and  $\langle\sigma_{x'z'}L_{z'}\rangle$  vanish. This result implies in particular that no net rotation of the electronic charge cloud around the internuclear axis can be produced in such collisions. The situation is, however, different for heteronuclear molecules.

The correlation between the direction of  $\mathbf{J}$  and the orientation of the electronic charge density has interesting consequences for dissociative photochemistry and has been extensively studied for several molecules (e.g., ClCN, H<sub>2</sub>O). For details we refer to the reviews by Delgado-Barrio (1993) and Schinke (1993).

A possible method of measuring stereochemical effects (such as the different population of  $\Lambda$ -doublet states) is to analyze the light emitted in the decay of the excited molecules. Consider for example a  $\Pi \rightarrow \Sigma$  transition in the high-rotation limit. The transition dipole  $\mathbf{d}$  lies along the axis of the respective electron lobes.  $\mathbf{d}$  is therefore parallel to  $\mathbf{J}$  for levels with  $\epsilon = -1$  and does not rotate, and  $\mathbf{d}$  is perpendicular to  $\mathbf{J}$  for the  $\epsilon = +1$  component and rotates with the molecule (see Fig. 7.5). One can therefore expect increasing polarization of the emitted light with increasing population of the  $\epsilon = -1$  level. We will return to this point in greater detail at the end of the following subsection.

### 7.7.3 *Combined Description of Rotational Polarization and Orbital Anisotropies*

#### 7.7.3.1 States with Definite $\Lambda$ as Basis Set Distribution Functions

In the preceding subsection we have studied the correlation between the spatial distribution of electronic orbitals and the direction of the angular momentum vectors. We will now develop a formalism in order to characterize rotational polarization for diatomics with electronic angular momentum. For simplicity we will concentrate on singlet states ( $\Omega = \Lambda$ ). For sharp values of  $\Lambda$  several results have been obtained in Sect. 7.6. However, because of their near degeneracy, the electronic states with  $\Lambda$  and  $-\Lambda$  will generally be coherently excited in collisions.

(Although the degeneracy of these states might be lifted by some small interactions, their energy difference will usually be much smaller than the spread of the projectile energy, resulting in a coherent excitation). In this section we will first develop the necessary formalism and then discuss how the various parameters can be determined experimentally. The molecules under consideration might have been excited in collisions with some reagent, or they may be fragments produced in photodissociation processes.

We will first take the states  $|\Lambda\rangle|\Lambda JM\rangle$  as basis set. The full information on the excited molecular ensemble is contained in the set of all relevant density matrix elements  $\langle\Lambda'JM'|\rho|\Lambda JM\rangle$  where we have abbreviated  $|\Lambda\rangle|\Lambda JM\rangle$  by  $|\Lambda JM\rangle$  in the density matrix elements, and where we have assumed sharp  $J$  for simplicity. (This assumption can easily be relaxed and rotational coherence can be taken into account as described in Sect. 4.3.) The elements of  $\rho$  are bilinear combinations of the relevant scattering amplitudes if the molecules have been excited by collisions with electrons, atoms, or molecules. The relevant expressions can be derived by applying the methods of Sects. 3.2 and 3.5 (see also the explicit derivations in Sect. 7.8.3).

The total density matrix can be written in the general form

$$\rho = \sum_{\substack{\Lambda' \Lambda \\ M' M}} \langle\Lambda'JM'|\rho|\Lambda JM\rangle |\Lambda'\rangle|\Lambda'JM'\rangle\langle\Lambda|\Lambda JM| \quad (7.87)$$

For example, the sum over  $\Lambda', \Lambda$  would run over the values  $|\Lambda|$  and  $-|\Lambda|$  if the molecules are in one of the states (7.79) with fixed  $\epsilon$ .

It is convenient for the following to take partial matrix elements of  $\rho$  between the electronic states and define for any pair  $\Lambda', \Lambda$  which contributes to the sum in (7.87)

$$\begin{aligned} \rho(\Lambda' \Lambda) &= \langle\Lambda'|\rho|\Lambda\rangle \\ &= \sum_{M' M} \langle\Lambda'JM'|\rho|\Lambda JM\rangle |\Lambda'JM'\rangle\langle\Lambda JM| \end{aligned} \quad (7.88)$$

Note that the elements  $\langle\Lambda'JM'|\rho|\Lambda JM\rangle$  contain the full information on the electronic and the rotational states.

For any pair  $\Lambda', \Lambda$  we define state multipoles similar to (4.31):

$$\begin{aligned} \bullet \quad &\langle T(\Lambda' \Lambda J)_{KQ}^\dagger \rangle \\ &= \sum_{M' M} (-1)^{J-M'} (2K+1)^{1/2} \begin{pmatrix} J & J & K \\ M' & -M & -Q \end{pmatrix} \langle\Lambda'JM'|\rho|\Lambda JM\rangle \end{aligned} \quad (7.89)$$

For  $\Lambda' = \Lambda$  the corresponding tensors  $\langle T(\Lambda J)_{KQ}^\dagger \rangle$  characterize the angular momentum distribution similar to Sects. 7.6.2 and 7.6.3. In addition, the multipoles with  $\Lambda' \neq \Lambda$  are required if the corresponding electronic states have been coherently excited. Physical interpretations of these multipoles will be given below.

Conversely, we obtain the expansion

$$\begin{aligned} \langle \Lambda' JM' | \rho | \Lambda JM \rangle &= \sum_{KQ} (-1)^{J-M'} (2K+1)^{1/2} \begin{pmatrix} J & J & K \\ M' & -M & -Q \end{pmatrix} \langle T(\Lambda' \Lambda J)_{KQ}^\dagger \rangle \quad (7.90) \end{aligned}$$

with  $K \leq 2J$ . The set of all relevant parameters  $\langle T(\Lambda' \Lambda J)_{KQ}^\dagger \rangle$  contains the full information on the rotational polarization and on the electronic orbital orientation and alignment.

The density matrix elements  $\langle \Lambda' JM' | \rho | \Lambda JM \rangle$  and the state multipoles (7.89) are the essential ingredients for any further theoretical developments. We will give examples below and in Sect. 7.8.

We will first derive some useful formulas. We start from (7.88), sandwich this equation between the “directed states”  $\langle \gamma \beta \alpha |$  and  $| \gamma \beta \alpha \rangle$ , and use (7.62a). We obtain

$$\begin{aligned} \langle 0 \beta \alpha | \rho(\Lambda' \Lambda) | 0 \beta \alpha \rangle &= \frac{2J+1}{4\pi} \sum_{M'M} \langle \Lambda' JM' | \rho | \Lambda JM \rangle D(0 \beta \alpha)_{\Lambda' M'}^{(J)} D(0 \beta \alpha)_{\Lambda M}^{(J)*} \quad (7.91a) \end{aligned}$$

with the choice  $\gamma = 0$ . The diagonal elements with  $\Lambda' = \Lambda$  are equal to the probability density of finding a molecule in the state  $\Lambda$  and with an axis pointing in the  $\beta - \alpha$  direction. Repeating essentially the same steps as in Sect. 7.6.2 and using Eqs. C17 and (7.90) we obtain

$$\begin{aligned} \bullet \quad \langle 0 \beta \alpha | \rho(\Lambda' \Lambda) | 0 \beta \alpha \rangle &= \frac{2J+1}{4\pi} = \sum_{KQQ'} (-1)^{J-\Lambda'} (2K+1)^{1/2} \begin{pmatrix} J & J & K \\ \Lambda' & -\Lambda & -Q' \end{pmatrix} \quad (7.92) \\ &\times \langle T(\Lambda' \Lambda J)_{KQ}^\dagger \rangle D(0 \beta \alpha)_{\Lambda' -\Lambda, Q}^{(K)} \end{aligned}$$

where  $Q'$  is fixed by  $Q' = \Lambda' - \Lambda$  and  $K$  must satisfy the conditions  $K \geq \Lambda' - \Lambda$  and  $K \leq 2J$ . The hermiticity condition (2.12) and (4.37) yields

$$\langle 0 \beta \alpha | \rho(\Lambda \Lambda') | 0 \beta \alpha \rangle = \langle 0 \beta \alpha | \rho(\Lambda' \Lambda) | 0 \beta \alpha \rangle^*$$

The probability density  $W(\gamma \beta \alpha)$  for the total sample (that is, independent of  $\Lambda$ ) is given by the relation

$$W(\gamma \beta \alpha) = \sum_{\Lambda} \langle 0 \beta \alpha | \rho(\Lambda) | 0 \beta \alpha \rangle$$

which gives

$$W(\beta\alpha) = \frac{2J+1}{(4\pi)^{1/2}} \sum_{KQ\Lambda} (-1)^{J-\Lambda} \begin{pmatrix} J & J & K \\ \Lambda & -\Lambda & 0 \end{pmatrix} \left\langle T(\Lambda J)_{KQ}^\dagger \right\rangle Y(\beta\alpha)_{KQ} \quad (7.93)$$

For sharp  $\Lambda$  (7.93) reduces to (7.63).

### 7.7.3.2 States with Definite Parity as Basis Set

It is sometimes more convenient to use the states (7.79) with definite parity as basis instead of using the set  $|\Lambda\rangle|\Lambda JM\rangle$  with definite  $\Lambda$ . Allowing for coherent excitation of the nearly degenerate states with  $\epsilon = \pm 1$ , we use the set of all relevant density matrix elements  $\langle \Lambda JM'\epsilon'|\rho|\Lambda JM\epsilon\rangle$  (with  $\Lambda = |\Lambda|$ ) to characterize the molecular ensemble. These elements can be transformed back into the elements  $\langle \Lambda' JM'|\rho|\Lambda JM\rangle$  by using (7.79).

To keep the following discussion simple we will assume that the value of  $|\Lambda|$  is fixed. We normalize the density matrix according to the condition

$$\text{tr } \rho = \sum_{M\epsilon} \langle \Lambda JM\epsilon|\rho|\Lambda JM\epsilon\rangle = 1 \quad (7.94)$$

It follows that  $\Sigma_M \langle \Lambda JM\epsilon|\rho|\Lambda JM\epsilon\rangle$  is equal to the probability of finding a molecule in a state with parity index  $\epsilon$ . For any pair  $\epsilon', \epsilon = \pm 1$  we define state multipoles by the expression

- $\langle T(\epsilon'\epsilon J^\dagger)\rangle_{KQ}$

$$= \sum_{M'M} \langle \Lambda JM'\epsilon'|\rho|\Lambda JM\epsilon\rangle (-1)^{J-M'} (2K+1)^{1/2} \begin{pmatrix} J & J & K \\ M' & -M & -Q \end{pmatrix} \quad (7.95)$$

(See for example [Dellen et al. \(1995\)](#). Multipoles with  $\epsilon' = \epsilon$  have been discussed by [Alexander and Davis \(1983\)](#).) These tensors  $\left\langle T(\epsilon J)_{KQ}^\dagger \right\rangle$  characterize the anisotropy of the angular momentum distribution for molecules in states with the corresponding parity index  $\epsilon$ . In particular, we have

$$\left\langle T(\epsilon J)_{00}^\dagger \right\rangle = \left( \frac{1}{2J+1} \right)^{1/2} \sum_M \langle \Lambda JM\epsilon|\rho|\Lambda JM\epsilon\rangle \quad (7.96a)$$

which shows that the multipoles with  $K = 0$  and sharp  $\epsilon$  are proportional to the probability of finding a molecule in the corresponding state.

We will now discuss the physical importance of the multipoles with  $\epsilon' = -\epsilon$ . Let us take the tensors with  $K = 1$  as an example and compare the transformation properties of the multipoles  $\left\langle T(\epsilon J)_{1Q}^\dagger \right\rangle$  with sharp  $\epsilon$  with the interference

parameters  $\langle T(\epsilon' \epsilon J)_{1Q}^\dagger \rangle$  with  $\epsilon' = -\epsilon$ . The three components  $\langle T(\epsilon J)_{1Q}^\dagger \rangle$  transform as components of an *axial* vector under reflections and are proportional to the expectation value  $\langle J_Q \rangle$  of the angular momentum vectors as discussed in Sect. 4.3.3. The multipoles  $\langle T(\epsilon' \epsilon J)_{1Q}^\dagger \rangle$  with  $\epsilon' = -\epsilon$  transform as components of a *polar* vector [as follows, for example, from (7.98)]. These parameters are related to the coherence between states with opposite parity and are proportional to the mean value  $\langle D_Q \rangle$  of the electric dipole moment  $\mathbf{D}$  induced during the excitation:

$$\langle D_Q \rangle \sim \text{Re}[\langle T(\epsilon' \epsilon J)_{1Q}^\dagger \rangle \langle J \epsilon || D || J \epsilon' \rangle] \quad (7.97)$$

with  $\epsilon' = +1$ ,  $\epsilon = -1$ , and where the last term is the reduced matrix element of  $D_Q$ , and  $\text{Re}$  denotes the real part (Dellen et al. 1995). This relation is completely similar to the corresponding *sp*-coherence terms for atomic hydrogen.

In conclusion, during the excitation process a certain anisotropy will be created for  $\mathbf{J}$ ,  $\mathbf{d}$ , and for the distribution of the electronic orbitals. The full set of state multipoles (7.95) characterizes these anisotropies and is a measure of the corresponding stereodynamical effects produced during the excitation. As an example let us briefly consider excitation by electron impact, assuming an initial isotropic ensemble of molecules. Here, a well-defined plane (scattering plane) is defined by the incoming and scattered electrons relative to which all vectors relevant for the process can be measured. Invariance with respect to reflection in the scattering plane requires the condition

- $\langle T(\epsilon' \epsilon J)_{KQ}^\dagger \rangle = \epsilon' \epsilon (-1)^{K+Q} \langle T(\epsilon' \epsilon J)_{K-Q}^\dagger \rangle$  (7.98)

Numerical  $R$  matrix calculations have been performed for the state multipoles for CO excitation. The results show that a considerable degree of anisotropy is created during the collision (Dellen et al. 1995).

#### 7.7.4 Vector Correlations. Analysis of Emitted Light

A method of measuring the orientation and alignment tensors (and obtaining information on the stereodynamics of the excitation process) is to analyze the light emitted by the excited molecules (or molecular fragments) in the subsequent decay. The rotational polarization of the excited molecules is related to the correlations between the vectors  $\mathbf{k}_0$ ,  $\mathbf{k}_1$ , and  $\mathbf{J}$ , where  $\mathbf{k}_0$  and  $\mathbf{k}_1$  are the initial and final relative momenta of molecules and projectiles in the excitation process respectively, and  $\mathbf{J}$  denotes the angular momentum vector of the final product of interest.

If only  $\mathbf{k}_0$  and  $\mathbf{k}_1$  are measured then the final vector  $\mathbf{k}_1$  is azimuthally symmetric about the initial vector  $\mathbf{k}_0$  (if the initial molecules have an isotropic distribution of

angular momenta). Likewise, the distribution of the final  $\mathbf{J}$  vectors of the observed molecules (or fragments) is axially symmetric about  $\mathbf{k}_0$  if  $\mathbf{k}_1$  is not measured, that is, if only the emitted light is observed without detecting the scattered projectiles. Because of the azimuthal symmetry only multipoles with  $Q = 0$  contribute (as discussed in Sect. 4.5.2).

In order to determine the triple vector correlation among  $\mathbf{k}_0$ ,  $\mathbf{k}_1$ , and  $\mathbf{J}$  one has to measure the product vectors  $\mathbf{k}_1$  and  $\mathbf{J}$  simultaneously. This can be achieved by coincidence experiments where the final molecules of interest and the emitted photons are detected in coincidence. In these experiments only a subset of excited molecules is observed (corresponding to the selected  $\mathbf{k}_1$  vector). The  $\mathbf{J}$  vectors of this subset will not have azimuthal symmetry about  $\mathbf{k}_0$ , and state multipoles with  $Q \neq 0$  will contribute to the characterization of the subset of interest. An increasing number of studies have addressed this aspect of inelastic collisions in atomic physics (see, for example, [Blum and Kleinpoppen 1979](#); [Andersen et al. 1988](#)) and in molecular physics (see, for example, [Simons 1987](#)). In this subsection we will outline the general theory.

Immediately after the excitation the excited molecular subensemble of interest may be characterized by the state multipoles (7.95). Using these multipoles we can obtain expressions for the angular distribution  $I(\Theta\phi)$  and polarization of the emitted light completely similar to the procedure explained in Chaps. 5 and 6.

Instead of using the Wigner–Eckart theorem (4.26) we apply the extended version (see, e.g., [Landau and Lifschitz 1965](#)):

$$\begin{aligned} \langle \Lambda_1 V_1 J_1 M_1 | d_{-Q} | \Lambda V J M \rangle &= [(2J_1 + 1)(2J + 1)]^{1/2} \begin{pmatrix} J_1 & 1 & J \\ -\Lambda_1 & -q & \Lambda \end{pmatrix} \\ &\times \begin{pmatrix} J_1 & 1 & J \\ -M_1 & -Q & M \end{pmatrix} \langle \Lambda_1 V_1 | d_{-q} | \Lambda V \rangle \end{aligned}$$

Here,  $d_Q$  and  $d_q$  are the components of the dipole moment  $\mathbf{d}$  in the laboratory and molecular system respectively (with  $q = \Lambda - \Lambda_1$  for emission processes), and  $V$  and  $V_1$  denote the vibrational quantum numbers for the initial and final states, respectively. The reduced matrix element of  $d_{-q}$  is independent of  $J$  and  $J_1$ . Furthermore, we use the relation

$$|\Lambda_1 V_1 | d_{-1} | \Lambda V \rangle = (-1)^{\Lambda_1 + \Lambda + 1} \langle -\Lambda_1 V_1 | d_q | -\Lambda V \rangle$$

[which can be derived similar to (7.103)a in Sect. 7.7.5]. Following the same procedure as in Chap. 5 we obtain, after some algebra, for the angular distribution of the emitted light for a  ${}^1\Pi \rightarrow \Sigma^+$  transition:

- $$\begin{aligned}
 I(\Theta\phi) &= \frac{C(w)}{\gamma} |\langle \Sigma^\dagger V_1 | d_{-1} | \Lambda = 1, V \rangle|^2 (-1)^{J_1+J+1} (2J+1)(2J_1+1) \\
 &\quad \times \begin{pmatrix} J_1 & 1 & J \\ 0 & -1 & 1 \end{pmatrix} (1 + (-1)^K) \cdot \sum_{KQ} (4\pi)^{1/2} \begin{pmatrix} 1 & 1 & K \\ 1 & -1 & 0 \end{pmatrix} \begin{Bmatrix} 1 & 1 & K \\ J & J & J_1 \end{Bmatrix} \\
 &\quad \times (1 - \epsilon(-1)^{J+J_1}) \left\langle T(\epsilon J)_{KQ}^\dagger \right\rangle Y_{KQ}(\Theta\phi)
 \end{aligned} \tag{7.99}$$

where  $C(w)$  is given by (5.9), and  $\gamma$  is the lifetime of the excited state. In deriving (7.99) we have assumed that condition (7.98) is satisfied.

Only terms with  $K = 0$  and  $K = 2$  contribute to (7.99). Of particular interest is the fact  $1 - \epsilon(-1)^{J+J_1}$  which follows from parity conservation in the decay. As discussed in Sect. 7.7.2 the parity in the initial state is  $\epsilon(-1)^J$ . The parity of the final  $\Sigma^+$ -state is  $(-1)^{J_1}$ . Since the dipole moment has negative parity we obtain the condition  $\epsilon(-1)^J = (-1)^{J_1+1}$ . The factor  $1 - \epsilon(-1)^{J+J_1}$  vanishes therefore for parity forbidden transitions. In particular, for  $J_1 = J$ , only multipoles with  $\epsilon = -1$  contribute to (7.99). The angular distribution depends only on the tensor components with  $\epsilon = +1$  if  $J_1 = J \pm 1$ . This result that the spectroscopic  $P, Q, R$ -branches probe uniquely one or the other  $\Lambda$ -doublet component is well known in molecular physics. Similar results hold for the Stokes parameters. Due to parity conservation the coherence terms  $\left\langle T(\epsilon' \epsilon J)_{KQ}^\dagger \right\rangle$  do not contribute to the angular distribution (7.99). These parameters, describing the coherence between states with opposite parity, can be measured by observing the emitted light in the presence of an external electric field. This is similar to the determination of the  $sp$ -coherence terms in atomic physics.

Let us specialize to an axially symmetric excitation process, taking the initial wave vector  $\mathbf{k}_0$  as quantization axis. Consequently, only cylindrically symmetric multipoles with  $Q = 0$  are nonvanishing. The linear polarization of the emitted light is then determined by the Stokes parameters  $\eta_3$  [ $\eta_1$  vanishes as follows from an inspection of (6.1c)]. Similar to the derivation of (7.99) we obtain

$$I\eta_3 = W(J_1 J) \left( \frac{3}{2} \right)^{1/2} (-1)^{J+J_1} \begin{Bmatrix} 1 & 1 & 2 \\ J & J & J_1 \end{Bmatrix} \left\langle T(\epsilon J)_{20}^\dagger \right\rangle \sin^2 \Theta \tag{7.100a}$$

with  $\epsilon = +1$  for the  $P, R$  branches, and  $\epsilon = -1$  for the  $Q$  branch.  $I$  is the intensity (7.99). The factor  $W(J_1 J)$  is defined by the expression

$$W(J_1 J) = \frac{C(\omega)}{\gamma} |\langle \Sigma^\dagger V_1 | d_{-1} | \Lambda = 1, V \rangle|^2 (2J+1)(2J_1+1) \begin{pmatrix} J_1 & 1 & J \\ 0 & -1 & 1 \end{pmatrix}^2$$

Equations 7.99 and 7.100a can be utilized to design an experiment that measures the alignment parameter. The most common method is to detect light emitted at an angle  $\Theta = \pi/2$  with respect to the  $z$  axis. The azimuthal angle  $\varphi$  is then irrelevant and we obtain from (7.99) that

$$I = W(J_1 J) \left[ \frac{2 \langle T(\epsilon J)_{00}^\dagger \rangle}{3(2J+1)^{1/2}} + \frac{(-1)^{J+J_1}}{6^{1/2}} \left\{ \begin{matrix} 1 & 1 & 2 \\ J & J & J_1 \end{matrix} \right\} \langle T(\epsilon J)_{20}^\dagger \rangle \right] \quad (7.100b)$$

with  $\Theta = \pi/2$ .

The light intensities at two settings of a linear polarizer are then measured in order to determine  $\langle T(\epsilon J)_{KQ}^\dagger \rangle$ , for example,  $I_{\parallel}$  and  $I_{\perp}$ , where  $I_{\parallel}(I_{\perp})$  denotes the emitted intensities of the light which has passed through a linear polarizer with transmission axis parallel (perpendicular) to  $z$ . The polarization ratio  $P$  is defined by (6.11) and (6.12):

$$P = \frac{I_{\parallel} - I_{\perp}}{I_{\parallel} + I_{\perp}} = \frac{I \eta_3}{I} \quad (7.100c)$$

Combining (7.100a)–(7.100c) we obtain

$$P = \frac{(-1)^{J+J_1} \left\{ \begin{matrix} 1 & 1 & 2 \\ J & J & J_1 \end{matrix} \right\} \left( \frac{3}{2} \right)^{1/2} \langle T(\epsilon J)_{20}^\dagger \rangle}{2 \langle T(\epsilon J)_{00} \rangle + \frac{(-1)^{J+J_1}}{6^{1/2}} \left\{ \begin{matrix} 1 & 1 & 2 \\ J & J & J_1 \end{matrix} \right\} \langle T(\epsilon J)_{20}^\dagger \rangle} \quad (7.100d)$$

which should be compared with (6.14).

It is convenient to normalize according to  $\text{tr } \rho(\epsilon) = 1$ , which gives  $\langle T(\epsilon J)_{00} \rangle = 1/(2J+1)^{1/2}$ . Introducing the Fano–Macek parameter  $A_0$  by applying (4.85) and (4.86), substituting the numerical value of the  $6j$  symbol, and taking the high- $J$  limit, we obtain

$$P = \frac{3A_0}{4 + A_0}$$

for the  $Q$  branch ( $\epsilon = -1$ ), and

$$P = \frac{3A_0}{8 - A_0}$$

for the  $P, R$  branches ( $\epsilon = +1$ ). Measurements of  $P$  allows therefore the determination of the alignment parameter.

Another interesting polarization ratio is the expression

$$R = \frac{I_{\parallel} - I_{\perp}}{I_{\parallel} + 2I_{\perp}}$$

where the denominator is given by

$$I_{\parallel} + 2I_{\perp} = \frac{W(J_1 J) \langle T(\epsilon J)_{00} \rangle}{(2J + 1)^{1/2}}$$

which follows from (6.10), (7.100a), and (7.100b). In the high- $J$  limit we substitute the semiclassical expression (7.9) for  $\langle T(\epsilon J)_{20} \rangle$  and obtain

$$R = \langle P_2(\cos \Theta_J) \rangle_{\epsilon=-1}$$

for the  $Q$  branch and

$$R = -\frac{1}{2} \langle P_2(\cos \Theta_J) \rangle_{\epsilon=+1}$$

for the  $P, R$  branches. The mean values of the legendre polynomial express the correlation between  $\mathbf{k}_0$  and  $\mathbf{J}$ . The result for the  $\epsilon = -1$  level would be twice as much as for the  $\epsilon = +1$  state if the rotational alignment would be the same. This is in accordance with the qualitative arguments given at the end of Sect. 7.7.2.

We note that the determination of multipoles of rank  $K > 2$  can be achieved by analyzing laser-induced fluorescence light (up to  $K = 4$ ). For a detailed discussion we refer to the papers by Case et al. (1978) and by Green and Zare (1983), where many examples can be found.

Finally, we refer briefly to the electron impact excitation of molecules. Here, orientation and alignment parameters have been measured for various  $H_2$  transitions by McConkey and his group (see, for example, Khakoo and McConkey 1987, and references therein), and calculated numerically by Meneses et al. (1995 and references therein). Numerical results for the multipoles  $\langle T(\epsilon J)_{KQ}^{\dagger} \rangle$  and for the coherence terms  $\langle T(\epsilon' \epsilon J)_{KQ}^{\dagger} \rangle$  have been reported by Dellen et al. (1995) for CO excitations. The results show that a considerable degree of anisotropy is created during the collision. In particular, the tensors  $\langle T(\epsilon J)_{KQ}^{\dagger} \rangle$  differ considerably for the two  $\Lambda$ -doublet states.

### 7.7.5 Photoabsorption and Photofragmentation

We will first consider absorption of linearly polarized light by diatomic molecules initially in a  $\Sigma^+$  state. The molecules may be in the gas phase with an initially isotropic axes distribution. We will assume that the rotational structure is not resolved and denote the state of a molecule with electronic quantum number  $\Lambda$  and instantaneous axis distribution  $\mathbf{n}$  ( $z'$  direction) by  $|\Lambda \mathbf{n}\rangle$ , suppressing the dependence on the vibrational quantum number. Dipole selection rules restrict the excited electronic states to either  $\Sigma$  states ( $\Lambda = 0$ ) or  $\Pi$  states ( $|\Lambda| = 1$ ). We remember that the third Euler angle  $\gamma$  has been set to zero so that molecular  $x'$  axis lies in the  $z - z'$  plane (Fig. 7.4).

Instead of using eigenstates  $|\pm \Lambda\rangle$  of the electronic orbital angular momentum operator  $L_z$  we will choose as basis states the linear combinations (7.76) (for  $|\Lambda| = 1$ ):

$$|II_{x'}\rangle = -\frac{1}{\sqrt{2}}[|\Lambda = +1\rangle - |\Lambda = -1\rangle] \quad (7.101a)$$

$$|II_{y'}\rangle = +\frac{i}{\sqrt{2}}[|\Lambda = +1\rangle + |\Lambda = -1\rangle] \quad (7.101b)$$

$|\Pi_{x'}\rangle$  is directed along  $x'$  and remains invariant under reflections in the molecular  $x' - z'$  plane, whereas  $|\Pi_{y'}\rangle$  is directed along the  $y'$  axis and changes its sign:

$$\sigma_{x'z'}|\Pi_{x'}\rangle = |\Pi_{x'}\rangle, \quad \sigma_{x'z'}|\Pi_{y'}\rangle = -|\Pi_{y'}\rangle \quad (7.102)$$

where  $\sigma_{x'z'}$  denotes the corresponding reflection operator.

Absorption of linearly polarized light (with  $\mathbf{E}$  parallel to  $z$ ) by a molecule with instantaneous axis direction  $\mathbf{n}$  and which undergoes a transition  $|\Sigma_0\mathbf{n}\rangle \rightarrow |f\mathbf{n}\rangle$  is described by matrix elements  $\sim \langle f\mathbf{n}|d_z|\Sigma_0\mathbf{n}\rangle$ , where  $|f\rangle$  denotes the final and  $|\Sigma_0\rangle$  the initial electronic state, and  $d_z$  denotes the relevant dipole operator. For simplicity we will assume a  $\Sigma^+$  state as initial state which remains invariant under reflections.

The ensemble of excited molecules is axially symmetric around the  $\mathbf{E}$  direction and invariant with respect to reflections in any plane though  $z$ . In particular, the  $z - z'$  plane is a symmetry plane for any orientation of  $z'$ . Since  $d_z$  remains invariant and since the  $z - z'$  plane coincides with the molecular  $x' - z'$  plane we have

$$\sigma_{x'z'}d_z\sigma_{x'z'} = d_z$$

Using (7.102) we obtain in particular

$$\begin{aligned} \langle \Pi_{y'}\mathbf{n}|d_z|\Sigma_0\mathbf{n}\rangle &= \langle \Pi_{y'}\mathbf{n}|\sigma_{x'z'}d_z\sigma_{x'z'}|\Sigma_0\mathbf{n}\rangle \\ &= -\langle \Pi_{y'}\mathbf{n}|d_z|\Sigma_0\mathbf{n}\rangle \end{aligned} \quad (7.103)$$

for any orientation of  $\mathbf{n}$ . Hence, the  $|\Pi_{y'}\rangle$  orbital cannot be excited.

Taking these results into account, we obtain for the (unnormalized) probability density  $W(\beta\alpha)'$  that a molecule with instantaneous axis in the  $\beta - \alpha$  direction absorbs a photon:

$$W(\beta\alpha)' = C(w)[|\langle \Sigma\mathbf{n}|d_z|\Sigma_0\mathbf{n}\rangle|^2 + |\langle \Pi_{x'}\mathbf{n}|d_z|\Sigma_0\mathbf{n}\rangle|^2]$$

where  $C(w)$  is given by (5.9).

Transformation to the molecular system (see Fig. 7.4) yields

$$d_z = d_{z'} \cos \beta - d_{x'} \sin \beta \quad (7.104)$$

Considering reflections in the molecular  $z' - y'$  plane we obtain the relations

$$\begin{aligned}\sigma_{z'y'}d_{z'y'}\sigma_{z'y'} &= d_{z'}, & \sigma_{z'y'}d_{x'}\sigma_{z'y'} &= -d_{x'} \\ \sigma_{z'y'}|\Pi_{x'}\rangle &= -|\Pi_{x'}\rangle, & \sigma_{z'y'}|\Pi_{y'}\rangle &= |\Pi_{y'}\rangle\end{aligned}$$

Substitution of these relations into the relevant matrix elements yields

$$\langle \Pi_{x'} | d_{z'} | \Sigma_0 \rangle = \langle \Sigma | d_{x'} | \Sigma_0 \rangle = 0 \quad (7.105)$$

Taking (7.104) and (7.105) into account we obtain from (7.103):

$$W(\beta\alpha)' = C(w)[|M(\Sigma)|^2 \cos^2 \beta + |M(\Pi)|^2 \sin^2 \beta] \quad (7.106)$$

which is independent of the azimuth angle  $\alpha$  of  $\mathbf{n}$ . We have used the abbreviations

$$|M(\Sigma)|^2 = |\langle \Sigma | d_{z'} | \Sigma_0 \rangle|^2, \quad |M(\Pi)|^2 = |\langle \Pi_{x'} | d_{x'} | \Sigma_0 \rangle|^2$$

for the absorption strengths.

Equation 7.106 expresses the relevant geometrical correlations between the transition dipole moment  $\mathbf{d}$ , the molecular axis  $\mathbf{n}$ , and the electric vector  $\mathbf{E}$ . The first term in (7.106) describes a  $\Sigma - \Sigma$  transition where  $\mathbf{d}$  is directed parallel to the molecular axis (parallel transition). The second term in (7.106) refers to a  $\Sigma - \Pi$  transition with  $\mathbf{d}$  perpendicular to  $\mathbf{n}$  (perpendicular transition). Photoabsorption to the  $\pi$ -excited states preferentially creates excited molecules with axes perpendicular to  $\mathbf{E}$ , whereas for a  $\Sigma - \Sigma$  transition light will be predominantly absorbed by molecules with axes parallel to the electric vector. The independence on the azimuth angle  $\alpha$  reflects the axial symmetry with regard to  $\mathbf{E}$ .

Expressing the trigonometric functions in (7.106) in terms of the Legendre polynomial  $P_2(\cos \beta)$ ,

$$\cos^2 \beta = \frac{1}{3}(1 + 2P_2), \quad \sin^2 \beta = \frac{2}{3}(1 - P_2)$$

we obtain finally for the (unnormalized) probability that a molecule with axes along the  $\beta - \alpha$  direction absorbs a photon

- $W(\beta\alpha)' = \frac{C(w)}{3}[|M(\Sigma)|^2 + 2|M(\Pi)|^2][1 + \beta_m P_2(\cos \beta)] \quad (7.107a)$

where the asymmetry parameter  $\beta_m$  is defined by the expressions (Dill et al. 1980)

- $\beta_m = \frac{2(|M(\Sigma)|^2 - |M(\Pi)|^2)}{|M(\Sigma)|^2 + 2|M(\Pi)|^2} \quad (7.107b)$

The asymmetry parameter measures the difference between the photoabsorption strengths.  $\beta_m$  is equal to +2 for a parallel transition and to -1 for a perpendicular

transition. The axis distribution  $W(\beta\alpha)'$  is aligned but not oriented in accordance with the general symmetry requirements of Sect. 4.5.2.

Equation 7.107 apply also to photofragmentation of molecules under axial-recoil conditions, that is, if the dissociation occurs sufficiently promptly that the fragments have the same direction as the molecular axis at the time of photoabsorption. The probability of observing the fragment of interest in a direction specified by  $\beta$  and  $\alpha$  is then given by (7.107a).

The discussion of this simple case exhibits the nature of the correlation between the transition dipole moment  $\mathbf{d}$  and the direction  $\mathbf{v}$  of the observed fragment. The essential point is that, according to (7.103), only the  $z$  component of  $\mathbf{d}$  contributes. If the transition is parallel then molecules with axis along  $\mathbf{E}$  will preferentially dissociate, and the fragments will be found preferentially in the  $\mathbf{E}$  direction. For a perpendicular transition the fragmentation peaks at right angles to  $\mathbf{E}$ . In the first case we have  $\beta_m = 2$  and  $W(\beta) \sim \cos^2 \beta$ , and in the second case  $\beta_m = -1$  and  $W(\beta) \sim \sin^2 \beta$ . Hence, because  $\mathbf{d}$  is aligned by the dissociating light,  $\mathbf{v}$  will also be aligned. This correlation between  $\mathbf{d}$  and  $\mathbf{v}$  results therefore in an anisotropic angular distribution of the fragments, even for an initially isotropic molecular ensemble, as was first pointed out by [Zare and Herschbach \(1963\)](#).

An important consequence is that the fragment angular distribution provides information about the electronic symmetry  $\Lambda$  of the dissociating state if that of the initial molecular state is known. If a fragment distribution  $W(\beta) \sim \cos^2 \beta$  is found experimentally then the parent molecules dissociate from a  $\Sigma$  state, and in case of  $W(\beta) \sim \sin^2 \beta$  the molecules dissociate from a  $\Pi$  state. Thus, molecular photofragmentation provide us with a useful spectroscopic tool.

Our discussion of photofragmentation covers only the most elementary aspects of the theory. For more information we refer to the review articles by [Green and Zare \(1982\)](#), [Houston \(1987\)](#), [Beswick \(1993\)](#), and in particular to the book by [Schinke \(1993\)](#) and references therein.

## 7.8 Dynamical Stereochemistry

### 7.8.1 General Expressions and Definition of Steric Factors

The dependence of chemical reactivity on the orientation and alignment of the reactants is a key issue in stereodynamics. Extensive investigations of the steric effects, that is, the difference between the reaction cross sections for favorable and unfavorable oriented or aligned molecules, relative to the cross section for isotropic ensembles, have been performed. A typical steric information is the “head-versus-tail” asymmetry of reactivity. For example, it was found that in the processes  $\text{K} + \text{CH}_3\text{I} \rightarrow \text{KI} + \text{CH}_3$  products are more likely to form if the atoms approach the iodine end of the molecule (“head”) than if they encounter the  $\text{CH}_3$  end (“tail”). In general, the information gained from observing the products’ angular distribution

and also their polarization has led to new insights into the details of chemical reactions. For the history of the subject and a review of recent developments, we refer to the articles by [Bernstein et al. \(1987\)](#), [Simons \(1987\)](#), [Levine and Bernstein \(1987\)](#), and [Loesch \(1995\)](#).

In the present subsection we will derive some basic formulas useful for the description of steric effects and for an exploitation of the spatial aspects of molecular processes. Our discussion will apply to elastic and inelastic collisions between polarized freely rotating molecules and electrons or atoms, and to reactive scattering processes like  $\text{Li} + \text{HF} \rightarrow \text{LiF} + \text{H}$ . We will first concentrate on the angular distribution of the final reagents (like the H atom in the Li–HF reaction). The polarization of the final particles will be considered in Sect. 7.8.3. In order to have a well-defined picture in mind we will consider processes with diatomic molecules, initially in their electronic ground state, although our results will also apply to symmetric tops.

Our key approximation is the following. The collision time between projectiles and molecules is assumed to be much shorter than the average rotation time of the free molecule. The incoming projectile “sees” therefore the instantaneous axis distribution of the molecular beam and is scattered by a molecule with fixed axis direction. The differential cross section of this “elementary” process is then calculated first and then averaged over the given instantaneous axis distribution. Trajectory calculations show that, for all but the lowest energy regime, this approximation is quite reasonable (see, for example, [Blais et al. 1985](#)). A more general approach without using this approximation is outlined in Sects. 7.8.3 and 7.8.4.

The prerequisite for measuring steric effects is the preparation of an anisotropic angular momentum or, equivalently, axes distribution of the molecular ensemble prior to the collision. We will describe this process in a coordinate system with axes  $x, y, z$  (*director system*). If the process by which the molecules have been prepared possesses an axis of symmetry, we will choose this as  $z$  axis. Examples are the direction of a static electric field if the electric focusing technique is applied. In laser pumping experiments with linearly polarized light the molecular angular momenta and axes will be symmetrically distributed around the electric field vector of the light. In free jet expansions the beam direction will be an axis of symmetry.

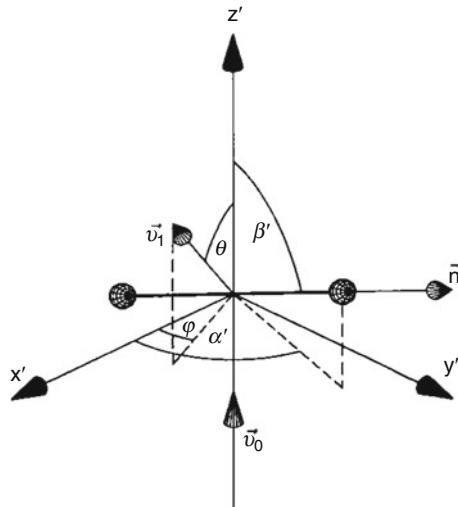
The probability density of finding a molecule with an instantaneous axis  $\mathbf{n}$  pointing in  $\beta - \alpha$  direction is given by the corresponding function  $W(\beta\alpha)$  where  $\beta$  is the polar angle of  $\mathbf{n}$  and  $\alpha$  is the azimuth in the director frame (Fig. 7.4). The distribution function  $W(\beta\alpha)$  can be characterized in terms of state multipoles [(7.23) for diatomics or (7.63) for symmetric tops] or in terms of the corresponding order parameters [(7.28)]. Let us start with the latter choice and write

$$W(\beta\alpha) = \sum_{KQ} \langle Y_{KQ}^* \rangle Y(\beta\alpha)_{KQ} \quad (7.108)$$

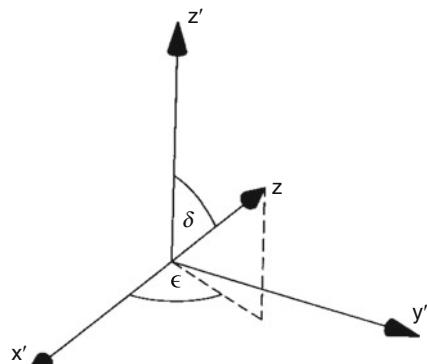
Next we will describe the reaction between molecules and projectiles. The basic theoretical quantity is the differential cross section in the center-of-mass frame. We introduce therefore a coordinate frame with  $x'y'z'$  axes where  $z'$  is parallel to the

initial relative velocity  $\mathbf{v}_0$  (assuming very narrow velocity and angular spreads of the beams).  $x'$  and  $y'$  are chosen perpendicular to  $z'$  and to each other (*collision system*). The scattering angle (that is, the angle between initial and final relative velocities  $\mathbf{v}_0$  and  $\mathbf{v}_1$ ) will be denoted by  $\Theta$ , and the azimuth angle of  $\mathbf{v}_1$  in the collision system will be denoted by  $\phi$ .  $\phi$  would be zero if the scattering plane ( $\mathbf{v}_0 - \mathbf{v}_1$  plane) were chosen as  $x' - z'$  plane (see Fig. 7.6). Polar and azimuth angle of the molecular axes in the collision system will be denoted by  $\beta'$  and  $\alpha'$  respectively (Fig. 7.6).  $\beta'$  is then the angle of attack. The relation between director and collision system is fixed by the three Euler angles  $\epsilon$ ,  $\delta$ ,  $\chi$ .

Here,  $\delta$  and  $\epsilon$  are polar and azimuth angles of  $z$  in the  $x'y'z'$  system respectively (Fig. 7.7). The third Euler angle  $\chi$  can always be set to zero if  $z$  is a symmetry axis of the molecular sample. In particular,  $\delta$  is the angle between  $z$  and  $\mathbf{v}_0$ , for example, between a focusing electric field and the relative initial velocity. If the molecular axes are symmetrically distributed around  $z$  with a positive alignment then  $\delta$  can be



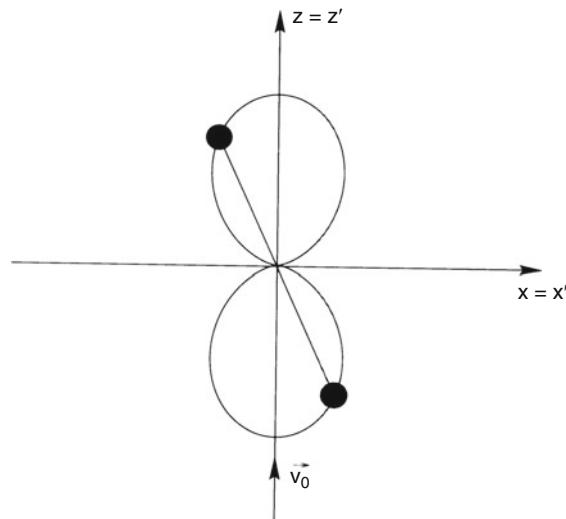
**Fig. 7.6** Polar angle ( $\beta'$ ) and azimuth angle ( $\alpha'$ ) of a molecular axis, and angles  $\Theta$  and  $\phi$  of  $\mathbf{V}_1$  in the collision system



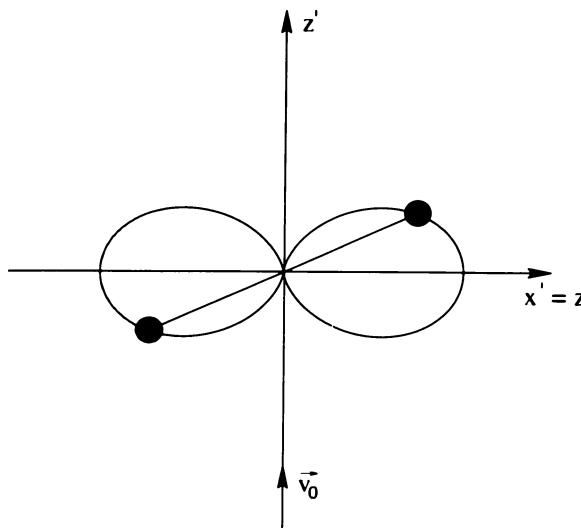
**Fig. 7.7** Relation between director system ( $xyz$ ) and collision system ( $x'y'z'$ )

considered as a mean angle of attack (see Fig. 7.9 below).  $\epsilon$  is the angle between  $z$  and the  $x' - z'$  plane and, considering the  $\epsilon$ -dependence of observables, will allow us to describe the “azimuthal steric effects.” If  $\chi = 0$  then the  $x$  axis lies within the  $z - z'$  plane.

As stated above, the elementary process is a reaction between the incoming projectile and a molecule whose instantaneous axis direction is specified by angles  $\beta$  and  $\alpha$  in the director frame, and  $\beta'$  and  $\alpha'$  in the collision system. The relevant differential cross section is most conveniently calculated in the collision



**Fig. 7.8** Geometry of experiment (i) (“end-side” collision: mean angle of attack  $\delta = 0$ )



**Fig. 7.9** Geometry of experiment (ii) (“broadside” collision: mean angle of attack  $\delta = \pi/2$ )

system (center-of-mass system) and will be denoted by  $\sigma(\beta'\alpha'\Theta\phi)$ , suppressing the dependence on other variables for brevity.

The experimental accessible differential cross section is  $\sigma(\Theta\phi)$ , which is obtained by multiplying  $\sigma(\beta'\alpha'\Theta\phi)$  with the probability density  $W(\beta'\alpha')$  of finding a molecule with axis pointing in the  $\beta' - \alpha'$  direction in the  $x'y'z'$  system and integrating over the axes distribution; that is,

$$\sigma(\Theta\phi) = \int_0^{2\pi} d\alpha' \int_0^\pi d\beta' \sin \beta' W(\beta'\alpha') \sigma(\beta'\alpha'\Theta\phi) \quad (7.109)$$

For inelastic collisions a sum over (unobserved) degenerate states must be included.

Equation 7.109 is our basic “ansatz.” We emphasize, however, that this “ansatz” cannot be applied if the initial molecules are in electronically excited and degenerate states. In such cases the coherence between the states must be taken into account and the corresponding density matrix elements would occur in (7.109) instead of the cross section.

In order to relate  $W(\beta'\alpha')$  to  $W(\beta\alpha)$  we write  $W(\beta'\alpha')$  in a form similar to (7.108):

$$W(\beta'\alpha') = \sum_{kq} \langle Y_{kq}^* \rangle Y(\beta'\alpha')_{kq} \quad (7.110)$$

where the order parameters  $\langle Y_{kq}^* \rangle$  are defined in the  $x'y'z'$  systems

$$\langle Y_{kq}^* \rangle = \int_0^{2\pi} d\alpha' \int_0^\pi d\beta' \sin \beta' W(\beta'\alpha') Y(\beta'\alpha')_{kq}^*$$

This set is related to the parameters  $\langle Y_{KQ}^* \rangle$ , defined by (7.108), by the relation (4.41):

$$\langle Y_{kq}^* \rangle = \delta_{Kk} \sum_Q \langle Y_{KQ}^* \rangle D(\chi \delta \epsilon)_{Qq}^{(K)*} \quad (7.111)$$

which redefines the axes distribution in the collision system as

$$W(\beta'\alpha') = \sum_{KQq} \langle Y_{KQ}^* \rangle D(\chi \delta \epsilon)_{Qq}^{(K)*} (\beta'\alpha')_{Kq} \quad (7.112)$$

Combining (7.109) and (7.112) we obtain the expression for the differential cross section in the form

$$\sigma(\Theta\phi) = \sum_{KQq} \langle Y_{KQ}^* \rangle D(\chi \delta \epsilon)_{Qq}^{(K)*} \int_0^{2\pi} d\alpha' \int_0^\pi d\beta' \sin \beta' Y(\beta'\alpha')_{Kq} \sigma(\beta'\alpha'\Theta\phi) \quad (7.113)$$

We note that the dependence of the cross section on the azimuth angle  $\phi$  can be given explicitly (see, for example, [Ostrawsky et al. 1995](#)) and we obtain finally

$$\begin{aligned} \sigma(\Theta\phi) = & \sum_{KQq} \langle Y_{KQ}^* \rangle D(\chi\delta\epsilon)_{Qq}^{(K)*} e^{i\phi q} \\ & \int_0^{2\pi} d\alpha' \int_0^\pi d\beta' \sin\beta' Y(\beta'\alpha')_{Kq} \sigma(\beta'\alpha'\Theta\phi = 0) \end{aligned} \quad (7.114)$$

In these and the following formulas we will suppress the dependence of  $\sigma(\Theta\phi)$  on the Euler angles  $\chi, \delta, \epsilon$ . The information on the stereodynamics of the reaction is given by the integral in (7.114) and we rewrite this equation in the form

$$\bullet \quad \sigma(\Theta\phi) = \sum_{KQq} \langle Y_{KQ}^* \rangle D(\chi\delta\epsilon)_{Qq}^{(K)*} e^{i\phi q} I(\Theta)_{Kq} \quad (7.115)$$

where the “steric factor”  $I(\Theta)_{Kq}$  is defined by the integral in (7.114).

The advantage of (7.114) and (7.115) is that geometrical and dynamical factors are separated. The instantaneous axis distribution of the initial molecular ensemble is characterized by the order parameters  $\langle Y_{KQ}^* \rangle$  in the director system, which allows us to take full advantage of the symmetries of the preparation process.

The differential cross sections  $\sigma(\beta'\alpha'\Theta\phi)$  and the steric factors refer to the collision system ( $\mathbf{v}_0$  as quantization axis), which is convenient for numerical calculations. The elements  $D(\chi\delta\epsilon)_{Qq}^{(K)}$  describe the geometry of the experiment, that is, the orientation of the molecular sample relative to the incoming relative velocity  $\mathbf{v}_0(z')$  and the  $x' - y'$  axes.  $\delta$  is the angle between  $z$  and  $\mathbf{v}_0$  (Fig. 7.7). If the initial molecular axes are symmetrically distributed around  $z$ , and if the alignment is positive,  $\delta$  can be considered as an average angle of attack.  $\epsilon$  is the angle between  $z$  and the  $x' - z'$  plane. By varying  $\epsilon$  the azimuth steric dependence of observables can be studied ([Stolte 1982](#)). The angle  $\chi$  is superfluous if  $z$  is a symmetry axis of the molecular axes distribution (see Sect. 7.6.1).  $\Theta$  and  $\phi$  are scattering angle and azimuth angle of the detected particle respectively. The  $\phi$  dependence is given explicitly by the exponential factor in (7.115).  $\phi$  would be zero if the velocity of the detected particle were within the  $x' - z'$  plane.

The sums in (7.115) run over all  $Q$  and  $q$  values satisfying  $-K \leq Q \leq K$  and  $-K \leq q \leq K$ . If all molecules in the sample of interest have the same sharp value  $J$  of angular momentum then  $K$  is restricted by the condition  $K \leq 2J$ . Often  $K$  is further limited by symmetry requirements.

Thus far we have expressed  $\sigma(\Theta\phi)$  in terms of the order parameters specifying the instantaneous initial axis distribution. One can also consider the dependence of  $\sigma(\Theta\phi)$  on the corresponding rotational polarization. This is of particular interest for ensembles with sharp  $J$  (for example, prepared by state-selective laser excitation).  $\sigma(\Theta\phi)$  can immediately be expressed in terms of the relevant state multipoles

$\langle T(J)_{KQ}^\dagger \rangle$  by substituting (7.34) into (7.115) for linear rotors, or of (7.64b) for symmetric tops. The obtained expressions allow us to study the correlation between initial and final momenta and  $\mathbf{J}$ , which involves both the scattering angle  $\Theta$  and (semiclassically) the rotational alignment angle  $\Theta_J$ . We will return to this point in Sect. 7.8.3 in more detail.

It should be noted, however, that (7.115) applies not only to ensembles with sharp  $J$  but also to ensembles of molecules with different  $J$  values [as is often the case in free jet expansion, or after applying the electric focusing method (see, for example, Volkmer et al. 1992)]. It is the instantaneous axis distribution of the *total* ensemble which is of importance for the collision, and a parametrization in terms of order parameters is then most convenient.

As stated above, our results must be modified if the rotation of the molecules during the approach motion of the projectiles cannot be neglected.

In the present subsection we have developed the theory up to (7.115). The next step would be to obtain more explicit analytical expressions for the steric factors. This can be done by applying standard techniques of scattering theory, in particular partial wave expansions, and will not be discussed here.

Finally, we give some symmetry properties of the steric factors which are useful for calculations. From the symmetry properties of the spherical harmonics follows

$$I(\Theta)_{K-q} = (-1)^q I(\Theta)_{kq}^* \quad (7.116a)$$

Furthermore, we note that the differential cross sections  $\sigma(\beta'\alpha'\Theta\phi = 0)$  refer to processes where  $\mathbf{V}_1$  lies within the  $x'-z'$  plane, and describe an “elementary collision” between projectile and, for example, a diatomic molecule with axis  $\mathbf{n}$  in the  $\beta' - \alpha'$  direction in the collision system. A reaction with a molecule oriented at angles  $\beta'$  and  $-\alpha'$  has the same probability; hence,  $\sigma(\beta', \alpha', \Theta, \phi = 0) = \sigma(\beta', -\alpha', \Theta, \phi = 0)$ . Since  $Y(\beta'\alpha')_{kq}^* = Y(\beta' - \alpha')_{kq}$ , it follows by substituting  $\alpha \rightarrow -\alpha$  in the integral in (7.114) that the steric factors are real

$$I(\Theta)_{Kq} = I(\Theta)_{kq}^* \quad (7.116b)$$

By combining (7.116a) and (7.116b) we obtain therefore

- $I(\Theta)_{Kq}^* = (-1)^q I(\Theta)_{K-q} \quad (7.116c)$

Further relations hold for center-of-mass forward and backward scattering. In these cases the cross sections  $\sigma(\beta'\alpha'\Theta\phi = 0)$  must be independent of  $\alpha'$ . The integration over  $\alpha'$  can then explicitly be performed and the integrals in (7.114) vanish unless  $q = 0$ . Hence,

- $I(0)_{Kq} = I(\pi)_{Kq} = 0 \quad (7.116d)$

if  $q \neq 0$ .

## 7.8.2 Discussion and Examples

### 7.8.2.1 Differential Cross Sections Steric Effects in Collisions

In order to make our result (7.115) more tangible we will discuss some examples of experimental interest. Let us first assume that a molecular ensemble has been prepared with an axially symmetric axis distribution. Only order parameters with  $Q = 0$  contribute then to (7.115).

Using (7.33c) and realizing that because of the axial symmetry around  $z$  the third Euler angle  $\chi$  becomes redundant and can be set to zero, we rewrite (7.115) as

$$\bullet \quad \sigma(\Theta\phi) = \sum_{Kq} \left( \frac{2K+1}{4\pi} \right)^{1/2} \langle P_K(\cos \beta) \rangle d(\delta)_{0q}^{(K)} e^{i(\phi-\epsilon)q} I(\Theta)_{Kq} \quad (7.117a)$$

$$\bullet \quad = \sum_{Kq} \langle P_K(\cos \beta) \rangle Y(\delta\epsilon)_{Kq}^* e^{i\phi q} I(\Theta)_{Kq} \quad (7.117b)$$

where we have applied (C.12) in deriving (7.117a).

By applying condition (7.116c) and (C.16c) we can rewrite (7.117a):

$$\begin{aligned} \sigma(\Theta\phi) &= \sum_K \left( \frac{2K+1}{4\pi} \right)^{1/2} \langle P_K(\cos \beta) \rangle P_K(\cos \delta) I(\Theta)_{K0} \\ &+ 2 \sum_{K,q>0} \left( \frac{2K+1}{4\pi} \right)^{1/2} \langle P_K(\cos \beta) \rangle d(\delta)_{0q}^{(K)} \cos((\phi-\epsilon)q) I(\Theta)_{Kq} \end{aligned} \quad (7.117c)$$

For forward and backward scattering (7.116d) apply. Consider, for example, backscattering in the center-of-mass system, say for rebound reactions. We obtain from (7.117c):

$$\bullet \quad \sigma(\pi) = \sum_K \left( \frac{2K+1}{4\pi} \right)^{1/2} \langle P_K(\cos \beta) \rangle P_K(\cos \delta) I(\pi)_{K0} \quad (7.118)$$

which is independent of  $\phi$  and  $\epsilon$ . This expression has a particularly simple structure. The differential cross section  $\sigma(\pi)$  is expanded in terms of Legendre polynomials of the angle  $\delta$ . For example,  $\delta$  would be zero if the  $z$  axis of the director system (for example, the direction of an orientating field) is parallel to the relative initial velocity  $\mathbf{v}_0$  (“head orientation”), and  $\delta = \pi$  if  $z$  is antiparallel to  $\mathbf{v}_0$  (“tail orientation”). The steric factors  $I(\pi)_{K0}$  can in principle be obtained by measuring the differential cross section and fitting its  $\delta$  dependence (see, for example, the review of Stolte 1982).

Expansions like (7.115) or (7.117) are particularly useful in situations where only a limited number of expansion coefficients contribute. In this case the description of

the angular dependence of the reaction products simplifies considerably. Consider, for example, a beam of molecules prepared in definite rotational states by optical pumping with linearly polarized laser light. In this case only order parameters with  $K = 0$  and  $K = 2$  and  $Q = 0$  contribute (see Sect. 7.5). We will further choose the scattering plane ( $\mathbf{v}_0 - \mathbf{v}_1$  plane) as the  $x' - z'$  plane of the collision system. The azimuth angle  $\phi$  of  $\mathbf{v}_1$  is then zero and the azimuth angle  $\epsilon$  is the angle between the  $z$  axis of the director system and the scattering plane. We will follow [Loesch and Stienkemeier \(1993\)](#) and consider the following three experimental geometries:

1.  $\mathbf{v}_0$  is parallel to the  $z$  direction of the director system (for example, parallel to the direction of an orientating electric field) and director and collision system coincide. This geometry is illustrated in Fig. 7.9a. In the figure a special axis distribution  $W(\beta\alpha) = \frac{3}{4} \cos^2 \beta$  has been assumed corresponding to  $\langle P_2 \rangle = \frac{2}{5}$  (see Fig. 7.2). The molecules are preferentially “end-side” aligned with respect to  $\mathbf{v}_0$ , and the molecules will preferentially encounter the attacking projectiles head-on. The polar angle  $\delta$  and azimuth angle  $\epsilon$  of  $z$  in the  $x'y'z'$  system are both zero,  $d(0)_{0q}^{(K)}$  vanishes except for  $q = 0$ , and (7.117) reduces to

$$\sigma_1(\Theta, \phi = 0) = \sigma_0 + \left( \frac{5}{4\pi} \right)^{1/2} \langle P_2(\cos \beta) \rangle I(\Theta)_{20} \quad (7.119a)$$

where  $\sigma_0 = (1/4\pi)^{1/2} I(\Theta)_{00}$  is the differential cross section for collisions with randomly oriented molecules.

2. We assume that the symmetry axis of the molecular axis distribution is perpendicular to  $\mathbf{v}_0$  and parallel to the  $x'$  axis (Fig. 7.9b); that is,  $z$  lies within the scattering plane. In this case we have  $\delta = \pi/2$ ,  $\epsilon = 0$ , and the molecules show “broadside” alignment relative to  $\mathbf{v}_0$ . Equation 7.117c yields

$$\begin{aligned} \sigma_2(\Theta, \phi = 0) = \sigma_0 - \frac{1}{2} \left( \frac{5}{4\pi} \right)^{1/2} \langle P_2(\cos \beta) \rangle I(\Theta)_{20} \\ + \left( \frac{15}{8\pi} \right)^{1/2} \langle P_2(\cos \beta) \rangle I(\Theta)_{22} \end{aligned} \quad (7.119b)$$

where we have inserted the explicit values

$$d\left(\frac{\pi}{2}\right)_{00}^{(2)} = -\frac{1}{2}, \quad d\left(\frac{\pi}{2}\right)_{0\pm 1}^{(2)} = 0, \quad d\left(\frac{\pi}{2}\right)_{0\pm 2}^{(2)} = \left(\frac{3}{8}\right)^{1/2}$$

Figure 7.9 illustrate the meaning of  $\delta$  as an average angle of attack.

3. In order to study the azimuthal steric effect, that is, the dependence on  $\epsilon$ , one has to consider geometries where the  $z$  axis lies outside the scattering plane. We consider the case where  $z$  is pointing along the  $y'$  axis corresponding to  $\epsilon = \pi/2$  and  $\delta = \pi/2$ .

Equation 7.117c yields

$$\begin{aligned}\sigma_3(\Theta, \phi = 0) = \sigma_0 - \frac{1}{2} \left( \frac{5}{4\pi} \right)^{1/2} \langle P_2(\cos \beta) \rangle I(\Theta)_{20} \\ - \left( \frac{15}{8\pi} \right)^{1/2} \langle P_2(\cos \beta) \rangle I(\Theta)_{22}\end{aligned}\quad (7.119c)$$

Under the experimental conditions assumed here the steric effects manifest themselves as differences between  $\sigma_0$ ,  $\sigma_1$ ,  $\sigma_2$ , and  $\sigma_3$ .

By combining (7.119) we obtain the relations (Loesch and Stienkemeier 1993)

$$\sigma_1 + \sigma_2 + \sigma_3 = 3\sigma_0 \quad (7.120a)$$

$$\sigma_2 - \sigma_3 = 2 \left( \frac{15}{8\pi} \right)^{1/2} \langle P_2(\cos \beta) \rangle I(\Theta)_{22} \quad (7.120b)$$

$$2\sigma_1 - (\sigma_2 + \sigma_3) = 3 \left( \frac{15}{4\pi} \right)^{1/2} \langle P_2(\cos \beta) \rangle I(\Theta)_{22} \quad (7.120c)$$

These expressions show that by combining the values of differential cross sections the steric factors  $I_{20}$  and  $I_{22}$  can be extracted from the measurements if the alignment is known. (A determination of  $I_{21}$  would require an experiment with  $\delta \neq 0$  and  $\delta \neq \pi/2$ .) In particular, (7.120c) gives the difference between the cross sections for “head-on” and “side-on” collisions.

By determining the difference between  $\sigma_2$  and  $\sigma_3$  the influence of the azimuthal steric dependence can be probed. Equation 7.120b shows that this azimuthal effect is proportional to  $I_{22}$ . In the geometry (ii) the molecular axes are lying preferentially within the scattering plane (assuming positive axis alignment as in Fig. 7.9b), and in case of geometry (iii) the axes are mainly aligned perpendicular to the collision plane. A positive value of  $I_{22}$  would then indicate that geometry (ii) is favored.

If the molecules would be oriented and not merely aligned one could also distinguish between the two “ends” of the molecule. Orientation is characterized by the order parameters with  $K$  odd. Orientation and alignment terms in (7.117) can be separated by reversing the direction of the symmetry axis ( $z$ ) of the molecular axis distribution (for example, by reversing the direction of an orientating electric field). The polar and azimuth angles  $\delta$  and  $\epsilon$  of  $z$  in the  $x'y'z'$  system are then transformed into  $\pi - \delta$  and  $\epsilon + \pi$  respectively. Using the symmetry properties of the spherical harmonics we obtain from (7.117b) that the terms with  $K$  odd change their sign.

### 7.8.2.2 Integrated Cross Sections

Besides the differential cross section  $\sigma(\Theta\phi)$  the total cross section  $\sigma_t$  is also of fundamental importance for collision studies. In order to obtain  $\sigma_t$  we have to integrate (7.115) over  $\Theta$  and  $\phi$ . Noting that only terms with  $q = 0$  survive the  $\phi$  integration and defining

$$I_{K0} = \int d\Theta \sin \Theta I(\Theta)_{K0}$$

we obtain

$$\sigma_t = \sum_{KQ} \langle Y_{KQ}^* \rangle D(\chi \delta \epsilon)_{Q0}^{(K)*} I_{K0} \quad (7.121)$$

If only terms with  $Q = 0$  contribute we obtain from (7.117):

$$\sigma_t = \sum_K \left( \frac{2K+1}{4\pi} \right)^{1/2} \langle P_K(\cos \beta) \rangle P(\cos \delta)_K I_{K0} \quad (7.122)$$

The total cross section for preferred head-on collisions ( $\delta = 0$ ) in case of (7.122) is

$$\sigma_{t1} = \sum_K \left( \frac{2K+1}{4\pi} \right)^{1/2} \langle P_K(\cos \beta) \rangle I_{K0}$$

For preferred side-on collision ( $\delta = \pi/2$ ) (7.122) yields

$$\sigma_{t2} = \sum_{K \text{ even}} \left( \frac{2K+1}{4\pi} \right) \langle P_K(\cos \beta) \rangle P(0)_K I_{K0}$$

where the sum includes only terms with  $K$  even. If only terms with  $K = 0$  and  $K = 2$  contribute to the molecular axis distribution we obtain

$$\sigma_{t1} - \sigma_{t2} = \frac{3}{2} \left( \frac{5}{4\pi} \right)^{1/2} \langle P_2(\cos \beta) \rangle I_{20}$$

for the difference of the cross sections for end-on and side-on collisions.

If the molecular initial ensemble is also oriented, and terms with  $K = 1$  contribute also to (7.122) we obtain for preferred head-on collisions ( $\delta = 0$ )

$$\sigma_{t4} = \sigma_{t0} + \left( \frac{3}{4\pi} \right)^{1/2} \langle P_1(\cos \beta) \rangle I_{10} + \left( \frac{5}{4\pi} \right)^{1/2} \langle P_2(\cos \beta) \rangle I_{20} \quad (7.123)$$

where  $\sigma_{t0}$  corresponds to  $K = 0$ .

The corresponding total cross section  $\sigma_{t5}$  for preferred tail-on collisions ( $\delta = \pi$ ) follows from (7.123) by changing the sign of the second term. The difference

is given by

$$\sigma_{l_4} - \sigma_{l_5} = 2 \left( \frac{3}{4\pi} \right)^{1/2} \langle \cos \beta \rangle I_{10}$$

Considerable steric effects have been found experimentally for many reactions, starting with the pioneering experiments by [Beuler and Bernstein \(1969\)](#) and [Brooks and Jones \(1966\)](#), and we refer to the literature cited above for further information.

### 7.8.3 Product Rotational Polarization. Quantum Mechanical Theory and Semiclassical Approximation

#### 7.8.3.1 Derivation of General Equations

So far we have discussed the angular distribution of the reaction products. Another accessible stereodynamic property is the spatial distribution of rotational angular momenta of the final products. We have already discussed in Sect. 7.7.4 the corresponding vector correlations. Here we will consider inelastic collisions between atoms A and diatomic molecules BC or reactions like  $A + BC \rightarrow AB + C$ . We will derive some general equations for the rotational polarization of the molecule AB in the exit channel and point out the relations to the results obtained in the previous sections. We will also allow for rotational polarization in the entrance channel, either for the atom or for the initial molecule. In order to have a definite case in mind let us assume that the initial molecular ensemble is polarized and that the atoms are initially in their ground state. (The case of initially aligned atoms will be considered below.)

In order to derive the relevant formulas we will follow the developments of Sect. 3.5 and apply the reduced density matrix formalism, which is most convenient for keeping track of the various coherencies. Our main results will be (7.132) and (7.134). Readers not so much interested in the mathematical formalism may proceed to these equations and the following more physical discussions.

The initially polarized molecular ensemble will be described in terms of the relevant state multipoles  $\langle T(J)_{KQ}^\dagger \rangle$ , defined in the director system introduced in Sect. 7.8.1. The components with respect to the collision system (with the initial relative wave vector  $\mathbf{k}_0$  as quantization axis) will be denoted by  $\langle T(J)_{Kq}^\dagger \rangle$ . If initial electronic orbital orientation and/or alignment must be taken into account, then the state multipoles  $\langle T(\Lambda' \Lambda J)_{KQ}^\dagger \rangle$ , defined in Sect. 7.7.3, must be used instead of  $\langle T(J)_{KQ}^\dagger \rangle$ .

We will denote the density matrix of the initial molecular ensemble by  $\rho$ . Assuming that the incident atoms are spinless and in their ground state, the density matrix  $\rho_{in}$  of the total system is given by the direct product

$$\rho_{in} = \rho \times |\mathbf{k}_0\rangle\langle\mathbf{k}_0| \quad (7.124a)$$

Taking matrix elements we obtain by applying (A.7) and (A.8) of Appendix A.1

$$\langle JM' \mathbf{k}_0 | \rho_{\text{in}} | JM \mathbf{k}_0 \rangle = \langle JM' | \rho | JM \rangle \quad (7.124\text{b})$$

where  $J$  and  $M$  denote angular momentum and its  $z$  component of the initial molecules respectively. The final molecular states will be characterized by the quantum numbers  $J_1 M_1$ .  $\mathbf{k}_1$  is the relative final wave vector and  $n_1$  will collectively denote the states of the final atoms which will be in excited states in general.

The density matrix  $\rho_{\text{out}}$ , describing the total final system, is related to  $\rho_{\text{in}}$  by (E.5):

$$\rho_{\text{out}} = T_{\rho_{\text{in}}} T^\dagger \quad (7.125)$$

where  $T$  denotes the transition operator. Taking matrix elements of (7.125) and applying the completeness relation for the initial states, we obtain

$$\begin{aligned} & \langle J'_1 M'_1 n'_1 \mathbf{k}_1 | \rho_{\text{out}} | J_1 M_1 n_1 \mathbf{k}_1 \rangle \\ &= \sum_{M' M} \langle J'_1 M'_1 n'_1 \mathbf{k}_1 | T | JM' \mathbf{k} \rangle \langle JM' | \rho | JM \rangle \langle JM \mathbf{k}_0 | T^\dagger | J_1 M_1 n_1 \mathbf{k}_1 \rangle \end{aligned} \quad (7.126)$$

where the  $T$ -matrix elements are the usual scattering amplitudes in the normalization (3.33). All quantum numbers are defined with respect to the collision system.

We will now consider a definite experimental situation. It will first be assumed that one of the final particles will be detected (so that  $\mathbf{k}_1$  is fixed) and that the excited states  $|n\rangle$  of the atom  $C$  will not be observed. We are interested in the rotational polarization of the final molecules. The information which can be obtained from the measurements under these conditions is contained in the relevant reduced density matrix  $\rho_1$ . As described in Sect. 3.2,  $\rho_1$  is obtained by considering those elements of  $\rho_{\text{out}}$  which are diagonal in all unobserved quantum numbers and by summing over the unobserved variables. In our present case of interest this procedure yields the elements

$$\langle J'_1 M'_1 | \rho | J_1 M_1 \rangle = \sum_{n_1} \langle J'_1 M'_1 n_1 \mathbf{k}_1 | \rho_{\text{out}} | J_1 M_1 n_1 \mathbf{k}_1 \rangle \quad (7.127)$$

suppressing the dependence of  $\rho_1$  on  $\mathbf{k}_1$  and  $\mathbf{k}_0$  for brevity.

The rotational polarization of the observed molecules will be characterized in terms of the relevant multipole components. Assuming high spectral resolution in the detection of the fluorescence light, so that quantum beats are not detected, it is sufficient to consider density matrix elements with  $J'_1 = J_1$  only. The corresponding multipoles will be denoted by  $\langle T(J_1)_{kq}^\dagger \rangle$  and will conveniently be defined in the collision system (so that  $q$  refers to  $\mathbf{k}_0$  as quantization axis):

$$\left\langle T(J_1)_{kq}^\dagger \right\rangle = \sum_{M'_1 M_1} (-1)^{J_1 - M'_1} (2k + 1)^{1/2} \begin{pmatrix} J_1 & J_1 & k \\ M'_1 & -M_1 & -q \end{pmatrix} \langle J_1 M'_1 | \rho_1 | J_1 M_1 \rangle \quad (7.128)$$

The initial molecular density matrix  $\rho$  is expanded in terms of multipoles  $\left\langle T(J)_{KQ'}^\dagger \right\rangle$  where  $Q'$  refers also to the collision frame:

$$\langle JM' | \rho | JM \rangle = \sum_{KQ'} (-1)^{J - M'} (2K + 1)^{1/2} \begin{pmatrix} J & J & K \\ M' & -M & -Q' \end{pmatrix} \left\langle T(J)_{KQ'}^\dagger \right\rangle \quad (7.129)$$

In order to take full advantage of the symmetry properties of the initial angular momentum distribution we transform to the director system by using (4.41),

$$\left\langle T(J)_{KQ'}^\dagger \right\rangle = \sum_Q \left\langle T(J)_{KQ}^\dagger \right\rangle D(\chi \delta \epsilon)_{QQ'}^{(K)*} \quad (7.130)$$

similar to (7.111). The angles  $\chi$ ,  $\delta$ , and  $\epsilon$  and their geometrical importance have been discussed in Sect. 7.8.1. Combining (7.126)–7.130 we obtain finally

$$\begin{aligned} T(J_1)_{kq}^\dagger \rangle = & \sum_{KQQ'} \left\langle T(J)_{KQ}^\dagger \right\rangle D(\chi \delta \epsilon)_{QQ'}^{(K)*} \sum_{\substack{M' M \\ M'_1 M_1 n_1}} (-1)^{J_1 - M'_1 + J - M'} ((2k + 1) \\ & \times (2k + 1))^{1/2} \begin{pmatrix} J_1 & J_1 & k \\ M'_1 & -M_1 & -q \end{pmatrix} \begin{pmatrix} J & J & K \\ M' & -M & -Q' \end{pmatrix} f(M'_1 M') f(M_1 M)^* \end{aligned} \quad (7.131)$$

$$\bullet = \sum_{KQQ'} \left\langle T(J)_{KQ}^\dagger \right\rangle D(\chi \delta \epsilon)_{QQ'}^{(K)*} A(\Theta \phi)_{KQ'}^{(kq)} \quad (7.132)$$

Here we have abbreviated the scattering amplitudes  $\langle J_1 M_1 n_1 k_1 | T | JM \mathbf{k}_0 \rangle$  by  $f(M_1 M)$ , and the “anisotropy coefficient”  $A(\Theta \phi)_{KQ'}^{(kq)}$  is defined by the second sum in (7.131).

The advantage of an expansion like (7.132) is that geometrical and dynamical elements are separated. The state multipoles  $\left\langle T(J)_{kq}^\dagger \right\rangle$  characterize the rotational polarization of the observed final product in the collision system (that is,  $q$  refers to  $\mathbf{k}_0$  as quantization axis). The parameters  $\left\langle T(J)_{KQ}^\dagger \right\rangle$  characterize the initial rotational polarization in the director system. The anisotropy coefficients contain the information on the dynamics of the collision and have to be calculated in the collision system which is convenient for numerical calculation. The rotation matrix elements describe the relation between director and collision system and specify the geometry of the experiment. Assume, for example, an aligned symmetric

distribution of  $\mathbf{J}$  vectors around the  $z$  axis of the director system. If the alignment of  $\mathbf{J}$  is positive then the  $\mathbf{J}$  vectors will point preferentially in the  $z$  direction.  $\delta$  is the angle between this preferred direction and the direction of the initial relative wave vector. If the  $x' - z'$  plane is chosen as scattering plane ( $\phi = 0$ ), then  $\epsilon$  is the angle between  $z$  and the collision plane.

If electronic orbital orientation and alignment must be taken into account we have to calculate the state multipoles  $\left\langle T (\Lambda'_1 \Lambda_1 J_1)_{kq}^\dagger \right\rangle$  or  $\left\langle T (\epsilon'_1 \epsilon_1 J_1)_{kq}^\dagger \right\rangle$  introduced in Sect. 7.7.3. The relevant general equations can be obtained completely similar to the derivation of (7.132).

The lower state multipoles ( $K \leq 2$ ) can be measured by observing the fluorescence light and determining its angular distribution and polarization. We refer to the discussion in Sect. 7.7.4 and to Chaps. 5 and 6 for more details.

The next step in the theoretical development would be to perform a partial wave expansion of the scattering amplitudes as a basis for numerical calculations of the anisotropy parameters. Lack of space forbids a discussion of the relevant calculations.

### 7.8.3.2 Discussion and Semiclassical Interpretations

In order to get a feeling for the physical importance of the multipoles (7.132) we will follow Levine and Bernstein (1987) and derive a simple physical picture for the production of rotational polarization in cases where the initial particles are unpolarized ( $K = 0$ ). The initial angular momenta  $\mathbf{J}$  of the molecules are then statistically distributed. The initial relative orbital angular momentum  $\mathbf{L}$  is preferentially directed perpendicular to the scattering plane ( $\mathbf{k}_0 - \mathbf{k}_1$  plane). Let us assume that many partial waves contribute to the reaction so that  $J \ll L$ . This is the case in reactions of the type  $\text{K} + \text{H Br} \rightarrow \text{K Br} + \text{H}$ . Angular momentum conservation requires  $\mathbf{J} + \mathbf{L} = \mathbf{J}_1 + \mathbf{L}_1$ . Since the reduced mass of the final products is much smaller than that of the initial particles for the reaction considered we have  $L_1 \ll L$ , which results in the angular momentum correlation  $J_1 \approx L$ . That is, the reactant orbital angular momentum appears as product rotational angular momentum, and  $\mathbf{J}_1$  will preferentially be aligned perpendicular to the scattering plane. The rotational state distribution of  $\text{K Br}$  is a reflection of the range of impact parameters that contribute to the reactive collision.

In this case a strong rotational polarization is required by essentially kinematically constraints. In fact, a significant fraction of the energy released in the reaction is in the form of rotational excitation of  $\text{K Br}$ . The produced anisotropy in the  $\mathbf{J}_1$  distribution will then result in a strong polarization of the emitted fluorescence light.

The  $\text{K} + \text{H Br}$  and similar reactions therefore produce quite high angular momenta for the alkali halides, typically  $\sim 100 \text{h}$ , so that the semiclassical approximation applies. If the final reagents are not observed (but only the fluorescence light emitted by the total ensemble of final molecules), then the initial relative wave vector  $\mathbf{k}_0$  would be a symmetry axis for the  $\mathbf{J}_1$  distribution, and the angular

momentum distribution would be invariant under reflections in any plane through  $\mathbf{k}_0$ . Consequently, as discussed in Sect. 4.5, only multipoles with  $k$  even and  $q = 0$  contribute. The semiclassical approximation (7.9) yields

$$\langle T(J_1)_{k0} \rangle = \left( \frac{2k+1}{4\pi} \right)^{1/2} \langle P_k(\cos \Theta_{J_1}) \rangle$$

for the parameters (7.132) where  $\Theta_{J_1}$  is the angle between  $\mathbf{J}_1$  and  $\mathbf{k}_0$ . The spatial distribution of  $\mathbf{J}_1$  vectors is then represented by the distribution function (7.10), which in our present case of interest reduces to the expression

$$W(\Theta_J) = \frac{1}{4\pi} [1 + 5\langle P_2(\cos \Theta_J) \rangle P_2(\cos \Theta_J) + 9\langle P_4(\cos \Theta_J) \rangle P_4(\cos \Theta_J) + \dots]$$

In several experiments  $\langle P_2 \rangle$  has been determined (for example, by analyzing the fluorescence light), and in some cases also  $\langle P_4 \rangle$ . In most cases investigated,  $\langle P_2 \rangle$  is negative and  $\langle P_4 \rangle$  positive, indicating that  $\mathbf{J}_1$  is preferentially aligned perpendicular to  $\mathbf{k}_0$ . (Bernstein et al. 1987).

If the state multipoles have been experimentally and theoretically determined, the corresponding parameters for the axes distribution follow (7.34) for linear rotors and (7.64b) for symmetric tops. The corresponding semiclassical relations are given by (7.35a) and (7.64c) respectively.

If scattered particles and emitted light are observed in coincidence, then the azimuthal symmetry around  $\mathbf{k}_0$  is disturbed and state multipoles with  $q \neq 0$  will contribute. This corresponds to a simultaneous measurement of  $\mathbf{k}_1$  and  $\mathbf{J}_1$  which allows us to determine the triple vector correlation among  $\mathbf{k}_0$ ,  $\mathbf{k}_1$ , and  $\mathbf{J}_1$ . In particular, information on the dihedral angle (that is, the angle between  $\mathbf{J}_1$  and the  $\mathbf{k}_0 - \mathbf{k}_1$  plane) can be extracted from the measurements.

### 7.8.4 Alignment-Induced Chemical Reactions

So far we have not specified the normalization of the final density matrix  $\rho_1$  of interest. In collision processes it is convenient to normalize according to (3.33), namely

$$\text{tr } \rho_1 = \sum_{M_1} \langle J_1 M_1 | \rho_1 | J_1 M_1 \rangle = \sigma(\Theta\phi) \quad (7.133a)$$

where  $\sigma(\Theta\phi)$  is the differential cross section. The monopole is then proportional to  $\sigma$ :

$$\langle T(J_1) \rangle_{00} = \frac{\sigma(\Theta\phi)}{(2J_1 + 1)^{1/2}} \quad (7.133b)$$

The differential cross section then follows from (7.132) and (7.133):

$$\bullet \quad \sigma(\Theta\phi) = \sum_{KQQ'} (2J_1 + 1)^{1/2} \left\langle T(J)_{KQ}^\dagger \right\rangle D(\chi \delta \epsilon)_{QQ'}^{(K)*} A(\Theta\phi)_{KQ'} \quad (7.134)$$

where the corresponding anisotropy coefficient is obtained by setting  $k = 0$  in (7.131).

Equation 7.134 is practically equivalent to (7.115), and the coefficients  $A_{KQ'}$  are equivalent to the steric factors defined by (7.115). In fact, (7.115) can be derived from (7.134) by transforming to the axis representation, applying the adiabatic approximation, and using (7.34). Expression (7.134) is, however, more general than (7.115) because the approximations, discussed in Sect. 7.8.1, are not contained in (7.134).

Equation 7.134 describes the influence of initial rotational polarization of the molecule BC on reactions like  $A + BC \rightarrow AB + C$ . It has been measured, for example, by optical pumping of the  $M$  substates of the HF molecule by IR polarized light for the reaction  $K + HF \rightarrow KF + H$ . The reaction cross section was then measured for two different HF polarizations (Hoffmeister et al. 1987). The type of information which can be obtained from the measurements is the orientational angle dependence of the reaction barrier.

Other experiments have been performed with initially aligned atoms. The corresponding expressions are given by (7.132) and (7.134), where then  $\left\langle T(J)_{KQ}^\dagger \right\rangle$  refer to rotational polarization of the atoms. In most experiments the initial atoms have been prepared in  $p$  states by optical pumping. Taking the direction of the electric vector of the pump laser as  $z$  axis of the director frame the atomic state is represented by a  $p_z$  orbital. The corresponding charge distribution is parallel to  $z$  (similar to Fig. 7.2). Since only one element of the density matrix  $\rho$  is nonvanishing (the one with  $J = 1, M = 0$ ) we obtain from (4.31) that, besides the monopole, only the alignment parameter  $\left\langle T(J)_{20}^\dagger \right\rangle$  is nonvanishing with value

$$\left\langle T(J)_{20}^\dagger \right\rangle = - \left( \frac{2}{3} \right)^{1/2}$$

The third Euler angle  $\chi$  can be put to zero and (7.134) can be rewritten in the form

$$\sigma(\Theta\phi) = \sigma_0 - \left( \frac{2}{3} \right)^{1/2} \sum_{Q'} d(\delta)_{0Q'}^{(2)} e^{i(\phi - \epsilon)Q'} A(\Theta)_{2Q'} \quad (7.135)$$

where we have used  $A(\Theta\phi)_{KQ'} = e^{i\phi Q'} A(\Theta)_{KQ'}$ , which follows from the symmetry conditions of the scattering amplitudes.

Let us choose the collision plane as  $x' - z'$  plane (corresponding to  $\phi = 0$ ). From the invariance of the  $T$  operator under reflections in this plane and the corresponding symmetry properties of the scattering amplitudes, it follows that the anisotropy coefficients satisfy the conditions

- $A(\Theta)_{KQ'} = (-1)^{K+Q'} A(\Theta)_{K-Q'}$  (7.136a)

- $A(\Theta)_{KQ'}^* = (-1)^K A(\Theta)_{KQ'}$  (7.136b)

Hence, the experiment under discussion is completely determined by three real independent parameters corresponding to  $Q' = 0, 1, 2$  for any scattering angle  $\Theta$ . These coefficients can be determined experimentally by measuring the cross section as a function of  $\delta$  and  $\epsilon$ . Assume, for example, that the electric vector of the laser is lying within the scattering plane and rotated within this plane. The azimuth angle  $\epsilon$  of the field vector is then zero, and  $\delta$  is the angle between the field direction and  $\mathbf{k}_0$ .

Using the conditions (7.136) and inserting the explicit analytical forms for the  $d$  matrices, we obtain from (7.135):

$$\sigma(\Theta) = \sigma_0 - \left( \frac{2}{3} \right)^{1/2} \left[ \frac{1}{2} (3 \cos^2 \delta - 1) A(\Theta)_{20} - 2 \left( \frac{3}{2} \right)^{1/2} A(\Theta)_{21} \sin \delta \cos \delta + 2 \left( \frac{3}{8} \right)^{1/2} A(\Theta)_{22} \sin^2 \delta \right] \quad (7.137)$$

For  $\delta = 0$  the  $p_z$  orbital is parallel to  $\mathbf{k}_0$ , and for  $\delta = \pi/2$  the orbital is perpendicular to  $\mathbf{k}_0$ . From both measurements the coefficients  $A_{20}$  and  $A_{22}$  can be extracted if  $\sigma_0$  has been determined before. (A determination of  $A_{21}$  requires  $\delta \neq 0$  and  $\delta \neq \pi/2$ .) It was found, for example, that the reaction between  $\text{Ca}({}^1 P)$  and  $\text{HCl}$  shows a marked preference for the perpendicular alignment of the charge cloud relative to  $\mathbf{k}_0$  (Retner and Zare 1982). Reactions like these represent interesting examples of alignment-induced chemical reactions.

Summarizing the contents of this section, our discussion has indicated how the theory of steric effects can be developed in a systematic way. The use of state multipoles allows us to describe the influence of rotational polarization and electronic orientation and alignment on molecular processes. The use of order parameters allows us to describe molecular axis distributions in a convenient way for a variety of cases. In general, the systematic application of multipoles and order parameters enables the results from many types of experiments to be treated in the same way.

# Chapter 8

## Quantum Theory of Relaxation

### 8.1 Density Matrix Equations for Dissipative Quantum Systems

#### 8.1.1 *Conditions of Irreversibility. Markoff Processes*

Consider a system which is not closed but in continuous contact with its surroundings, exchanging energy, polarization and so forth. If initially the system is in a nonequilibrium state then—under certain conditions which will be specified below—it will at some later time go over into an equilibrium state determined by external conditions such as temperature. This gradual evolution into an equilibrium state is called a *relaxation process*. In the present chapter we will consider some methods for studying processes of this kind.

Relaxation phenomena are irreversible processes. The fundamental quantum mechanical equations of motion, the Schrödinger and Liouville equations, describe a reversible evolution in the course of time, and hence a major problem is that of the solution of the question how irreversibility can arise if the behavior of microscopic particles is strictly reversible. In recent years there has been success in answering this question. A detailed treatment of the modern theory is outside the scope of this book and the reader is referred to modern textbooks on statistical physics for a more detailed account.

We will start with the concepts introduced in Sect. 3.2. Consider a system  $S$  interacting with an unobserved system  $R$ . We will denote the density matrix characterizing the total system by  $\rho(t)$  and the total Hamiltonian by  $H = H_S + H_R + V$ , where  $H_S$  and  $H_R$  are the Hamiltonians for the uncoupled systems  $S$  and  $R$ , respectively, and  $V$  describes the interactions between  $S$  and  $R$ . In the interaction picture the time evolution of  $\rho(t)$  is given by (2.79) or, alternatively, by (2.80). Inserting (2.80) back into (2.79) gives

$$\dot{\rho}(t)_I = -(i/\hbar)[V(t)_I, \rho(0)] - (i/\hbar)^2 \int_0^t dt' [V(t)_I, [V(t')_I, \rho(t')_I]] \quad (8.1)$$

where  $\dot{\rho}(t)_I$  is the time derivation of  $\rho(t)_I$ , and  $\rho(t)_I$  and  $V(t)_I$  are operators in the interaction picture which are related to their Schrödinger picture counterparts by (2.75) and (2.61), respectively, with  $H_0$  replaced by  $H_S + H_R$ .

The reduced density matrix  $\rho(t)_S$ , describing the system of interest  $S$ , is obtained from  $\rho(t)$  by taking the trace over all variables of the unobserved system  $R$  according to (3.7). Hence, in the interaction picture,

$$\rho(t)_{SI} = \text{tr}_R \rho(t)_I \quad (8.2)$$

and from (8.1)

$$\dot{\rho}(t)_{SI} = -(i/\hbar)\text{tr}_R[V(t)_I, \rho(0)_I] - (1/\hbar)^2 \int_0^t dt' \text{tr}_R[V(t)_I, [V(t')_I, \rho(t')_I]] \quad (8.3)$$

In writing (8.1) and (8.3) it has been assumed that the interaction is switched on at time  $t = 0$ . Prior to this  $S$  and  $R$  are uncorrelated and the total density matrix is given by the direct product

$$\rho(0) = \rho(0)_S \rho(0)_R = \rho(0)_I \quad (8.4)$$

(see Appendix A.1).

The coupling between the two systems may result in a reversible exchange of energy, polarization, etc. An example has been discussed in Sect. 5.4, the coupling of orbital angular momentum to an undetected spin system. In order for an irreversible process to occur further conditions must be imposed on the unobserved system in order to prevent the energy initially in the system  $S$  from returning from the unobserved system  $R$  to  $S$  in any finite time.

At this point we follow Fano (1957) and make the first of two key assumptions. *It is assumed that  $R$  has so many degrees of freedom that the effects of the interaction with  $S$  dissipate away quickly and will not react back onto  $S$  to any significant extent so that  $R$  remains described by a thermal equilibrium distribution at constant temperature, irrespective of the amount of energy and polarization diffusing into it from the system  $S$ .* In other words, it is assumed that the reaction of  $S$  on  $R$  is neglected [so that the  $R$  system is represented by  $\rho(0)_R$  at all times] and the correlations between  $S$  and  $R$ , induced by the interaction, are neglected. In this case  $\rho(t)_I$  can be replaced by the simpler density matrix

- $\rho(t)_I \rightarrow \overline{\rho(t)_I} = \rho(t)_{SI} \rho(0)_R \quad (8.5)$

at any time  $t$  without introducing any significant error in the calculation of  $\rho(t)_{SI}$ .  $\rho(0)_R$  is represented by the density matrix (2.89):

$$\rho(0)_R = \exp(-\beta H_R)/Z \quad (8.6)$$

Equations 8.5 represents our *basic condition of irreversibility*.

In the following we will consider the behavior of a “small” system  $S$ , the dynamical system, coupled to a “large” system  $R$  with many degrees of freedom. Throughout this chapter we will refer to the large system as the “heat bath” or “reservoir.” For example, atoms in a gas will collide with other atoms and these can act as a heat reservoir for the atoms considered. Light in a cavity is in interaction with the walls which then play the role of a heat bath for the light. In magnetic resonance experiments the spin variables interest with other degrees of freedom (the “lattice”) and these other variables form the heat reservoir.

Replacing  $\rho(t)_I$  in (8.3) by the approximate density matrix (8.5) gives

$$\begin{aligned} \dot{\rho}(t)_{SI} = & -(i/\hbar)\text{tr}_R[V(t)_I, \rho(0)_S \rho(0)_R] \\ & - (1/\hbar)^2 \int_0^t dt' \text{tr}_R[V(t)_I, [V(t')_I, \rho(t')_{SI} \rho(0)_R]] \end{aligned} \quad (8.7)$$

It should be noted that the corrections neglected in (8.5) and (8.7) can be treated systematically by successive approximations. If the interaction term  $V$  is zero then system and reservoir are uncorrelated and  $\rho(t)_I = \rho(t)_I$ . If  $V$  is small (that is,  $|V| \ll |H_S|, |V| \ll |H_R|$ ) then we can write

$$\rho(t) = \rho(t)_{SI} \rho(0)_R + \Delta\rho \quad (8.8)$$

such that  $\Delta\rho$  is small of order  $V$ . If (8.8) is inserted in the integral in (8.3) and only terms of order  $V^2$  are retained then (8.7) is obtained. Equation 8.7 is therefore the equation of motion for the dynamic system up to second order in the interaction.

Equation 8.7 contains  $\rho(t')_{SI}$  in the integral, and hence the behavior of the system depends on its past history from  $t' = 0$  to  $t' = t$ . The motion of the system  $S$  is, however, damped by the coupling to the reservoir and damping destroys the knowledge of the past behavior of the system. We therefore make our second key assumption:  $\dot{\rho}(t)_{SI}$  depends only on  $\rho(t)_{SI}$ , its present value. In other words, it is assumed that the system loses all memory of its past. Hence, in (8.7) we can make the substitution

- $\rho(t')_{SI} \rightarrow \rho(t)_{SI}$  (8.9)

This substitution is the *Markoff approximation* and gives

- $$\begin{aligned} \dot{\rho}(t)_{SI} = & -(i/\hbar)\text{tr}_R[V(t)_I, \rho(0)_S \rho(0)_R] \\ & - (1/\hbar)^2 \int_0^t dt' \text{tr}_R[V(t)_I, [V(t')_I, \rho(t')_{SI} \rho(0)_R]] \end{aligned} \quad (8.10)$$

We will consider the Markoff approximation in more detail in the following section.

### 8.1.2 Time Correlation Functions. Discussion of the Markoff Approximation

The next step in the analysis of (8.9) is to consider the coefficients of  $\rho(t)_{SI}$  in this equation. The development here follows that of [Loisell \(1973\)](#) to whom reference should be made for more detailed treatment of specific points (see also [Sargent et al. 1974; Haken 1970](#)).

Let us assume that the interaction operator can be written in the form

$$V = \sum_i Q_i F_i \quad (8.11)$$

where the  $F_i$  are reservoir operators and the  $Q_i$  are operators acting only on the variables of the dynamic system. In the interaction picture

$$\begin{aligned} V(t)_I &= \exp[i(H_S + H_R)t/\hbar]V \exp[-i(H_S + H_R)t/\hbar] \\ &= \sum_i F(t)_i Q(t)_i \end{aligned} \quad (8.12)$$

where

$$F(t)_i = \exp(iH_R t/\hbar) F_i \exp(-iH_R t/\hbar) \quad (8.13a)$$

and

$$Q(t)_i = \exp(iH_S t/\hbar) Q_i \exp(-iH_S t/\hbar) \quad (8.13b)$$

Inserting the expression (8.12) into (8.10) using the fact that the operators  $F_i$  and  $Q_i$  commute and using the cyclic property of the trace gives

$$\begin{aligned} \dot{\rho}(t)_{SI} &= -(i/\hbar) \sum_i \{ Q(t)_i \rho(0)_{SI} \text{tr}_R (F(t)_i \rho(0)_R) \\ &\quad - \rho(0)_{SI} Q(t)_i \text{tr}_R (F(t)_i \rho(0)_R) \} \\ &\quad - (1/\hbar)^2 \sum_{ij} \int_0^t dt' \{ (Q(t)_i Q(t')_j \rho(t)_{SI} - Q(t')_j \rho(t)_{SI} Q(t)_i) \text{tr}_R \\ &\quad \times (F(t)_i F(t')_j \rho(0)_R) - (Q(t)_i \rho(t)_{SI} Q(t')_j) \\ &\quad - \rho(t)_{SI} Q(t')_j Q(t)_i \text{tr}_R (F(t')_j F(t)_i \rho(0)_R) \} \end{aligned} \quad (8.14)$$

Consider first the expectation values

$$\begin{aligned}\langle F(t)_i \rangle &= \text{tr}_R (F(t)_i \rho(0)_R) \\ &= \sum_N \langle N | F(t)_i | \rangle \langle N | \rho(0)_R | N \rangle\end{aligned}\quad (8.15)$$

where the trace has been conveniently expressed in terms of eigenstates  $|N\rangle$  of  $H_R$  so that the equilibrium density matrix (8.6) is diagonal in this representation. Assuming that the interaction operators  $F_i$  have no diagonal elements in this representation (since otherwise the free Hamiltonian could be redefined to include those parts) we then have

$$\langle F(t)_i \rangle = 0 \quad (8.16)$$

This is equivalent to the assumption that the interaction does not produce an average frequency shift. It then follows that the first term in (8.14) vanishes.

Next consider the functions

$$\langle F(t)_i F(t')_j \rangle = \text{tr}_R (F(t)_i F(t')_j \rho(0)_R) \quad (8.17)$$

These are *time correlation functions*, that is, expectation values of products of physical quantities taken at different times, which characterize the correlation which exists on average between interactions occurring at times  $t$  and  $t'$ . Since the reservoir is assumed to be large and such that it quickly dissipates the effects of the interaction it is expected that the reservoir will quickly “forget” its interactions with the system S. Thus it is expected that  $\langle F(t)_i F(t')_j \rangle$  will be nonzero for some time interval  $t - t' \lesssim \tau$ , where  $\tau$  is typical of the reservoir and is called the *correlation time* of the reservoir. Interactions at times  $t$  and  $t'$  become progressively less correlated for  $t - t' > \tau$  and become uncorrelated for  $t - t' \gg \tau$  in which case, using (8.16),

$$\langle F(t)_i F(t')_j \rangle \approx \langle F(t)_i \langle F(t')_j \rangle \approx 0 \quad (8.18)$$

The correlation function  $\langle F(t)_i F(t')_j \rangle$  is therefore a maximum at  $t - t'$  and decreases with increasing  $t - t'$ .

The correlation time  $\tau$  is a measure of the time during which, on average, some memory of the interaction is retained. The nature of  $\tau$  depends on the nature of the reservoir. In the case of gases, for example,  $\tau$  may be given by the mean time between two collisions. Similarly, in magnetic resonance experiments any nuclei will interact with the magnetic moment of the neighboring nuclei, and, in the case of liquids,  $\tau$  is given by the mean time for which a given pair of nuclei is near to each other before diffusing away.

Finally, we note that the correlation functions (8.17) are *stationary*, that is, they depend only on the time difference  $t - t'$ . This can be shown from (8.13a) by using the cyclic property of the trace and the fact that the equilibrium density matrix (8.6) commutes with  $H_R$ :

$$\begin{aligned}
\langle F(t)_i F(t')_j \rangle &= \text{tr}_R[\exp(iH_R t/\hbar) F_i \exp(-iH_R t/\hbar) \exp(-iH_R t'/\hbar) F_j \\
&\quad \times \exp(-iH_R t'/\hbar) 2\rho(0)_R] \\
&= \text{tr}_R\{\exp[iH_R(t-t')/\hbar] F_i \exp[-iH_R(t-t')/\hbar] F_j \rho(0)_R\} \\
&= \langle F(t-t')_i F_j \rangle
\end{aligned} \tag{8.19}$$

We will now use these results and reconsider the Markoff approximation. Because of the property (8.18) the integral in (8.7) is effectively only nonzero for a time interval  $t - t' \lesssim \tau$ , that is, between times  $t' \approx t - \tau$  and  $t' = t$ . It follows that values of  $\rho(t')_{SI}$  at times  $t'$  outside this interval have little or no influence on  $\dot{\rho}(t)_{SI}$  at time  $t$ . The system is therefore capable of memorizing its state for time intervals only which are not much larger than the correlation time. Usually one is interested in the macroscopic behavior of the system rather than in its detailed changes. If  $\tau$  is much smaller than a characteristic time  $1/\gamma$  (the damping time or decay time), required for  $\rho(t)_{SI}$  to change appreciably on a macroscopic scale,

$$\tau \ll 1/\gamma \tag{8.20}$$

then  $\rho(t')_{SI} \approx \rho(t)_{SI}$  in the integrand of (8.7) and the Markoff approximation holds.

Substitution of  $\rho(t)_{SI}$  for  $\rho(t')_{SI}$  in (8.7) therefore implies that we do not try to describe details of the system motion for time intervals comparable to  $\tau$ . The quantity of interest is

$$\frac{\Delta \rho(t)_{SI}}{\Delta t} = \frac{\rho(t + \Delta t)_{SI} - \rho(t)_{SI}}{\Delta t} \tag{8.21}$$

where two values of the system density matrix are compared at times  $t$  and  $t + \Delta t$ , where  $\Delta t$  is much larger than  $\tau$  but still sufficiently small that the change in  $\rho(t)_{SI}$  is linear in  $\Delta t$ . If it is possible to find an interval  $\Delta t$  which satisfies this condition then  $\Delta \rho / \Delta t$  can be replaced by the time derivative (8.10) provided that it is understood that we never use this equation to describe the changes of  $\rho(t)_{SI}$  over time intervals less than  $\tau$ . In this sense one often refers to the Markoff approximation as a “coarse-grained” average and the time derivative (8.10) is often called a “coarse-grained” derivative.

### 8.1.3 The Relaxation Equation. The Secular Approximation

We now return to the further development of (8.14). Applying the relation (8.19) and introducing the variable  $t'' = t - t'$ ,  $dt'' = -dt'$ , the integral  $\int_0^t dt' \dots$  is transformed into the integral  $\int_0^t dt'' \dots$ . The correlation function  $\langle F(t'')_i F_j \rangle$  is effectively zero for  $t'' \gg \tau$  and, hence, the upper integration limit can be extended to infinity with negligible error under the Markoff approximation. Using (8.16) we obtain

$$\begin{aligned}\dot{\rho}(t)_{SI} = & -(1/\hbar)^2 \sum_{ij} \int_0^\infty dt'' \{ [Q(t)_i, Q(t-t'')_j] \rho(t)_{SI} \langle F(t'')_i F_j \rangle \\ & - [Q(t)_i, \rho(t)_{SI} Q(t-t'')_j] \langle F_j F(t'')_i \rangle \}\end{aligned}\quad (8.22)$$

It should be noted that all information on the reservoir is contained in the correlation functions. Taking matrix elements between eigenstates  $|m\rangle$  of  $H_S$  and applying (8.13b) gives

$$\langle m | Q(t)_i | n \rangle = \exp(i \omega_{mn} t) \langle m | Q_i | n \rangle \quad (8.23)$$

where

$$\omega_{mn} = (E_m - E_n)/\hbar$$

Introducing the notation

$$\Gamma_{mkln}^+ = (1/\hbar)^2 \sum_{ij} \langle m | Q_i | k \rangle \langle l | Q_j | n \rangle \int_0^\infty dt'' \exp(-i \omega_{ln} t'') \langle F(t'')_i F_j \rangle \quad (8.24a)$$

$$\Gamma_{mkln}^- = (1/\hbar)^2 \sum_{ij} \langle m | Q_j | k \rangle \langle l | Q_i | n \rangle \int_0^\infty dt'' \exp(-i \omega_{mkt''}) \langle F_j F(t'')_i \rangle \quad (8.24b)$$

we obtain after some algebra

$$\begin{aligned}\langle m' | \dot{\rho}(t)_{SI} | m \rangle = & \sum_{n'n} \langle n' | \rho(t)_{SI} | n \rangle \\ & \times \left\{ - \sum_k \delta_{mn} \Gamma_{m'kkn'}^+ + \Gamma_{nmm'n'}^+ + \Gamma_{nmm'n'}^- - \sum_k \delta_{n'm'} \Gamma_{nkkm}^- \right\} \\ & \exp[i(\omega_{m'n'} + \omega_{mn})t]\end{aligned}\quad (8.25a)$$

which can be written in the form

$$\langle m' | \dot{\rho}(t)_{SI} | m \rangle = \sum_{n'n} \langle n' | \rho(t)_{SI} | n \rangle R_{m'mn'n} \exp[i(E_{m'} - E_m - E_{n'} + E_n)t/\hbar] \quad (8.25b)$$

where the  $t$ -independent parameters  $R_{m'mn'n}$  are defined by the braces in (8.25a).

In this equation the time-dependent exponential vanishes if

$$E_{m'} - E_m - E_{n'} + E_n = 0 \quad (8.26)$$

Equation 8.25 is often approximated by the equation

$$\langle m' | \dot{\rho}(t)_{SI} | m \rangle = \sum_{n'n} \langle n' | \rho(t)_{SI} | n \rangle R_{m'mn'n} \quad (8.27)$$

where the prime on the summation sign indicates that only the *secular terms* are kept, that is, those terms satisfying (8.26). This approximation means that the “coarse-grained” derivative is taken over time intervals  $\Delta t$  which are long compared to a period of the free motion of the system

$$\Delta t \gg \frac{1}{\omega_{mn}}$$

so that the system goes through many cycles during  $\Delta t$ .

We will now consider the secular terms in more detail. Following Loisell (1973) we will consider the case in which there are no regularities in the level spacing of the system. Equation 8.26 is then satisfied in any of the following cases: (1)  $m' = n'$ ,  $m = n$ ,  $m' \neq m$ ; (2)  $m' = m$ ,  $n' = n$ ,  $m' \neq n'$ ; (3)  $m' = m = n' = n$ . In these cases

$$\begin{aligned} \langle m' | \rho(t)_{SI} | m \rangle &= [\langle m' | \rho(t)_{SI} | m \rangle R_{m'mm'm}]' + \delta_{m'm} \sum_n' \langle n | \rho(t)_{SI} | n \rangle R_{mmnn} \\ &\quad + \delta_{m'm} \langle m' | \rho(t)_{SI} | m' \rangle R_{m'm'm'm'} \end{aligned} \quad (8.28a)$$

where the prime on the bracket indicates that this term contributes only if  $m' \neq m$  and the prime on the summation sign indicates that the term  $m = n$  must be omitted. If the prime on the bracket is dropped the third term of (8.28a) is automatically included, which gives

•

$$\langle m' | \dot{\rho}(t)_{SI} | m \rangle = \delta_{m'm} \sum_{n \neq m} \langle n | \rho(t)_{SI} | n \rangle \cdot W_{mn} - \gamma_{m'm} \langle m' | \rho(t)_{SI} | m \rangle \quad (8.28b)$$

where (for  $m = n$ )

$$W_{mn} = \Gamma_{nnnn}^+ + \Gamma_{nnnn}^- \quad (8.29a)$$

and

$$\gamma_{m'm} = \sum_k (\Gamma_{m'kkm'}^+ + \Gamma_{mkkm}^-) - \Gamma_{mmnm'}^+ - \Gamma_{mmnm'}^- \quad (8.29b)$$

It is left as an exercise for the reader to show that

$$(\Gamma_{mnkl}^-)^* = \Gamma_{lknm}^+ \quad (8.30)$$

from which it follows that the parameters  $W_{mn}$  are real.

In the approximation (8.28) the off-diagonal elements of the density matrix obey the equation

$$\langle m' | \dot{\rho}(t)_{SI} | m \rangle = -\gamma_{m'm} \langle m' | \rho(t)_{SI} | m \rangle \quad (8.31)$$

The hermiticity condition (2.12) implies

$$\gamma_{m'm} = \gamma_{mm'}^* \quad (8.32)$$

The physical importance of parameters  $W_{mn}$  and  $\gamma_{mn}$  will be considered in the following sections. Equation 8.28 is transformed into the Schrödinger picture by substituting

$$\rho(t)_{SI} = \exp(iH_s t/\hbar) \rho(t)_s \exp(-iH_s t/\hbar)$$

which gives

•

$$\begin{aligned} \langle m' | \dot{\rho}(t)_S | m \rangle &= - (i/\hbar) \langle m' | H_S, \rho(t)_S | m \rangle \\ &+ \delta_{m'm} \sum_n \langle n | \rho(t)_S | n \rangle W_{mn} - \gamma_{m'm} \langle m' | \rho(t)_S | m \rangle \end{aligned} \quad (8.33)$$

where the first term describes the motion of the unperturbed system.

The equations of motion of reduced density matrices are often called the *generalized Master equations*. Master equations were first introduced into quantum statistical physics by [Pauli \(1928\)](#). In their original form as used by Pauli they are rate equations for the diagonal elements of  $\rho(t)_s$  (see Sect. 8.2). For a survey and rigorous proofs we refer to the review by [Haake \(1973\)](#).

Equations 8.25, 8.28, and (8.33) play a very important role in physical kinetics. They describe the *irreversible* behavior of a system and are therefore quite unlike the detailed equations of motion, the Schrödinger and Liouville equations. It will be useful to recall briefly the essential steps in deriving the “kinetic” equations starting with the general (8.3). The basic assumption is that the effects of the interaction between system and reservoir dissipate away quickly so that the reservoir effectively remains in thermal equilibrium and is represented by the density matrix (8.6). This assumption leads to (8.7), which is an integrodifferential equation for the elements of  $\rho(t)_{SI}$ . The time interval for which the integral in this relation is essentially nonzero corresponds to a correlation time  $\tau$  for  $V(t)_I$ . If  $\tau$  is small compared to a characteristic time  $1/\gamma$  required for the system to change appreciably then the Markoff approximation  $\rho(t')_{SI} \approx \rho(t)_{SI}$  can be applied and the upper integration limit can be extended to infinity. *The Markoff approximation enables the integrodifferential (8.7) to be reduced to a set of linear differential equations for the elements of  $\rho(t)_{SI}$  with time-independent coefficients  $R_{m'mn'n}$ .* On retaining only the secular terms (8.28) is obtained.

We have presented the derivation of (8.25) and (8.33) in some detail in order to show the assumptions made and the limits of applicability of these equations.

## 8.2 Rate (Master) Equations

In order to obtain an interpretation of some of the parameters occurring in (8.25) and (8.28) we will consider the rate of change of the diagonal elements of a density matrix  $\rho(t)_S$  describing a system of atoms (or nuclei) interacting with some “reservoir.” Retaining only the secular terms and noting that for the diagonal elements the Schrödinger picture is equivalent to the interaction picture and using the notation

$$\langle m' | \rho(t)_S | m \rangle = \rho(t)_{m'm}$$

it is found from (8.28) and (8.29b) that

$$\dot{\rho}(t)_{mm} = \sum_{n \neq m} \rho(t)_{nn} W_{mn} - \rho(t)_{mm} \sum_{k \neq m} (\Gamma_{mkkm}^+ + \Gamma_{mkkm}^-)$$

Using (8.29a) and changing the summation index from  $k$  to  $n$  in the second term gives

- 
- $$\dot{\rho}(t)_{mm} = \sum_{n \neq m} \rho(t)_{nn} W_{mn} - \rho(t)_{mm} \sum_{n \neq m} W_{nm} \quad (8.34)$$

Equation 8.34 can be interpreted as follows. The diagonal element  $\rho(t)_{mm}$  gives the probability of finding the atomic level  $|m\rangle$  occupied at time  $t$ . This probability increases in time owing to transitions from all other levels  $|n\rangle$  to  $|m\rangle$ . It decreases as a result of transitions from  $|m\rangle$  to all other states  $|n\rangle$ . Thus the rate of change of the diagonal elements must be given in general by a relation of the form

$$\dot{\rho}(t)_{mm} = \text{gain in } |m\rangle - \text{loss from } |m\rangle$$

The “gain” factor is obtained by multiplying  $\rho(t)_{nn}$  by the corresponding transition rate  $W(n \rightarrow m)$  for the transition  $|n\rangle \rightarrow |m\rangle$  summed over all states  $|n\rangle$ . The “loss” factor is obtained by multiplying  $\rho(t)_{mm}$  by the transition rate  $W(m \rightarrow n)$  and summing over all  $n$ . Thus *the parameters  $W_{mn}$  in (8.34) can be interpreted as the probability per unit time that a transition between atomic levels  $|n\rangle \rightarrow |m\rangle$  is induced by the interaction with the reservoir.*

Equation 8.34 is often called the *Pauli Master equation*. The conditions under which this equation hold have been specified in the preceding section. In particular, in order to be able to apply the Markoff approximation it is necessary that the probability of a transition occurring at a given time  $t$  depend only on the state of the system at that time and not on its previous history. Equation 8.34 plays a prominent role in modern statistics and has been applied to many problems in physics, chemical kinetics, and biology (see, for example, Haken 1978).

It is instructive to consider the transition rates  $W_{mn} = \Gamma_{nmmn}^+ + \Gamma_{nmmn}^-$  in more detail by inspecting (8.24). Using (8.13a) and expressing  $\text{tr}_R$  in terms of the eigenstates  $|N\rangle$  of the reservoir Hamiltonian  $H_R$  it is found that

$$\begin{aligned}
& \int_0^\infty dt'' \exp(-i\omega_{mn}t'') \text{tr}_R [F(t'')_i F_j \rho(0)_R] \\
&= \sum_{N'N} \langle N' | F_i | N \rangle \langle N | F_j | N' \rangle \langle N' | \rho(0)_R | N' \rangle \\
&\quad \times \int_0^\infty dt'' \exp[i(E_{N'} - E_N - \hbar\omega_{mn})t'']/\hbar
\end{aligned} \tag{8.35a}$$

and the integral occurring in the quantity  $\Gamma_{nmnn}^-$  is given by

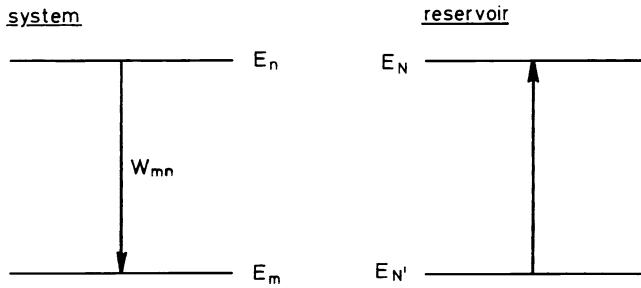
$$\begin{aligned}
& \int_0^\infty dt'' \exp(i\omega_{mn}t'') \text{tr}_R [F_j F(t'')_i \rho(0)_R] \\
&= \sum_{N'N} \langle N' | F_j | N \rangle \langle N | F_i | N' \rangle \langle N' | \rho(0)_R | N' \rangle \\
&\quad \times \int_0^\infty dt'' \exp[i(E_{N'} - E_N - \hbar\omega_{mn})t'']/\hbar
\end{aligned} \tag{8.35b}$$

where  $t''$  has been replaced by  $-t''$  in the integral. Using (8.11)

$$\sum_i \langle m | Q_i | n \rangle \langle N' | F_i | N \rangle = \langle mN' | V | nN \rangle \tag{8.35c}$$

and inserting (8.35) into (8.24) gives

$$\begin{aligned}
W_{mn} &= \Gamma_{nmnn}^+ + \Gamma_{nmnn}^- \\
&= (1/\hbar^2) \sum_{ijNN'} \langle n | Q_i | m \rangle \langle m | Q_i n | \rangle \langle N' | F_i | N \rangle \langle N | F_j | N' \rangle \langle N' | \rho_R | N' \rangle \\
&\quad \times \int_0^\infty dt'' \exp[i(E_{N'} - E_N - \hbar\omega_{mn})t'']/\hbar \\
&+ (1/\hbar^2) \sum_{ijNN'} \langle n | Q_j | m \rangle \langle m | Q_i | n \rangle \langle N' | F_j | N \rangle \langle N | F_i | N' \rangle \langle N' | \rho(0)_R | N' \rangle \\
&\quad \times \int_0^\infty dt'' \exp[i(E_{N'} - E_N - \hbar\omega_{mn})t'']/\hbar \\
&= (1/\hbar^2) \sum_{NN'} \langle nN' | V | Mn \rangle \langle mN | V | nN' \rangle \\
&\quad \times \langle N' | \rho(0)_R | N' \rangle \int_{-\infty}^{+\infty} dt'' \exp[i(E_{N'} - E_N - \hbar\omega_{mn})t'']/\hbar \\
&= (2\pi/\hbar) \sum_{NN'} |\langle mN | V | nN' \rangle|^2 \langle N' | \rho(0)_R | N' \rangle \delta(E_{N'} - E_N - \hbar\omega_{mn}) \tag{8.36}
\end{aligned}$$



**Fig. 8.1** See text for explanations

In (8.36) the element  $|\langle mN|V|nN'\rangle|^2$  is the probability of an atom making a transition from level  $|n\rangle$  to the level  $|m\rangle$  while the reservoir simultaneously undergoes a transition from a state  $|N'\rangle$  with energy  $E_{N'}$ , to a state  $|N\rangle$  with energy  $E_N$  where, in order to ensure energy conservation,  $E_N - E_{N'} = E_n - E_m$  (see Fig. 8.1). These probabilities are then averaged over the thermal distribution of the reservoir in order to obtain the net transition rates  $W_{mn}$  for the atomic system. Equation 8.36 is known as the “golden rule” for the transition rates.

Since  $V$  is Hermitian the transition probabilities  $|\langle nN'|V|mN'\rangle|^2$  satisfy the condition

$$|\langle nN'|V|mN\rangle|^2 = |\langle mN|V|nN'\rangle|^2 \quad (8.37)$$

that is, a transition  $|n\rangle|N'\rangle \rightarrow |m\rangle|N\rangle$  has the same probability of occurring as the reverse transition. The condition (8.37) in general does not, however, apply to the probabilities  $W_{mn}$ , describing the net transition  $|n\rangle \rightarrow |m\rangle$  averaged over the reservoir states. Since the reservoir remains in thermal equilibrium (as discussed in Sect. 8.1.1) the reservoir is more likely to be in the lower state  $|N'\rangle$  of Fig. 8.1 than in the upper state  $|N\rangle$ . Hence if  $E_n > E_m$ , a transition from an atomic level  $|n\rangle$  to a level  $|m\rangle$  is more probable than the inverse transition and, in general,

$$W_{mn} \neq W_{nm} \quad (8.38)$$

Let us discuss these results in more detail. From (2.92)

$$\langle N'| \rho(0)_R | N' \rangle = \exp(-\beta E_{N'}) / Z \quad (8.39)$$

which gives

$$W_{mn} = (2\pi/\hbar Z) \sum_{NN'} |\langle mN|V|nN'\rangle|^2 \exp(-\beta E_{N'}) \delta(E_{N'} - E_N - \hbar\omega_{mn}) \quad (8.40a)$$

and for the reverse transition

$$W_{mn} = (2\pi/\hbar Z) \sum_{NN'} |\langle nN' | V | mN \rangle|^2 \exp(-\beta E_N) \delta(E_N - E_{N'} - \hbar\omega_{mn}) \quad (8.40b)$$

Using the symmetry property (8.37) and energy conservation  $E_N = E_{N'} + E_n - E_m$ , (8.40b) can be written in the form

$$W_{nm} = \exp[-\beta(E_n - E_m)](2\pi/\hbar Z) \times \sum_{N'N} |\langle mN | V | nN' \rangle|^2 \exp(-\beta E_{N'}) \delta(E_{N'} - E_N - \hbar\omega_{mn})$$

and from (8.40a) it follows then that

$$\frac{W_{mn}}{W_{nm}} = \frac{\exp(-\beta E_m)}{\exp(-\beta E_n)} \quad (8.41)$$

Hence if  $E_n > E_m$  a transition from an atomic level  $|n\rangle$  to a level  $|m\rangle$  is more probable than the inverse transition.

For example, consider a two-level system, an atomic ground state  $|1\rangle$  with energy  $E_1$  and an excited state  $|2\rangle$  with energy  $E_2$ . From (8.34) and (8.41) we obtain

$$\begin{aligned} \dot{\rho}(t)_{11} &= W_{12}\rho(t)_{22} - W_{21}\rho(t)_{11} \\ &= W_{21}\{\exp[-\beta(E_1 - E_2)]\rho(t)_{22} - \rho(t)_{11}\} \\ &= -\dot{\rho}(t)_{22} \end{aligned} \quad (8.42)$$

Equilibrium is established when the net population of the two levels is constant, that is, when  $\dot{\rho}_{11} = \dot{\rho}_{22} = 0$ . In this case it follows from (8.42) that the population probabilities are given by a Boltzmann distribution

$$\frac{\rho_{11}}{\rho_{22}} = \frac{\exp(-\beta E_1)}{\exp(-\beta E_2)} \quad (8.43)$$

That is, when the initial distribution differs from (8.43) the transitions caused by relaxation processes tend to produce the thermal equilibrium distribution (8.43) in which the system is more likely in the lower state  $|1\rangle$  than in the upper state  $|2\rangle$ .

Finally, we note that the result (8.38) follows formally from the fact that the reservoir operators  $F_i$  and  $F_j$  in (8.24) do not in general commute. [Otherwise, by interchanging  $F_i$  and  $F_j$  and  $m$  and  $n$  in (8.24) it follows that  $\Gamma_{nnmn}^\pm = \Gamma_{mnnm}^\pm$  and  $W_{mn} = W_{nm}$ .] On the other hand, in theories in which the reservoir is treated classically and its effect on the system described in terms of random functions of the time rather than in terms of noncommuting operators, it follows that  $W_{mn} = W_{nm}$ .

This is a serious shortcoming of all semiclassical theories of relaxation. A further discussion of this point can be found, for example, in [Abragam \(1961\)](#).

### 8.3 Kinetics of Stimulated Emission and Absorption

In this section and [Sect. 8.4](#) we will discuss the physical importance and the application of the basic [\(8.28\)](#), [\(8.33\)](#), and [\(8.34\)](#). We will consider the interactions between atoms or molecules with external electromagnetic fields in the presence of relaxation processes. This kind of problem is particularly important in the analysis of quantum electronic devices.

We will confine ourselves to cases in which the energy differences between the atomic or molecular states are sufficiently small for the frequency  $\nu$ , associated with the transition, to lie in the Hertzian range (that is,  $\nu \sim 10^9 - 10^{12}$  Hz, corresponding to wavelengths  $\lambda \sim 1$  mm). This range includes in particular *radiofrequencies* ( $10^4 - 10^9$  Hz) and *microwaves* ( $10^9 = 10^{12}$  Hz). The principal spectral transitions in this range are rotational lines of molecules in the millimeter and centimeter range, electronic paramagnetic resonance, and nuclear magnetic resonance. The atomic transitions studied correspond to Zeeman levels produced by external magnetic fields or to natural fine- and hyperfine-structure states. In the following we will use the abbreviation rf to denote frequencies in this range.

One of the special features of transitions in the microwave and radiofrequency region is the *predominance of stimulated emission*. It follows from Einstein's theory of radiation that the ratio between induced and spontaneous transitions is proportional to  $\rho(\nu)\lambda^3$  where  $\rho(\nu)$  is the spectral radiation density. In the optical region  $\rho(\nu)$  and  $\lambda$  are small and—with the exception of the special case of lasers—spontaneous emission dominates. In the rf range  $\lambda$  is large and waves can be produced with large  $\rho(\nu)$ , so that stimulated emission dominates and spontaneous emission can often be neglected. A further difference between optical and rf lines is that the width of optical lines from conventional light sources is determined by the Doppler effect. For rf transitions the Doppler effect is small and compared to other broadening effects can often be neglected as will be discussed below.

We will now illustrate the application of the basic equations, derived in [Sect. 8.1](#) and [8.2](#), with some simple examples using two-level systems, an atomic or molecular ground state  $|1\rangle$  of energy  $E_1$ , and an excited state  $|2\rangle$  of energy  $E_2$ . In magnetic resonance experiments the energy difference between the two spin states is produced by a homogeneous static field  $\mathbf{H}_0$ . The atomic system is axially symmetric with respect to the quantization axis, which is defined by the direction of  $\mathbf{H}_0$  and hence there is no coherence between the two levels. The corresponding density matrix is therefore diagonal in the representation in which the basis states are  $|1\rangle$  and  $|2\rangle$ . In thermal equilibrium the population of the two states is determined by a Boltzmann distribution.

If a rf field is applied it will produce transitions between the states. We will assume that the field is perpendicular to the quantization axis so that there is a privileged *transverse* direction. In this case a coherent superposition of the states  $|1\rangle$  and  $|2\rangle$  will be produced as discussed in Chaps. 4 and 6 and, hence, the reduced density matrix  $\rho(t)_S$  of the atomic system of interest will no longer be diagonal.

In addition to the interaction with the external field relaxation processes must be taken into account. The various random interactions between neighboring atoms tend to establish or maintain thermal equilibrium in the medium, that is, a distribution of atoms among the two levels conforming to Boltzmann's law. In vapor these interactions occur in collisions between the atoms of the vapor and the walls of the container. In magnetic resonance problems fluctuating fields are produced by the magnetic dipoles of the atoms. In solids there are always interactions between neighboring atoms which are vibrating about their equilibrium positions constituting a reserve of energy. In the following it will always be assumed that the basic approximations of Sect. 8.1 apply. In particular it will be assumed that the "surroundings" of the atoms under consideration can always be considered as a heat reservoir at thermal equilibrium.

It is therefore necessary to consider two competing processes. The relaxation tends to reestablish thermal distribution of atoms between the two levels. Since the transition probabilities for stimulated emission and absorption are equal the external field tries to equalize the populations (in the absence of spontaneous emission). Eventually, a dynamic equilibrium is established resulting from the competition between these processes in which the population of level  $|2\rangle$  is higher than in thermal equilibrium. The relaxation causes more transitions  $|2\rangle \rightarrow |1\rangle$  than in the reverse direction and the rf field continually produces more transitions from the lower to the higher level than in the opposite direction. There are therefore more transitions in which photons are absorbed than transitions involving stimulated emission. Energy is therefore continually transferred from the field to the atomic system, while the latter continually restores it to the "reservoir" in form of heat. This absorption of radiation can then be measured using rf spectroscopy.

When an atomic system is under the influence of an external electromagnetic field then, if relaxation is neglected, its Hamiltonian can be written as

$$H(t) = H_0 + V(t) \quad (8.44)$$

where  $H_0$  is the Hamiltonian in the absence of the alternating field (in magnetic resonance problems the static field  $H_0$  will be included in  $H_0$ ). The interaction between the atoms or molecules with the applied field will be represented by

$$V(t) = V \cos \omega t = (1/2)V[\exp(i\omega t) + \exp(-i\omega t)] \quad (8.45)$$

In the case of electric dipole transitions, for example, the interaction operator is given by

$$V(t) = -e\mathbf{r}\mathbf{E}(t) = e\mathbf{r}\mathbf{E} \cos \omega t \quad (8.46a)$$

where  $e\mathbf{r}$  is the atomic dipole operator and  $\mathbf{E}(t)$  the electric field strength. In the case of the interaction between paramagnetic atoms or ions with an alternating electromagnetic field having a magnetic field vector  $\mathbf{H}(t)$  is

$$V(t) = -\mu\mathbf{H}(t) = -\mu\mathbf{H} \cos \omega t \quad (8.46b)$$

where  $\mu$  is the magnetic dipole moment of the atoms (see Sect. 2.5). It should be noted that the time dependence assumed in Eq. (8.45) ensures the hermiticity of the operators (8.46). For transverse fields the matrix elements  $\langle m'|V|m\rangle$  are only nonzero if  $m' \neq m$ ,  $m = 1, 2$ .

In the absence of any relaxation process the equation of motion for the reduced density matrix of interest is given by the Liouville (2.56), which we now write in the form

$$[\dot{\rho}(t)_{m'm}] = -i\omega_{m'm}\rho(t)_{m'm} - (i/\hbar)\langle m'|[V(t), \rho(t)_S]|M\rangle \quad (8.47a)$$

where  $\omega_{m'm} = (E_m' - E_m)/\hbar$ . The interaction between the atoms and their surroundings is usually taken into account by adding the relevant relaxation term

$$\rho(t)_{m'm} = \sum_{nn'} R_{m'mn'n} \rho(t)_{n'n} \rho(t) \quad (8.47b)$$

to the expression (8.47a) to give the total equation of motion:

•

$$\begin{aligned} \dot{\rho}(t)_{m'm} = & -i\omega_{m'm}\rho(t)_{m'm} - (i/\hbar)\langle m'|[V(t), \rho(t)_S]|m\rangle \\ & + \sum_{nn'} R_{m'mn'n} \rho(t)_{n'n} \end{aligned} \quad (8.48)$$

which is the relevant Master equation. *It should be noted that this relation assumes that the coupling between the various terms in the time evolution of  $\rho(t)_S$  can be ignored.*

In the optical region an additional term  $(\dot{\rho}_{m'm})_{\text{sp}}$  must be added to (8.48) to represent the effect of spontaneous decay. Since this is essentially a random process, which is caused by the fluctuations of the vacuum field, spontaneous emission can be represented by

$$\dot{\rho}_{m'm} = -\Gamma_{m'm}\rho_{m'm}$$

where  $\Gamma_{m'm}$  is the spontaneous decay rate of the excited level.

Using (8.42) the equations for the diagonal elements can be written in the form

$$\dot{\rho}(t)_{11} = -(i\hbar)\langle 1|[V(t), \rho(t)_S]|1\rangle + W_{12}\rho(t)_{22} - W_{21}\rho(t)_{11} \quad (8.49a)$$

$$\dot{\rho}(t)_{22} = -(i\hbar)\langle 2|[V(t), \rho(t)_S]|2\rangle + W_{21}\rho(t)_{11} - W_{12}\rho(t)_{22} \quad (8.49b)$$

In these equations the first term

$$(\dot{\rho}_{mm})_{\text{rad}} \equiv -(i/\hbar)\langle m|V(t), \rho(t)_S]|m\rangle \quad (8.50)$$

is the rate of change of the population probability of the level  $|m\rangle$  induced by the rf field and the other terms describe the influence of the relaxation processes.

It follows from (8.33) that the off-diagonal terms are described by

$$\begin{aligned} \dot{\rho}(t)_{21} &= \dot{\rho}(t)_{12}^* \\ &= -i(\omega_{21} - i\gamma_{21})\rho(t)_{21} - (i/\hbar)\langle 2|[V(t), \rho(t)_S]|1\rangle \\ &= -i(\omega_{21} - i\gamma_{21})\rho(t)_{21} \\ &\quad - (i/2\hbar)\langle 2|V|1\rangle[\exp(i\omega t) + \exp(-i\omega t)](\rho_{11} - \rho_{22}) \end{aligned} \quad (8.51)$$

where (8.45) has been applied together with the fact that the diagonal elements of  $V$  vanish.

Equations 8.49 and (8.51) give the rate of change of the density matrix elements under the combined influence of the external field and relaxation. Dynamic equilibrium is established when  $\dot{\rho}_{11} = \dot{\rho}_{22} = 0$ , that is, when the effects of the stimulated emission and absorption are balanced by the relaxation processes. We will now study this “stationary” solution in some detail.

Let us first consider (8.51). In the interaction representation the elements  $\rho_I(t)_{m'm}$  are related to  $\rho(t)_{m'm}$  by

$$\rho(t)_{21} = \exp(i\omega_{21}t)\rho_I(t)_{21} \quad (8.52)$$

where (2.75) has been used. Inserting this relation into (8.51) and multiplying both sides with  $\exp(i\omega_{21}t)$  we obtain

$$\begin{aligned} \dot{\rho}_I(t)_{21} &= -\gamma_{21}\rho_I(t)_{21} \\ &\quad - (i/2\hbar)\langle 2|V|1\rangle\{\exp[i\omega_{21} + \omega)t] + \exp[i\omega_{21} - \omega)t]\}[\rho(t)_{11} - \rho(t)_{22}] \end{aligned} \quad (8.53a)$$

In the resonance region  $\omega_{21} \approx \omega$  the dominant contribution will come from the low-frequency term  $\exp[i(\omega_{21} - \omega)t]$  and, in first-order approximation, the rapidly varying terms  $\exp[i(\omega_{21} + \omega)t] \approx \exp(2i\omega t)$  can be neglected (this is referred to as the “rotating wave approximation”). Equation 8.53a then simplifies to

$$\begin{aligned} \dot{\rho}(t)_{21} &= -\gamma_{21}\rho(t)_{21} - (i/2\hbar)\langle 2|V|1\rangle \exp[i(\omega_{21} - \omega)t] \\ &\quad + \exp[i(\omega_{21} + \omega)t][\rho(t)_{11} - \rho(t)_{22}] \end{aligned} \quad (8.54)$$

In order for the system to be in a steady state the density matrix elements must be independent of the time at which they are calculated. Since the “driving” term in (8.54) varies as  $\exp[i(\omega_{21} - \omega)t]$  we seek a solution of the form

$$\rho_I(t)_{21} = \exp[i(\omega_{21} - \omega)t]\rho(\omega)_{21} \quad (8.55a)$$

corresponding to

$$\rho(t)_{21} = \exp(-i\omega t)\rho(\omega)_{21} \quad (8.55b)$$

in the Schrödinger picture. When inserting (8.55a) into the expression (8.54) the time-dependent exponential factors cancel and

$$\begin{aligned} \rho(\omega)_{21} &= -\frac{i}{2\hbar^2} \langle 2|V|1\rangle \frac{\rho_{21} - \rho_{22}}{i(\omega_{21} - \omega) + \gamma_{21}} \\ &= \frac{1}{2\hbar} \langle 2|V|1\rangle \frac{\rho_{11} - \rho_{22}}{\omega - \omega_{21} + i\gamma_{21}} \end{aligned} \quad (8.56a)$$

The elements  $\rho(t)_{12}$  can be determined in a similar way. It should be noted that in this case the term  $\sim \exp(i\omega t)$  gives the dominant contribution in the rotated wave approximation. Hence

$$\rho(t)_{21} = \exp(i\omega t)\rho(\omega)_{12} \quad (8.56b)$$

and

$$\rho(\omega)_{12} = -\frac{1}{2\hbar} \langle 2|V|1\rangle^* \frac{\rho_{11} - \rho_{22}}{\omega - \omega_{21} - i\gamma_{21}^*} \quad (8.56c)$$

where the relation (8.32) has been applied.

It follows from the above discussion that the rotating wave approximation is obtained by setting

$$\begin{aligned} \langle 2|V(t)|1\rangle &= (1/2)\langle 2|V|1\rangle \exp(-i\omega t) \\ \langle 1|V(t)|2\rangle &= (1/2)\langle 1|V|2\rangle \exp(i\omega t) \end{aligned} \quad (8.57)$$

for the interaction (8.45) and using (8.55b) and (8.56b) for the density matrix elements. The higher-order terms  $\sim \exp(2i\omega t)$  neglected here are the basic source of nonlinear effects in quantum electronics.

Consider now (8.49) which describe the diagonal density matrix elements. Equation 8.50 can be rewritten as follows: Applying again the rotating wave approximation, using (8.55b), (8.56b), and (8.57), and substituting (8.56) for the off-diagonal elements we obtain

$$\begin{aligned} [\dot{\rho}(t)_{22}]_{\text{rad}} &= -\frac{i}{\hbar} \langle 2|V(t)|1\rangle \rho(t)_{12} + \frac{i}{\hbar} \langle 1|V(t)|2\rangle \rho(t)_{21} \\ &= -\frac{i}{2\hbar^2} |\langle 2|V(t)|1\rangle|^2 (\rho_{11} - \rho_{22}) \left( \frac{1}{\omega - \omega_{21} - i\gamma_{21}^*} - \frac{1}{\omega - \omega_{21} + i\gamma_{21}} \right) \\ &= \frac{1}{\hbar^2} |\langle 2|V|1\rangle|^2 \frac{\gamma'_{21}}{(\omega - \omega_{21} - \gamma''_{21})^2 + \gamma'^2_{21}} (\rho_{11} - \rho_{22}) \end{aligned} \quad (8.58a)$$

where  $\gamma'_{21}$  ( $\gamma''_{21}$ ) denotes the real (imaginary) part of the relaxation parameter  $\gamma_{21}$ .

Similarly,

$$[\dot{\rho}(t)_{11}]_{\text{rad}} = -\frac{1}{\hbar^2} |\langle 2 | V | 1 \rangle|^2 \frac{\gamma'_{21}}{(\omega - \omega_{21} - \gamma''_{21})^2 + \gamma'^2_{21}} (\rho_{22} - \rho_{11}) \quad (8.58b)$$

Equations 8.59 describe the change of the population probability of the two levels induced by the rf field. Comparing both expressions it can be seen that

$$[\dot{\rho}(t)_{11}]_{\text{rad}} = -[\dot{\rho}(t)_{22}]_{\text{rad}} \quad (8.59)$$

This result can be readily understood by noting that the field can increase the number of atoms in level  $|1\rangle$  only by inducing transitions  $|2\rangle \rightarrow |1\rangle$  and, vice versa, a “gain” in the population of level  $|2\rangle$  is due to induced transitions  $|1\rangle \rightarrow |2\rangle$ .

Defining

$$\begin{aligned} W(\omega)_{21} &= \frac{1}{\hbar^2} |\langle 2 | V | 1 \rangle|^2 \frac{\gamma'_{21}}{(\omega - \omega_{21} - \gamma''_{21})^2 + \gamma'^2_{21}} \\ &= W(\omega)_{12} \end{aligned} \quad (8.60)$$

then, in the steady-state case, (8.49) can be written in the form

$$\begin{aligned} \dot{\rho}(t)_{11} &= [W_{12} + W(\omega)_{12}] \rho_{22} - [W_{21} + W(\omega)_{21}] \rho_{11} = 0 \\ \dot{\rho}(t)_{22} &= [W_{12} + W(\omega)_{12}] \rho_{11} - [W_{21} + W(\omega)_{21}] \rho_{22} = 0 \end{aligned} \quad (8.61)$$

In Sect. 8.2 it was shown that the parameters  $W_{12}$  and  $W_{21}$  are the probabilities for the transitions  $|2\rangle \rightarrow |1\rangle$  and  $|1\rangle \rightarrow |2\rangle$ , respectively, caused by the relaxation mechanism. Similarly, the parameters  $W(\omega)_{12}$  and  $W(\omega)_{21}$  are the probabilities for a transition  $|2\rangle \rightarrow |1\rangle$  and  $|1\rangle \rightarrow |2\rangle$  induced by an alternating field with frequency  $\omega$ . We can therefore consider  $\rho(t)_{22} [W_{12} + W(\omega)_{12}]$  and  $\rho(t)_{11} [W_{21} + W(\omega)_{21}]$  in (8.61) as the rates at which the population probability of level  $|1\rangle$  increases and decreases under the combined influence of the external field and the relaxation processes.

If the intensity of the rf field is sufficiently high then the population probabilities  $\rho(t)_{11}$  and  $\rho(t)_{22}$  can be considerably different from their values  $\rho_{11}^{(0)}$  and  $\rho_{22}^{(0)}$  at thermal equilibrium. In this case the atoms are said to be *pumped* by the field. If the intensity of the field is weak then the diagonal elements remain close to their values at thermal equilibrium and on the right-hand sides of (8.56a), c

$$\rho_{mm} \approx \rho_{mm}^{(0)} \quad (8.62)$$

The power absorbed per unit time from the field by the atoms is

$$\begin{aligned}\frac{dE}{dt} &= E_1[\dot{\rho}(t)_{11}]_{\text{rad}} + E_2[\dot{\rho}(t)_{22}]_{\text{rad}} \\ &= (E_1 - E_2)[\dot{\rho}(t)_{11}]_{\text{rad}}\end{aligned}\quad (8.63)$$

where the relaxation (8.59) has been applied. If  $[\dot{\rho}(t)_{11}]_{\text{rad}} < 0$  the induced transitions  $|1\rangle \rightarrow |2\rangle$  exceed the number of downward transitions  $|2\rangle \rightarrow |1\rangle$  and the corresponding energy is absorbed from the rf field. Since  $E_2 > E_1$  then in this case  $dE/dt > 0$ . Conversely, if  $[\dot{\rho}(t)_{11}]_{\text{rad}} < 0$  more energy is given out by the stimulated emission process than is absorbed and  $dE/dt < 0$ .

Substitution of (8.58a) into (8.63) yields

$$\frac{dE}{dt} = \frac{1}{\hbar^2}(E_2 - E_1)|\langle 2|V|1\rangle|^2 \frac{\gamma'_{21}}{(\omega - \omega_{21} - \gamma''_{21})^2 + \gamma'^2_{21}} (\rho_{11} - \rho_{22}) \quad (8.64a)$$

and for weak fields

$$\frac{dE}{dt} = \frac{1}{\hbar^2}(E_2 - E_1)|\langle 2|V|1\rangle|^2 \frac{\gamma'_{21}}{(\omega - \omega_{21} - \gamma''_{21})^2 + \gamma'^2_{21}} (\rho_{11}^{(0)} - \rho_{22}^{(0)}) \quad (8.64b)$$

Since  $\rho_{11}^{(0)} > \rho_{22}^{(0)}$  at thermal equilibrium it follows from (8.64b) that  $dE/dt > 0$  and energy is absorbed from the field. In this case (8.64b) shows that the presence of relaxation has two effects on the absorption line: (1) a *line shift* caused by the imaginary part  $\gamma''_{21}$  and (2) a *line broadening* due to the real part  $\gamma'_{21}$  of the parameter  $\gamma_{21}$ .

If, in any circumstances,  $\rho(t)_{11} < \rho(t)_{22}$ , which in the case of lasers and masers is called *population inversion*, then  $dE/dt < 0$ . This means that on passing through the medium radiation is not attenuated by absorption but *amplified* by the stimulated emission. The operation of lasers and masers is based on this effect.

## 8.4 The Bloch Equations

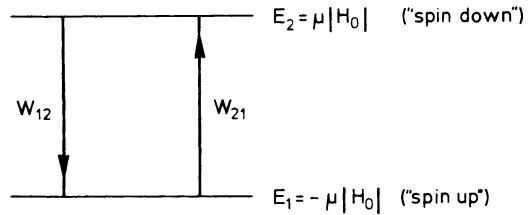
### 8.4.1 Magnetic Resonance

In this section we will apply (8.48) to magnetic resonance problems. The simplest possible system in which a magnetic resonance can be observed is a two-level system, for example, atoms or molecules with orbital angular momentum zero and spin-1/2, or atoms with no electronic angular momentum and nuclear spin-1/2.

If a static external magnetic field  $\mathbf{H}_0$  is applied in the  $z$  direction then the energies of the two spin states  $|1\rangle$  and  $|2\rangle$ , corresponding to “spin up” and “spin down,” are given by

$$E_1 = \mu|\mathbf{H}_0|, \quad E_2 = \mu|\mathbf{H}_0| \quad (8.65)$$

**Fig. 8.2** Energy level splitting in a static magnetic field



(see Fig. 8.2, where it has been assumed that the magnetic moment  $\mu$  is positive). The energy splitting is

$$\Delta E = E_2 - E_1 = 2\mu|H_0| \quad (8.66)$$

It follows that if a transverse electromagnetic field with magnetic field strength  $\mathbf{H}_1(t)$  oscillating at an angular frequency  $\omega_L$  and satisfying the resonance condition

$$\hbar\omega_L = \Delta E \quad (8.67)$$

(Larmor frequency) is applied to the system absorption of this energy will occur as electrons (or nuclei) are excited from the lower to the upper level. The required frequencies are well into the microwave region in the case of paramagnetic or electron spin resonance. Radiofrequencies are required in the case of nuclear magnetic resonance.

The number of atoms in the upper state is increased by the incoming radiation but this increase is reduced through relaxation effects which transfer energy from the excited state to the “surroundings” and attempt to reestablish the conditions of thermal equilibrium. The effect of these competing factors on the spin density matrix  $\rho(t)_S$  is described by (8.48) where now  $H_0$  includes the static field  $\mathbf{H}_0$ :

$$H_0 = H'_0 - \mu \cdot \mathbf{H}_0 \quad (8.68)$$

The Hamiltonian  $H'_0$  of the unperturbed spin states does not appear in the equation of motion because of the degeneracy of these states. Using (8.46b) the interaction between the spin and the external fields is represented by the Hamiltonian

$$H(t) = -\mu \cdot \mathbf{H}_0 + V(t) = -\mu \cdot (\mathbf{H}_0 + \mathbf{H}(t)_1) \quad (8.69)$$

First of all we will consider (8.49) in the absence of the rf field. In this case

$$\dot{\rho}(t)_{11} = W_{12}\rho(t)_{22} - W_{21}\rho(t)_{11} = -\dot{\rho}(t)_{22} \quad (8.70)$$

It will be assumed that each spin under consideration reacts to the external fields independently of all other spins and that the “surroundings” can be considered as a heat reservoir at thermal equilibrium. Adding and subtracting the term  $W_{12}\rho_{11}$  to (8.70) then, since  $\rho_{11} + \rho_{22} = 1$ , it follows that

$$\dot{\rho}(t)_{11} = W_{12} - (W_{12} + W_{21})\rho(t)_{11} \quad (8.71a)$$

and

$$\dot{\rho}(t)_{22} = W_{21} - (W_{12} + W_{21})\rho(t)_{22} \quad (8.71b)$$

which gives

$$\dot{\rho}(t)_{11} - \dot{\rho}(t)_{22} = (W_{12} - W_{21}) - (W_{12} - W_{21})[\rho(t)_{11} - \rho(t)_{22}] \quad (8.72)$$

In thermal equilibrium  $\dot{\rho}_{11} = \dot{\rho}_{22} = 0$  and it follows from (8.72) that

$$\rho_{11}^{(0)} - \rho_{22}^{(0)} = \frac{W_{12} - W_{21}}{W_{12} + W_{21}} \quad (8.73)$$

where  $\rho_{11}^{(0)}$  and  $\rho_{22}^{(0)}$  denote the population probability of levels  $|1\rangle$  and  $|2\rangle$ , respectively, at thermal equilibrium (in the presence of the static field). Defining the parameter  $T_1$  by

•

$$T_1 = 1/(W_{12} + W_{21}) \quad (8.74)$$

Equation 8.72 can be written as

$$\dot{\rho}(t)_{11} - \dot{\rho}(t)_{22} = \frac{(\rho_{11}^{(0)} - \rho_{22}^{(0)}) - [\rho(t)_{11} - \rho(t)_{22}]}{T_1} \quad (8.75)$$

Note that  $T_1$  is real [because of (8.30)].

The rf field can be taken into account by adding the relevant terms to (8.75):

$$\begin{aligned} \dot{\rho}(t)_{11} - \dot{\rho}(t)_{22} = & -\frac{i}{\hbar}[(1|[V(t), \rho(t)_S]|1) - (2|[V(t), \rho(t)_S]|2)] \\ & + \frac{(\rho_{11}^{(0)} - \rho_{22}^{(0)}) - [\rho(t)_{11} - \rho(t)_{22}]}{T_1} \end{aligned} \quad (8.76)$$

We will discuss the off-diagonal elements in an approximation where the imaginary part of  $\gamma_{12}$  (that is, the line shift) is neglected. In this case, defining

•

$$T_2 = \frac{1}{\gamma_{12}} \quad (8.77)$$

the off-diagonal elements obey the equation

$$\begin{aligned} \dot{\rho}(t)_{21} = & (-i\omega_{12} + 1/T_2)\rho(t)_{21} - (i/\hbar)\langle 2|[V(t), \rho(t)_S]|1\rangle \\ = & \dot{\rho}(t)_{12}^* \end{aligned} \quad (8.78)$$

which can be rewritten as

$$\dot{\rho}(t)_{21} = -\frac{i}{\hbar} \langle 2|[H(t), \rho(t)_S]|1\rangle + \frac{\rho(t)_{21}}{T_2} \quad (8.79)$$

where  $H(t)$  is the Hamiltonian (8.69).

The macroscopic magnetization  $\mathbf{M}$  is given by (2.94),

$$M_i = N\gamma\hbar(\sigma_i)/2 \quad (8.80a)$$

( $i = x, y, z$ ), where  $\sigma_i$  is the corresponding Pauli matrix,  $N$  the total number of atoms per unit volume, and  $\gamma$  the gyromagnetic ratio. Using the expressions for the Pauli matrices [(1.7)  $\mathbf{M}$  is given explicitly by

$$\begin{aligned} M_x &= \frac{1}{2}N\gamma\hbar(\rho_{12} + \rho_{21}), & M_y &= \frac{1}{2}N\gamma\hbar i(\rho_{12} - \rho_{21}), \\ M_z &= \frac{N\gamma\hbar}{2}(\rho_{11} - \rho_{22}) \end{aligned} \quad (8.80b)$$

In the absence of relaxation effects the equation of motion for the magnetization  $\mathbf{M}$  is given by (2.88) with  $\mathbf{P}$  replaced by  $\mathbf{M}$  and  $\mathbf{H}$  replaced by  $\mathbf{H}_0 = \mathbf{H}_1(t)$ . Adding the relaxation terms and using (8.75), (8.79), and (8.80b) we obtain

•

$$\frac{dM_x}{dt} = \gamma[\mathbf{M} \times (\mathbf{H}_0 + \mathbf{H}(t)_1)]_x - \frac{M_x}{T_2} \quad (8.81a)$$

$$\frac{dM_y}{dt} = \gamma[\mathbf{M} \times (\mathbf{H}_0 + \mathbf{H}(t)_1)]_y - \frac{M_y}{T_2} \quad (8.81b)$$

$$\frac{dM_z}{dt} = \gamma[\mathbf{M} \times \mathbf{H}(t)_1]_z + \frac{M_z^{(0)} - M_z}{T_1} \quad (8.81c)$$

where

$$M_z^{(0)} = \frac{W_{12} - W_{21}}{W_{12} + W_{21}} \quad (8.82)$$

As shown by (8.81c)  $M_z^{(0)}$  is the value of  $M_z$  at thermal equilibrium ( $dM_z/dt = 0$ ) in the absence of the rf field.

The set of (8.81) are the *Bloch equations* and were first derived by [Bloch \(1946\)](#) for  $N$ -level atoms. The main feature of the general Bloch equation is that the effect of the relaxation processes is described in terms of two real parameters,  $T_1$  and  $T_2$ .

The principal aim of the discussion given above is to elucidate the various approximations which are incorporated in the Bloch equations. These approximations are not always valid and relaxation is not in general as simple as expressed by (8.81). Nevertheless, these equations describe the observed phenomena to a good

approximation in a large number of cases. It should be noted that the macroscopic magnetization  $\mathbf{M}$  obeys the same equation as in classical phenomenological theories and it can be shown that the values of  $\mathbf{M}$  are equal to the values calculated in classical models. This is a consequence of the fact that spontaneous emission is neglected in (8.48). A detailed discussion of this point can be found in [Abragam \(1961\)](#). Finally, we note that  $W_{12} = W_{21}$  in semiclassical theories (as discussed in Sect. 8.2f), from which follows  $M_z^{(0)} = 0$ , which does not agree with experiment.

### 8.4.2 Longitudinal and Transverse Relaxation. Spin Echoes

A detailed discussion of the Bloch equations can be found in many treatments of magnetic resonance phenomena and we will confine ourselves to a discussion of the physical nature of the parameters  $T_1$  and  $T_2$ .

Let us assume that at a certain time (say, at  $t = 0$ ) the field  $\mathbf{H}(t)_1$  is removed. In the absence of  $\mathbf{H}_1$  the Bloch equations reduce to

$$\begin{aligned}\frac{dM_x}{dt} &= \omega_L M_y - \frac{M_y}{T_2} \\ \frac{dM_y}{dt} &= \omega_L M_x - \frac{M_y}{T_2} \\ \frac{dM_z}{dt} &= \frac{M_z^{(0)} - M_z}{T_1}\end{aligned}\tag{8.83}$$

with  $\omega_L = \gamma|\mathbf{H}_0|$ . In the absence of any relaxation process  $\mathbf{M}$  would precess freely around the static field  $\mathbf{H}_0$  with a frequency of  $\omega_L$ .  $M_z$  would remain constant and  $M_x$  and  $M_y$  rotate with constant magnitude in the  $x - y$  plane. Because of the various interactions between the spins and their surroundings the spin system will relax to thermal equilibrium. It can be shown that a solution of (8.83) is given by

$$\begin{aligned}M(t)_x &= A \sin(\omega_L t + \varphi) \exp(-t/T_2) \\ M(t)_y &= A \cos(\omega_L t + \varphi) \exp(-t/T_2) \\ M(t)_z &= (B - M_z^{(0)}) \exp(-t/T_1) + M_z^{(0)}\end{aligned}\tag{8.84}$$

where  $A$ ,  $B$ , and  $\varphi$  are integration constants. Equation 8.84 show that, as a consequence of relaxation,  $M_x$  and  $M_y$  will vanish with a time constant  $T_2$  and  $M_z$  will reach its equilibrium value with a time constant  $T_1$ .  $T_2$  therefore accounts for the decay of  $M_x$  and  $M_y$ , which are perpendicular to  $\mathbf{H}_0$ , and for this reason  $T_2$  is called the *transverse relaxation time*.  $T_1$  accounts for the decay of the longitudinal component  $M_z$  of  $\mathbf{M}$  and is termed the *longitudinal relaxation time*.

That  $M_x$  and  $M_y$  vanish at thermal equilibrium is due to the fact that there is no preferred transverse direction. The directions of the individual transverse components therefore vary in a random way from one atom to another and the net resultant is zero. The fact that  $M_z$  is different from zero is related to the axial symmetry of the system due to the static field  $\mathbf{H}_0$  which produces the difference in energy between the two levels.

The physical nature of  $T_1$  and  $T_2$  can be understood by noting that relaxation is caused by different mechanisms. First of all, the *spin–lattice interaction* includes all processes in which energy is exchanged between the spin system and its surroundings, for example the lattices in a crystal. In general, all degrees of freedom except the spins are called a *lattice*. A transfer of energy from the spin system to the lattice is associated with transitions from the upper to the lower spin state and causes the population number of the two spin states, and hence  $M_z$ , to change. *Longitudinal relaxation is therefore associated with an energy transfer from the spin system to the lattice.*  $T_1$  is thus a measure of the time required for the system to reach an energy equilibrium with its environment.

A second type of interaction, known as *spin–spin interaction*, includes all mechanisms whereby the spins can exchange energy among themselves rather than transferring it to the lattice as a whole. For example, in an elastic collision in which one atom undergoes a transition  $|1\rangle \rightarrow |2\rangle$  and the other one a transition  $|2\rangle \rightarrow |1\rangle$  the energy of the spin system and the value of  $M_z$  do not change. Such collisions therefore do not contribute to longitudinal relaxation but destroy the coherence between the spin states (see Chap. 3); the off-diagonal elements of the spin density matrix and the transverse components of  $\mathbf{M}$  are therefore reduced. *Transverse relaxation is therefore associated with a loss of coherence of the spin system.* Note that any process contributing to  $T_1$  will in general also destroy the coherence so that  $T_1 \geq T_2$ . Magnetic resonance techniques allow the determination of the relaxation times and enable information on the various relaxation processes to be obtained (see, for example, [Abragam 1961](#); [Corney 1977](#)).

The physical meaning of  $T_2$  can be understood in terms of the following simple model (which does not, however, include all the aspects of transverse relaxation). Immediately after the removal of the rf field the individual spins start precessing around  $\mathbf{H}_0$ . Without relaxation processes all component spins would rotate with the same frequency  $\omega_L$  and the initial values of the magnitudes  $M_x$  and  $M_y$  would be constant in time. The various random interactions of the magnetic dipoles produce a magnetic field at each atom giving rise to a fluctuating component in addition to the external field  $\mathbf{H}_0$ , either aiding or opposing  $\mathbf{H}_0$  and causing the individual precession rates to be either faster or slower. As a result the spins get out of step and in the course of time their distribution spreads over a wider and wider range in the  $x - y$  plane and the net transverse component eventually vanishes.  $T_2$  is a measure of the time required for the spins to become completely random to each other. A direct measurement of  $T_2$  is the most unambiguous method of investigating the mechanisms by which coherence is lost.

This simple model of transverse relaxation readily explains a phenomenon known as the *spin echo*. Suppose that a set of nuclear magnetic dipoles is such

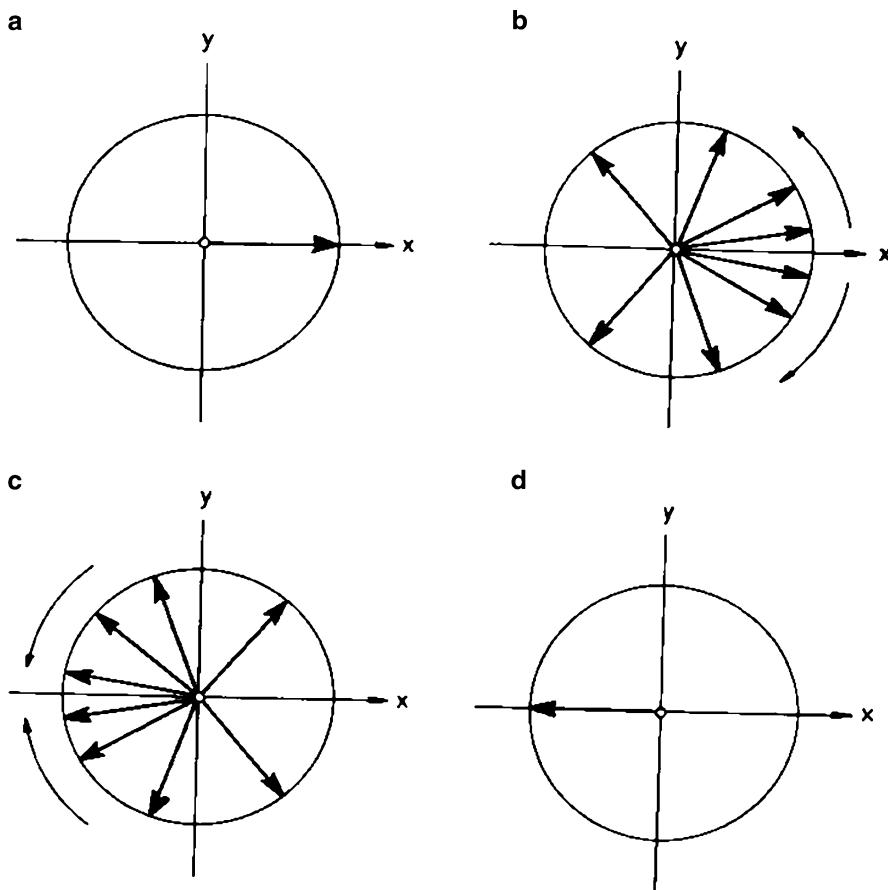


Fig. 8.3 Illustration of spin echoes

that the magnetization  $\mathbf{M}$  of the dipoles points in the direction of the static field ( $z$  axis). A resonant radiofrequency field is applied as a pulse of such a duration that it rotates  $\mathbf{M}$  from the  $z$  to the  $x$  direction (“ $\pi/2$  pulse”; Fig. 8.3a). When the pulse is switched off the individual spins precess about the direction of the static field. It is convenient to discuss the motion of the spins in a coordinate system which rotates with the Larmor frequency about the  $z$  axis. In the absence of any relaxation process the spins would rotate freely around  $\mathbf{H}_0$  with the Larmor frequency, that is, they would appear to be at rest when viewed from the rotating system. Since the precession frequency is slightly different for each of the component moments because of relaxation processes the spins get out of phase and become distributed in the  $x - y$  plane (Fig. 8.3b). After a time  $t < T_2$  a second pulse is applied with such a duration that the direction of all spins are reversed (“ $\pi$  pulse”). That is, the component spins are just turned over as shown by Fig. 8.3c. Because the spins keep

rotating with their initial speed the spins converge back to one vector (Fig. 8.3d), producing a “pulse” of magnetization in this direction, which appears as an “echo” of the first high-frequency pulse.

Abragam (1961) has given the following analog of this phenomenon. Suppose a group of ants is crawling around the edge of a pancake. They all start together in a small area but, because of their different speeds, they will progressively spread out around the circumference (“ $T_2$  process”). If the pancake is turned over (“ $\pi$  pulse”), the ants are turned around but continue to crawl in the same direction. Eventually, all the ants will again end up bunched together with the exception of those which have fallen off the pancake (“ $T_1$  process”).

### 8.4.3 The “Optical” Bloch Equations

As we discussed briefly at the beginning of this section there is a close analogy between a two-level atom and a spin-1/2 system (in a static magnetic field in the  $z$  direction). The “spin-down” state corresponds to the atomic ground level and the “spin-up” state to the excited level. The formalism developed above for magnetic resonance phenomena can be generalized to any two-level system driven by a resonant transverse field. This approach can be used to describe experiments in the microwave or optical region when coherent fields (maser, laser) are employed.

The relevance of the Bloch equations to the description of the maser was first recognized by Feynmann et al. (1957). Following these authors we define a fictitious quantity, the “pseudospin vector”  $\mathbf{v}$ , with components  $v_i$ , analogously to (8.80b):

$$\begin{aligned} v_1 &= \text{tr}[\rho(t)_S \sigma_x] = \rho(t)_{12} + \rho(t)_{21}, & v_2 &= \text{tr}[\rho(t)_S \sigma_y] = i[\rho(t)_{12} - \rho(t)_{21}] \\ v_3 &= \text{tr}[\rho(t)_S \sigma_z] = \rho(t)_{11} - \rho(t)_{22} \end{aligned} \quad (8.85)$$

In these equations  $\rho(t)_S$  denotes the density matrix of the atomic two-level system. As shown by (8.85)  $v_3$  depends on the difference of the population numbers and  $v_1$  and  $v_2$  characterize the coherence between the two states.

Starting with (8.49) and (8.51) it can then be shown, in an analogous way to the derivation of (8.81), that the components  $v_i$  obey the following set of equations, which are termed the “generalized” or “optical” Bloch equations:

$$\begin{aligned} \frac{dv_1}{dt} &= [\boldsymbol{\omega} \times \mathbf{V}]_1 - \frac{v_1}{T_2} \\ \frac{dv_2}{dt} &= [\boldsymbol{\omega} \times \mathbf{v}]_2 - \frac{v_2}{T_2} \\ \frac{dv_3}{dt} &= [\boldsymbol{\omega} \times \mathbf{v}]_3 - \frac{v_3}{T_1} \end{aligned} \quad (8.86)$$

where the “vector”  $\omega$  was components

$$\omega_1 = (V_{12} + V_{21})/\hbar, \quad \omega_2 = (V_{12} - V_{21})/\hbar, \quad \omega_3 = (-E_1 - E_2)/\hbar \quad (8.87)$$

and  $V_{ij} = \langle i | V | j \rangle$  are the matrix elements of the operator  $V$  introduced in Sect. 8.3 which describes the interaction between the atoms and the electromagnetic field. The relaxation times are defined as in (8.74) and (8.77).

The use of (8.86) enables a geometrical interpretation of electric dipole transitions in a two-level system to be made in a similar way to the description of magnetic resonance phenomena. Without the relaxation terms (8.86) can be interpreted as a precession of the “vector”  $\mathbf{v}$  about the “vector”  $\omega$ . The relaxation terms have similar meanings to those in the previous section. The relaxation of  $v_3$  (time constant  $T_1$ ) is associated with the various ways in which energy can be exchanged between the atoms and their environment. The relaxation of  $v_1$  and  $v_2$  (time constant  $T_2$ ) corresponds to a loss of coherence caused by the various dephasing processes. This geometrical interpretation can be used to explain photon echoes by considering the precession of the vector  $\mathbf{v}$  between two applied pulses. Furthermore, (8.87) can be used to treat electromagnetic transitions in very strong radiation fields where perturbation methods cannot be applied. It should be noted, however, that, as in the case of the Bloch (8.81), the (8.86) do not describe all phenomena associated with transitions in a two-level system. For a detailed discussion of (8.86) and their applications the reader is referred, for example, to the book by [Walther \(1976\)](#).

## 8.5 Some Properties of the Relaxation Matrix

### 8.5.1 General Constraints

In Sect. 8.1 it was shown that, under the Markoff approximation, the rate of change of the density matrix with respect to time can be represented by a set of coupled linear differential equations, which is in the interaction picture

$$\dot{\rho}_I(t)_{m'm} = \sum_{nn'} R_{m'mn'n} \rho_I(t)_{n'n} \quad (8.88)$$

$$[\langle m' | \rho(t)_{SI} | m \rangle \equiv \rho_I(t)^{m'm}]$$

In the secular approximation (8.28b) we have

$$R_{m'mn'n} = W_{mn} \delta_{n'n} - \gamma_{m'm} \delta_{n'n'} \delta_{mn}$$

where the first term contributes only if  $m \neq n$ .

The set of the (time-independent) coefficients  $R_{m'mn'n}$  is called the *relaxation matrix*. It follows from the discussions in the preceding sections that, for example,  $R_{mmnn}$  determines the rate of transfer of atoms from the level  $|n\rangle$  to the level  $|m\rangle$ . Following Happer (1972) we will now show that physical considerations place some important constraints on the elements of the relaxation matrix.

In doing this some of the general results obtained in the previous sections will be rederived and generalized.

1. If the relaxation mechanism does not alter the number of atoms present then it follows from the probability interpretation of the diagonal elements that

$$\sum_m \dot{\rho}(t)_{mm} = \sum_{nn'} \left( \sum_m R_{mmn'n} \right) \rho_I(t)_{n'n} = 0$$

Since in general  $\rho_I(t)_{n'n} \neq 0$  then

$$\sum_m R_{mmn'n} = 0 \quad (8.89)$$

for any  $n'$  and  $n$ .

2. Consider the equation corresponding to (8.88) for the complex conjugate:

$$\dot{\rho}_I(t)_{m'm}^* = \sum_{nn'} R_{m'mn'n}^* \rho_I(t)_{n'n}^* \quad (8.90a)$$

Applying the hermiticity condition it follows that

$$\dot{\rho}_I(t)_{mm'} = \sum_{nn'} R_{m'mn'n}^* \rho_I(t)_{nn'} \quad (8.90b)$$

Equations 8.88 and 8.90b imply that

$$\sum_{n'n} \rho_I(t)_{nn'} (R_{m'mn'n}^* - R_{mm'nn'}) = 0$$

which gives

$$R_{m'mn'n}^* = R_{mm'nn'} \quad (8.91)$$

3. The diagonal elements of the density matrix are nonnegative and cannot exceed unity (see Sect. 2.2). In order to ensure that these conditions are met the following conditions must be satisfied:

$$R_{mmmm} \leq 0 \quad (8.92a)$$

$$R_{nnnn} \geq 0 \quad (8.92b)$$

for any orthogonal set of atomic states  $|m\rangle$  and  $|n\rangle$ . The validity of these conditions can be seen as follows: Suppose that at a certain time  $t$  only a single level  $|m\rangle$  is populated as described by (8.92a). For any state  $n \neq m$  it is then

$$\dot{\rho}_{nn} = R_{nnmm} \rho(t)_{mm}$$

Since  $\rho(t)_{mm}$  has its minimum value at time  $t$ , then it can only increase or remain zero as described by (8.92b).

### 8.5.2 Relaxation of State Multipoles

If the system under consideration possesses certain symmetry properties under rotations it is convenient to express the relaxation (8.88) in terms of state multipoles. For simplicity we will confine ourselves to the case of an atomic system which is in the ground state with sharp angular momentum  $J$ , and relaxation processes which cause transitions within this single multiplet.

In a similar way to (4.31) state multipoles can be defined as

$$\left\langle T(J, t)_{KQ}^\dagger \right\rangle = \sum_{MM'} (-1)^{J-M'} (2K+1) \begin{pmatrix} J & J & K \\ M' & -M & -Q \end{pmatrix} \rho_I(t)_{M'M}$$

and using the inverse relaxation (4.34) the relaxation equation (8.88) can be written as

$$\frac{\partial \left\langle T(J, t)_{KQ}^\dagger \right\rangle}{\partial t} = \sum_{K'Q'} R_{KQK'Q'} \left\langle T(J, t)_{K'Q'}^\dagger \right\rangle \quad (8.93)$$

where

$$\begin{aligned} R_{KQK'Q'} &= \sum_{\substack{M'M \\ m'm}} R_{M'Mm'm} (-1)^{2J-M'-m'} [(2K+1)(2K'+1)]^{1/2} \\ &\quad \times \begin{pmatrix} J & J & K \\ M' & -M & -Q \end{pmatrix} \begin{pmatrix} J & J & K' \\ m' & -m & -Q' \end{pmatrix} \end{aligned} \quad (8.94)$$

From the hermiticity condition (8.91) it follows that

$$R_{KQK'Q'} = (-1)^{Q+Q'} R_{K-QK'-Q'} \quad (8.95)$$

Equation 8.93 describes the time evolution of state multipoles in the presence of interactions which causes relaxation. An example of this which is of particular interest is that in which the atomic system under consideration is in an environment which is, on the average, *isotropic*. Isotropic conditions often prevail when a

polarized ensemble relaxes toward a random ensemble. It was shown in Chap. 4 that a rotationally invariant interaction cannot alter the rank  $K$  and component  $Q$  of the tensors. Because the relaxation processes are independent of the choice of the quantization axis the relaxation rates must then be independent on  $Q$ . This gives the symmetry condition:

$$R_{KQK'Q'} = -\gamma_K \delta_{K'K} \delta_{Q'Q} \quad (8.96)$$

where  $\gamma_K$  is the relaxation rate for all components of the tensor of rank  $K$ . Equation 8.95 implies that  $\gamma_K$  is *real*,

$$\gamma_K^* = \gamma_K \quad (8.97a)$$

and it can be shown that

$$\gamma_K \geq 0 \quad (8.97b)$$

Using the symmetry condition (8.96), (8.93) can be simplified and all  $(2K + 1)$  components of a tensor of rank  $K$  decay at the same rate:

$$\frac{\partial \langle T(J, t)_{KQ}^\dagger \rangle}{\partial t} = -\gamma_K \langle T(J, t)_{KQ}^\dagger \rangle \quad (8.98a)$$

or

$$\langle T(J, t)_{KQ}^\dagger \rangle = \langle T(J, 0)_{KQ}^\dagger \rangle \exp(-\gamma_K t) \quad (8.98b)$$

Since the monopole  $\langle T(J, t)_{00} \rangle$  is proportional to the trace of the density matrix (which is constant if no atoms are removed from the multiplet  $J$ ) it follows that

$$\gamma_0 = 0 \quad (8.99)$$

and hence all multipoles with  $K > 0$  will vanish in the course of time, and at thermal equilibrium all substates will be equally populated. If the multiplet under consideration is not the ground state then radiative decay must also be taken into account.

In conclusion we have seen that *under isotropic conditions, each multipole is decoupled from all other multipoles and relaxes with a characteristic relaxation rate  $\gamma_K$ .* The number of independent rates is therefore reduced to  $(2J + 1)$ . This number is still large if  $J$  is high but often not all of the parameters are of interest. A considerable simplification occurs, for example, when the atoms have been excited by dipole radiation. In this case only atomic orientation and alignment can be produced (see Chap. 5) and, irrespective of the value of  $J$ , it is only necessary to consider the corresponding relaxation rates  $\gamma_1$  and  $\gamma_2$ . This is the case in most optical pumping experiments.

In some cases the relaxation process is not isotropic but axially symmetric with respect to a preferred axis, for example, if the relaxation process is itself anisotropic or an external field is present as in the case of magnetic resonance experiments. When the high-frequency field is switched off the atoms then relax in the presence

of the static magnetic field which is producing the energy difference between the substates.

It has been shown in Chap. 4 that the component  $Q$  of the state multipoles is conserved in an interaction with axial symmetry. In this case (8.93) becomes

$$\frac{\partial \langle T(J, t)_{KQ}^\dagger \rangle}{\partial t} = \sum_{K'} R_{KQK'Q} \langle T(J, t)_{K'Q}^\dagger \rangle \quad (8.100)$$

This expression shows that tensors with different rank and the same component are mixed by the relaxation processes. In particular, orientation and alignment parameters with the same  $Q$  will combine with each other.

The state multipole formalism is of considerable interest for the description of relaxation in atomic and nuclear physics. For a more detailed discussion and applications to particular cases we refer, for example, to the reviews by [Omont \(1977\)](#) and [Baylis \(1979\)](#), and to the references cited in these papers.

## 8.6 The Liouville Formalism

The purpose of this section is to describe some mathematical techniques that are particularly useful in nonequilibrium quantum statistics. These techniques are connected with the Liouville representation of Density matrices.

The elements of the Hilbert space are the state vectors  $|\psi\rangle$ . Consider now the set of all linear operators  $A, B, \dots$  acting on the states  $|\psi\rangle$ . Any linear combination of linear operators is also a linear operator. Thus the set of all linear operators span another linear space, called the *Liouville space*, if an inner product is defined by the relation

- $$\langle A | B \rangle = \text{tr } A^\dagger B \quad (8.101)$$

We will use the notation  $|A\rangle, |B\rangle, \dots$  to emphasize that these operators are to be considered elements in the Liouville space.

Consider a set of basis vectors  $|m'\rangle, |m\rangle, \dots$  in Hilbert space. A basis in the Liouville space is then represented by the set of all operators  $|m'\rangle\langle m|$  which can be obtained by combining all elements of the set  $|m\rangle$ . Following [Gabriel \(1969\)](#) and using the “Dirac” notation  $|m'm\rangle$  for  $|m'\rangle\langle m|$  and  $\langle m'm|$  for  $|m\rangle\langle m'|$  and using (8.101) we find the orthogonality relation

$$\langle m'm | n'n \rangle = \text{tr}\{|m\rangle\langle m'|n\rangle\langle n|\} = \delta_{m'n'}\delta_{mn} \quad (8.102)$$

and the completeness relation

$$\sum_{m'm} |m'm)(m'm| = \mathbf{1} \quad (8.103)$$

where  $\mathbf{1}$  is the unit operator in Liouville space. It follows then that

$$(m'm|A) = \text{tr}[|m\rangle\langle m'|A] = \langle m'|A|m\rangle \quad (8.104)$$

that is, the inner product of any Liouville vector  $A$  with the basis vectors  $|m'm\rangle$  is given by the usual matrix element  $\langle m'|A|m\rangle = A_{m'm}$  in Hilbert space.

When the angular symmetries of the system under consideration are important it is convenient to use the elements  $|T(J'J)_{KQ}\rangle$  as basis vectors. This set is orthonormal,

$$\begin{aligned} (T(J'J)_{K'Q'}|T(J'J)_{KQ}) &= \text{tr} \left\{ T(J'J)_{K'Q'}^\dagger T(J'J)_{KQ} \right\} \\ &= \delta_{J'J} \delta_{K'K} \delta_{Q'Q} \end{aligned} \quad (8.105)$$

in accordance with (4.24) and complete

$$\sum_{J'JKQ} |\langle T(J'J)_{KQ}\rangle(T(J'J)_{KQ}| = \mathbf{1} \quad (8.106)$$

Applying the operator (8.106) to the density matrix, considered as a vector  $|\rho\rangle$  in the Liouville space, gives immediately the expansion:

$$|\rho\rangle = \sum_{J'JKQ} |T(J'J)_{KQ}\rangle(T(J'J)_{KQ}| \rho) \quad (8.107)$$

The state multipoles are then interpreted as the inner products

$$\left\langle T(J'J)_{KQ}^\dagger \right\rangle = (T(J'J)_{KQ}|\rho) \quad (8.108)$$

which can be transformed into the usual form (4.33) by using (8.101). Equations 8.107 and 8.108 correspond to the expansion (4.32).

To make calculations in the Liouville space it is necessary to introduce operators  $\hat{Q}$  which transform a vector  $|A\rangle$  into another vector

$$\hat{Q}|A\rangle = |\hat{Q}A\rangle \quad (8.109)$$

The operators  $\hat{Q}$  are often referred to as “superoperators.” In an arbitrary basis

$$\begin{aligned}
 (m'm|\hat{Q}|A) &= \sum_{n'n} (m'm|\hat{Q}|n'n)(n'n|A) \\
 &= \sum_{n'n} Q_{m'mn'n} A_{n'n}
 \end{aligned} \tag{8.110}$$

where the completeness relation (8.103) and (8.104) has been used. The elements of any superoperator are thus characterized by four indices.

As an example consider the general relaxation (8.88):

$$\dot{\rho}_{m'm} = \sum_{n'n} R_{m'mn'n} \rho_{n'n}$$

Interpreting the matrix elements as inner products between Liouville vectors according to (8.104) we write

$$(m'm|\dot{\rho}) = \sum_{n'n} (m'm|\hat{R}|n'n)(n'n|\rho)$$

Substitution of the identity operator (8.103) yields then

$$(m'm|\dot{\rho}) = (m'm|\hat{R}|\rho)$$

or

$$|\dot{\rho}\rangle = \hat{R}|\rho\rangle \tag{8.111}$$

where  $\hat{R}$  is the relaxation superoperator.

Of particular importance in nonequilibrium quantum statistics is the *Liouville operator*  $\hat{L}$ , defined for a given Hamiltonian  $H$  by

- $\hat{L}|A\rangle = (1/\hbar)[H, A]\rangle \tag{8.112}$

for any operator  $A$  where  $[H, A]$  denotes the usual commutator in Hilbert space. A convenient basis  $|i, j\rangle$  for  $\hat{L}$  can be constructed from the eigenstates  $|i\rangle, |j\rangle, \dots$  of the Hamiltonian. In this basis

$$\begin{aligned}
 \hat{L}|ij\rangle &= \hat{L}|i\rangle\langle j| \\
 &= (1/\hbar)[H, |i\rangle\langle j|] \\
 &= \omega_{ij}|ij\rangle
 \end{aligned} \tag{8.113}$$

which shows that the eigenvalues of the Liouville operator are identical to the possible frequencies  $\omega_{ij}$  of the system.

The equation of motion (2.52) of the density matrix can be rewritten in the Liouville notation:

$$|\dot{\rho}\rangle = -(i/\hbar)[H, |\rho\rangle]$$

or

•

$$|\dot{\rho}\rangle = -i \hat{L}|\rho\rangle \quad (8.114)$$

The formal solution of (8.114) is

$$|\rho(t)\rangle = |\rho(0)\rangle \exp(-i \hat{L}t) \quad (8.115)$$

with the time evolution superoperator

$$\hat{U}(t) = \exp(-i \hat{L}t) \quad (8.116)$$

Equation 8.115 should be compared with the traditional form (2.52).

Equations 8.107 and 8.115 allow a compact representation of the perturbation coefficients defined by (4.118). Assuming that the system of interest is described by a density matrix

$$|\rho(0)\rangle = \sum_{KQ} \left\langle T(J)_{KQ}^\dagger \right\rangle |T(J)_{KQ}\rangle$$

at time  $t = 0$  and by

$$|\rho(t)\rangle = \sum_{kq} \left\langle T(J, t)_{kq}^\dagger \right\rangle |T(J)_{kq}\rangle$$

at time  $t$  we obtain from (8.108) and 8.115

$$\begin{aligned} \left\langle T(J, t)_{kq}^\dagger \right\rangle &= (T(J)_{kq}|\rho(t)\rangle) \\ &= (T(J)_{kq}|\hat{U}(t)|\rho(0)\rangle) \\ &= \sum_{KQ} \left\langle T(J)_{KQ}^\dagger \right\rangle G(t)_{KQ}^{Qq} \end{aligned} \quad (8.117)$$

where the perturbation coefficient in Liouville notation is represented by

$$G(t)_{KQ}^{Qq} = (T(J)_{kq}|\hat{U}(t)|T(J)_{KQ}\rangle) \quad (8.118)$$

The formalism presented here has been applied by various authors to the theory of angular correlations perturbed by relaxation effects (see, for example, the papers by [Gabriel \(1969\)](#), and [Bosse and Gabriel \(1974\)](#)).

The real advantage of the Liouville operator appears in the resolvent form. The resolvent method, which adopts the concepts and techniques of scattering theory to the Liouville representation of density matrices, allows to represent the formalism in a compact form. For an introduction into this method we refer to the original paper by [Zwanzig \(1960\)](#).

## 8.7 Linear Response of a Quantum System to an External Perturbation

Physical problems are concerned with the determination of the unknown properties of a system. In order to do this one lets an external agent act on the system and observes the reaction of the system. That is, the observer puts a question to the system and the system responds. Starting with such general consideration the response formalism has been developed. This formalism was first applied by Kubo to the theory of irreversible processes in order to study transport phenomena, for example, the effect of external forces on equilibrium systems disturbing the equilibrium state and causing the system to conduct heat or electricity, or otherwise respond to the stimulus. In the present section a brief introduction into this formalism will be given.

Let a quantum system described by a density matrix  $\rho(t)$  be subjected to the action of an external perturbation  $V(t)$ . In the theory of irreversible processes it is usually assumed that the system was in statistical equilibrium with a heat bath in the remote past ( $t \rightarrow -\infty$ ), which is expressed by the initial condition

$$\rho(t) \rightarrow \rho_0 \quad (8.119)$$

for  $t \rightarrow -\infty$ , where  $\rho_0$  is the equilibrium density matrix of the system. The time evolution of the density matrix is given by the Liouville equation (2.52). Assuming that  $V(t)$  is sufficiently small then in first-order perturbation theory the solution of the Liouville equation can be written in the form

$$\rho(t) = \rho_0 - (i/\hbar) \int_{-\infty}^t dt' \exp[iH_0(t'-t)/\hbar] [V(t'), \rho_0] \exp[-iH_0(t'-t)/\hbar] \quad (8.120)$$

which is obtained by transforming (2.81) back into the Schrödinger picture by using (2.61) and (2.75). In this approximation the change is the expectation value  $\langle A \rangle$  of an operator  $A$  is given by

$$\begin{aligned} \Delta\langle A(t) \rangle &= \text{tr}\{\rho(t)A\} - \text{tr}\rho_0A \\ &= -\frac{i}{\hbar} \text{tr} \left\{ \int_{-\infty}^t \exp \left[ \frac{iH_0(t'-t)}{\hbar} \right] [V(t'), \rho_0] \exp \left[ -\frac{iH_0(t'-t)}{\hbar} \right] A dt' \right\} \end{aligned} \quad (8.121)$$

The quantity  $\Delta\langle A(t) \rangle$  can be regarded as the first-order response of the system to an external perturbation. It should be noted that the Hamiltonian  $H_0 = V(t)$  refers only to the system itself and the influence of the heat bath is not taken into account.

Suppose that  $V(t)$  can be represented in the form

$$V(t) = f(t)B \quad (8.122)$$

where  $f(t)$  is an external driving force (for example, an electric field) and  $B$  an operator on the system (for example, the dipole operator). Inserting (8.122) into (8.121) gives

$$\begin{aligned}\Delta\langle A(t)\rangle &= (i/\hbar) \int_{-\infty}^t dt' \operatorname{tr}\{[B, \rho_0]A(t'-t)\}f(t') \\ &= (i/\hbar) \int_{-\infty}^t \operatorname{tr}\{\rho_0[A(t'-t), B]\}f(t')dt'\end{aligned}\quad (8.123)$$

where the cyclic property of the trace has been used and where

$$A(t'-t) = \exp\{-iH_0(t'-t)/\hbar\}A \exp[iH_0(t'-t)/\hbar] \quad (8.124)$$

The upper limit of integration in (8.123) can be extended to infinity by introducing the *Green's function*

- $\langle\langle A(t)B(t')\rangle\rangle = -(i/\hbar)\theta(t-t')\operatorname{tr}\{\rho_0[A(t)B(t')]\}$  (8.125)

where  $\theta(t-t')$  is the step function.  $\Delta\langle A(t)\rangle$  can then be written in the form

- $\Delta\langle A(t)\rangle = \int_{-\infty}^{\infty} \langle\langle A(t'-t)B\rangle\rangle f(t')dt'$  (8.126)

Equation 8.126 shows that the effect of an external perturbation on the mean values of observables can be described by Green's functioning coupling the observed quantity with the perturbation.

An interpretation of the Green's function can be obtained by considering a unit pulse at time  $t_1$ , that is, by letting  $f(t')$  become  $\delta(t'-t_1)$  [where  $\delta(t'-t_1)$  denotes Dirac's delta function]. In this case it follows from (8.126) that

$$\Delta\langle A(t)\rangle = \langle\langle A(t_1-t)B\rangle\rangle \quad (8.127)$$

The Green's function  $\langle\langle A(t'-t)B\rangle\rangle$  is therefore the change  $\Delta\langle A(t)\rangle$  by the time  $t$  due to a unit pulse at time  $t'$ . Equation 8.126 can then be interpreted as the linear superposition of responses produced by pulses at times  $t'$  with amplitudes  $f(t')$ . The range of values of  $t'$  in (8.126) is  $t' < t$  (otherwise the step function vanishes). The response has therefore a *causal* character since only the effects of the perturbation at past moments of the time are taken into account. For this reason the quantity (8.125) is called the *retarded Green's function*.

Equation 8.126 is called the *Kubo formula* for the linear response of a system. The important point to note is that this equation expresses nonequilibrium properties in terms of averages over equilibrium states. One could also define the nonlinear response of a system to an external agent. In this case, however, the Green's functions are no longer properties of the unperturbed system.

As a special case consider a periodic perturbation

$$V(t) = -V_0 \exp(-i\omega t + \varepsilon t) B \quad (8.128)$$

where  $V_0$  is the amplitude and  $\varepsilon$  an infinitesimally small quantity which ensures  $V(t) \rightarrow 0$  for  $t \rightarrow -\infty$ . In the case of the periodic perturbation (8.128), (8.126) takes the form

$$\begin{aligned} \Delta\langle A(t) \rangle &= V_0 \exp(-i\omega t + \varepsilon t) \int_{-\infty}^{\infty} dt' \langle \langle A(t' - t) B \rangle \rangle \\ &\quad \times \exp[-i\omega(t' - t) + \varepsilon(t' - t)] \\ &= V_0 \exp(-i\omega t + \varepsilon t) \int_{-\infty}^{\infty} \langle \langle A(\tau) B \rangle \rangle \exp(-i\omega\tau + \varepsilon\tau) d\tau \quad (8.129a) \end{aligned}$$

$$= V_0 \exp(-i\omega t + \varepsilon t) \langle \langle AB \rangle \rangle_{\omega} \quad (8.129b)$$

where  $\tau = t' - t$  and  $\langle \langle AB \rangle \rangle_{\omega}$  is defined by the integral in (8.129a). The *generalized susceptibility*  $\chi(\omega)$  which describes the influence of the periodic perturbation (8.128), is defined by

$$\Delta\langle A(t) \rangle = \chi(\omega) V_0 \exp(-i\omega t + \varepsilon t) \quad (8.130)$$

Comparing (8.129b) and (8.130) we obtain

$$\chi(\omega) = \langle \langle AB \rangle \rangle_{\omega} \quad (8.131)$$

This is Kubo's formula for the generalized susceptibility.

The equations derived here can be used as a starting point for the investigation of transport phenomena. Under appropriate conditions it is possible to connect the response formalism with the Onsager theory of irreversible processes. Assuming that the external perturbation is so weak that the discussion can be restricted to first-order perturbation theory it has been shown that transport coefficients can be evaluated using an equilibrium density matrix. For example, the electric conductivity is directly related to the response of a system to an external field and this response in turn is related to time correlation functions. A discussion of these topics falls outside the scope of this book. For a detailed account with many applications the reader is referred particularly to the treatment given by Zubarev (1974).

# Appendices

## A.1 Appendix A: The Direct Product

An important quantity in matrix algebra is the direct product  $C = A \times B$  of two matrices  $A$  and  $B$ , where each element of  $C$  is formed by replacing each element  $a_{ij}$  of  $A$  by the matrix  $a_{ij}B$ . Thus if  $A$  is  $N$  dimensional and  $B$   $n$  dimensional then  $C$  is an  $(N \times n)$ -dimensional matrix. For example, if

$$A = \begin{pmatrix} a_{11} & a_{12} \\ a_{21} & a_{22} \end{pmatrix}, \quad B = \begin{pmatrix} b_{11} & b_{12} \\ b_{21} & b_{22} \end{pmatrix}$$

then the direct product  $A \times B$  is given by the four-dimensional matrix

$$A \times B = \begin{pmatrix} a_{11}B & a_{12}B \\ a_{21}B & a_{22}B \end{pmatrix} \quad (\text{A.1a})$$

where each “element”  $a_{ij}B$  stands for the two-dimensional matrix

$$a_{ij}B = \begin{pmatrix} a_{ij}b_{11} & a_{ij}b_{12} \\ a_{ij}b_{21} & a_{ij}b_{22} \end{pmatrix} \quad (\text{A.1b})$$

It can be shown that, if  $A$  and  $C$  are  $m \times m$  matrices and  $B$  and  $D$   $n \times n$  matrices, then the usual matrix product of  $A \times B$  and  $C \times D$  is given by

$$(A \times B) \cdot (C \times D) = (AC) \times (BD) \quad (\text{A.2a})$$

An important trace relation is

$$\text{tr}(A \times B) = \text{tr}A \text{ tr } B \quad (\text{A.2b})$$

Application of the relations (A.2) enables the use of explicit matrix representations to be avoided in most calculations.

The definition (A.1) can also be applied to row vectors which can be considered as matrices with one row only. For example, when the spin states are written in the standard representation, the direct product of the spin-1 state  $|+1\rangle$  and the spin-1/2 state  $| - 1/2\rangle$  is given by

$$\begin{pmatrix} 1 \\ 0 \\ 0 \end{pmatrix} \times \begin{pmatrix} 0 \\ 1 \\ 0 \\ 0 \end{pmatrix} = \begin{pmatrix} 0 \\ 1 \\ 0 \\ 0 \\ 0 \\ 0 \end{pmatrix} \quad (\text{A.3})$$

which we will write in the form  $| - 1\rangle | - 1/2\rangle = |1, - 1/2\rangle$ . (A.4)

More generally, consider two linear spaces  $R$  and  $r$ , spanned by basis vectors  $|N\rangle$  and  $|n\rangle$ , respectively [that is, any state vector in the space  $R(r)$  can be written as a linear combination of the states  $|N\rangle(|n\rangle)$ ]. The combined space can be spanned by the set of all direct product states

$$|N, n\rangle = |N\rangle|n\rangle \quad (\text{A.5})$$

that is, by all, possible pairs formed from all basis vectors  $|N\rangle$  and  $|n\rangle$ .

For example, an ensemble of spin-1 particles may be in the state  $|+1\rangle$  and an ensemble of spin-1/2 particles in the state  $| - 1\rangle$ . When both systems are well separated and not interacting the state of the combined system is represented by the direct product  $|+1, - 1/2\rangle$ . This simple representation does not apply when the two systems interact (see Sect. 3.1). However, any state vector  $|\psi\rangle$  representing the state of the coupled system, can always be written as a sum of direct products

$$|\psi\rangle = \sum_{Mm} a(M, m)|M\rangle|m\rangle \quad (\text{A.6})$$

with  $M = \pm 1, 0$  and  $m = \pm 1/2$ .

The direct product states have the following important properties. A scalar product is defined by

$$\langle N', n' | N, n \rangle = \langle N' | N \rangle \langle n' | n \rangle$$

The matrix elements of an operator  $Q(R)$ , acting only on the space  $R$ , are given by

$$\langle N', n' | Q(R) | N, n \rangle = \langle N', | Q(R) | N \rangle \langle n' | n \rangle \quad (\text{A.7})$$

and for a direct product

$$\langle N', n' | Q(R) \times Q(r) | N, n \rangle = \langle N' | Q(R) | N \rangle \langle n' | Q(r) | n \rangle \quad (\text{A.8})$$

Consider now a mixture of states  $|N, n\rangle$  represented by a density matrix

$$\rho = \sum_{Nn} W_{Nn} |N, n\rangle \langle N, n| \quad (\text{A.9})$$

where  $W_{Nn}$  is the probability of finding the system in the state  $|N, n\rangle = |N\rangle|n\rangle$ . The two systems are *uncorrelated* if

$$W_{Nn} = W_N W_n \quad (\text{A.10})$$

that is, when the probability of finding one system in a state  $|N\rangle$  is independent of the probability of finding the other system in a state  $|n\rangle$ . When (A.10) holds then, from (A.5) and (A.9),

$$\begin{aligned} \rho &= \left( \sum_N W_N |N\rangle \langle N| \right) \left( \sum_n W_n |n\rangle \langle n| \right) \\ &= \rho(N) \times \rho(n) \end{aligned} \quad (\text{A.11})$$

That is, *in the special case of uncorrelated systems the total density matrix is represented by the direct product of the individual matrices*.

As an example, consider two ensembles of particles with spins  $S_1$  and  $S_2$ , respectively. Before any interaction the two systems are uncorrelated and represented by density matrices  $\rho(S_1)$  and  $\rho(S_2)$ , respectively. The combined system then is characterized by the density matrix

$$\rho_{\text{ih}} = \rho(S_1) \times \rho(S_2)$$

Expanding the density matrices  $\rho(S_1)$  and  $\rho(S_2)$  in terms of spin tensors as discussed in Sect. 4.4 we obtain

$$\begin{aligned} \rho_{\text{in}} &= \left[ \sum_{KQ} \left\langle T(S_1)_{KQ}^\dagger \right\rangle T(S_1)_{KQ} \right] \left[ \sum_{kq} \left\langle T(S_2)_{kq}^\dagger \right\rangle T(S_2)_{kq} \right] \\ &= \sum_{\substack{KQ \\ kq}} \left\langle T(S_1)_{KQ}^\dagger \right\rangle \left\langle T(S_2)_{kq}^\dagger \right\rangle [T(S_1)_{KQ} \times T(S_2)_{kq}] \end{aligned} \quad (\text{A.12})$$

Using (A.2b), (4.24), and (4.25) we obtain for the trace

$$\begin{aligned} \text{tr}[\rho_{\text{in}} \cdot T(S_1)_{K'Q'} \times \mathbf{1}] &= \sum_{\substack{KQ \\ kq}} \left\langle T(S_1)_{KQ}^\dagger \right\rangle \left\langle T(S_2)_{kq}^\dagger \right\rangle \\ &\quad \cdot \text{tr}[T(S_1)_{KQ} \times T(S_2)_{kq}] \left[ T(S_1)_{K'Q'}^\dagger \times \mathbf{1} \right] \\ &= [1/(2S_2 + 1)^{1/2}] \left\langle T(S_1)_{K'Q'}^\dagger \right\rangle \cdot \langle T(S_2)_{00} \rangle \end{aligned}$$

Application of (4.42) then finally gives

$$\left\langle T(S_1)_{K'Q'}^\dagger \right\rangle = \text{tr } \rho_{\text{in}} \left[ T(S_1)_{K'Q'}^\dagger \times \mathbf{1} \right] \quad (\text{A.13})$$

Similarly, the spin tensors characterizing the second system only are given by

$$\left\langle T(S_2)_{kq}^\dagger \right\rangle = \text{tr } \rho_{\text{in}} \left[ \mathbf{1} \times T(S_2)_{kq}^\dagger \right] \quad (\text{A.14})$$

Equations A.12, A.13, and (A.14) are used, for example, in scattering theory to describe the initial state of polarized particles.

## B.1 Appendix B: State Multipoles for Coupled Systems

Consider two interacting systems with angular momenta  $J$  and  $I$ , respectively. The two systems may consist of, for example, two different ensembles of particles such as electrons with spin  $I = 1/2$  and atoms with spin  $J$  or of two different characteristics of the same state (for example, an atomic state with electronic angular momentum  $J$  and nuclear spin  $I$ ).

State multipoles describing the coupled system can be constructed by first coupling the states  $|JM\rangle$  and  $|Im\rangle$  to eigenstates of the total angular momentum operator  $F$  and then using these eigenstates to construct tensor operators  $T(F'F)_{KQ}$  using (4.3) with state multipoles corresponding to (4.31).

It is often more convenient to represent the total density matrix  $\rho$  in a different way. We take the set of all tensor operators  $T(J)_{KQ}$  and  $T(I)_{kq}$  which describe the separate systems (with  $K \leq 2J$  and  $k \leq 2I$ ) and construct the set of all direct products  $T(J)_{KQ} \times T(I)_{kq}$  as in Appendix A.1. Any operator acting on the composite space, spanned by the direct products  $|JM|Im\rangle$ , can then be expanded in terms of this set. Hence

$$\rho = \sum_{\substack{KQ \\ kq}} \left\langle T(J)_{KQ}^\dagger \times T(I)_{kq}^\dagger \right\rangle [T(J)_{KQ} \times T(I)_{kq}] \quad (\text{B.1})$$

The state multipoles are obtained from (B.1) calculating the trace

$$\left\langle T(J)_{KQ}^\dagger \times T(I)_{kq}^\dagger \right\rangle = \text{tr } \rho \left[ T(J)_{KQ}^\dagger \times T(I)_{kq}^\dagger \right] \quad (\text{B.2})$$

according to Appendix A.1.

When the two systems are uncorrelated

$$\left\langle T(J)_{KQ}^\dagger \times T(I)_{kq}^\dagger \right\rangle = \left\langle T(J)_{KQ}^\dagger \right\rangle \left\langle T(I)_{kq}^\dagger \right\rangle \quad (\text{B.3})$$

as follows from Appendix A.1.

In many cases the parameters

$$\left\langle T(J)_{KQ}^\dagger \times \mathbf{1} \right\rangle = (2I + 1)^{1/2} \left\langle T(J)_{KQ}^\dagger \times T(I)_{00} \right\rangle \quad (\text{B.4})$$

are of particular interest. In (B.4) and (4.14) has been used, and  $\mathbf{1}$  is the  $(2I + 1)$ -dimensional unit matrix. Using (A.8)b it can readily be shown that

$$\begin{aligned} \left\langle T(J)_{KQ}^\dagger \times \mathbf{1} \right\rangle &= \text{tr } \rho \cdot [T(J)_{KQ} \times \mathbf{1}] \\ &= \text{tr} \left[ \rho(J) T(J)_{KQ}^\dagger \right] \end{aligned} \quad (\text{B.5})$$

where  $\rho(J)$  is the reduced density matrix describing the  $J$  system alone

$$\langle JM' | \rho(J) | JM \rangle = \sum_m \langle JM', Im | \rho | JM, Im \rangle$$

Hence, when only the  $J$  system is of interest and the  $I$  system undetected, only the set of multipoles  $\left\langle T(J)_{KQ}^\dagger \times \mathbf{1} \right\rangle = \left\langle T(J)_{KQ}^\dagger \right\rangle$  need be considered. Similarly, when only the  $I$  system is observed then the parameters of interest are the multipoles  $\left\langle \mathbf{1} \times T(I)_{kq}^\dagger \right\rangle = \left\langle T(I)_{kq}^\dagger \right\rangle$ . Examples of this are given in Sect. 4.7. As another example, consider scattering experiments with polarized particles of spin  $J$  and  $I$ , respectively. The set of all spin tensors  $\left\langle T(J)_{KQ}^\dagger \times \mathbf{1} \right\rangle$  and  $\left\langle \mathbf{1} \times T(I)_{kq}^\dagger \right\rangle$  can be used to characterize the polarization states of the  $J$  and  $I$  systems, respectively, when the other one is either undetected or unpolarized. When polarization measurements are performed on both systems in coincidence then some or all of the parameters with both  $K$  and  $k$  nonzero must also be considered. Using (E.5) and expressing  $\rho_{\text{out}}$  according to (B.2) and  $\rho_{\text{in}}$  according to (A.12) the spin tensors of the final particles can then be related to those of the initial ones.

Finally, we give the relation describing the transformation between the “coupled” tensors  $T(F'F)_{K'Q'}$  and the “uncoupled” operators  $T(J)_{KQ} \times T(I)_{kq}$ :

$$\begin{aligned} T(F'F)_{K'Q'} &= \sum_{\substack{KQ \\ kq}} [(2K + 1)(2k + 1)(2F' + 1)(2F + 1)]^{1/2} (KQ, kq | K'Q') \\ &\times \left\{ \begin{array}{c} K \ k \ K' \\ J \ I \ F' \\ J \ I \ F \end{array} \right\} T(J)_{KQ} \times T(I)_{kq} \end{aligned} \quad (\text{B.6})$$

where  $\{\dots\}$  denotes a  $9j$  symbol. The inverse relation can be obtained by using the orthogonality properties of the  $9j$  symbol:

$$T(J)_{KQ} \times T(I)_{kq} = \sum_{\substack{FF' \\ K'Q'}} [(2K+1)(2k+1)(2F'+1)(2F+1)]^{1/2} (KQ, kq | K'Q') \\ \times \left\{ \begin{array}{ccc} K & k & K' \\ J & I & F' \\ J & I & F \end{array} \right\} T(F'F)_{K'Q'} \quad (\text{B.7})$$

As a special case, for  $k = 0$  (B.7) gives

$$T(J)_{KQ} \times \mathbf{1} = (2I+1)^{1/2} [T(J)_{KQ} \times T(I)_{00}] \\ = \sum_{F'F} [(2F'+1)(2F+1)]^{1/2} (-1)^{F+J+K+I} \left\{ \begin{array}{ccc} F' & F & K \\ J & J & I \end{array} \right\} \quad (\text{B.8})$$

A similar relation holds for the tensor operators  $\mathbf{1} \times T(I)_{kq}$  describing only the I system with the J system undetected.

## C.1 Appendix C: Formulas from Angular Momentum Theory

### Clebsch–Gordon Coefficients

$$\sum_{JM} (J_1 M'_1, J_2 M'_2 | JM) (J_1 M_1, J_2 M_2 | JM) = \delta_{M'_1 M_1} \delta_{M'_2 M_2} \quad (\text{C.1a})$$

$$\sum_{M_1 M_2} (J_1 M_1, J_2 M_2 | J' M') (J_1 M_1, J_2 M_2 | JM) = \delta_{J' J} \delta_{MM'} \quad (\text{C.1b})$$

Symmetry properties:

$$(J_1 M_1, J_2 M_2 | JM) = (-1)^{J_1 + J_2 - J} (J_1 - M_1, J_2 - M_2 | J - M) \quad (\text{C.2a})$$

$$= (-1)^{J_1 + J_2 - J} (J_2 M_2, J_1 M_1 | JM) \quad (\text{C.2b})$$

$$= [(2J+1)/(2J_2+1)]^{1/2} (-1)^{J_1 - M_1} (J_1 M_1, J - M | J_2 - M_2) \quad (\text{C.2c})$$

$$= [(2J+1)/(2J_1+1)]^{1/2} (-1)^{J_2 - M_2} (J - M, J_2 M_2 | J_1 - M_1) \quad (\text{C.2d})$$

### 3j Symbols

Definition:

$$\left( \begin{array}{ccc} J_1 & J_2 & J \\ M_1 & M_2 & M \end{array} \right) = [1/(2J+1)^{1/2}] (-1)^{J_1 - J_2 - M} (J_1 M_1, J_2 M_2 | J - M) \quad (\text{C.3})$$

Orthogonality relations:

$$\sum_{JM} (2J+1) \begin{pmatrix} J_1 & J_2 & J \\ M_1 & M_2 & M \end{pmatrix} \begin{pmatrix} J_1 & J_2 & J \\ M'_1 & M'_2 & M \end{pmatrix} = \delta_{M'_1 M_1} \delta_{M'_2 M_2} \quad (\text{C.4a})$$

$$\sum_{M_1 M_2} \begin{pmatrix} J_1 & J_2 & J' \\ M_1 & M_2 & M' \end{pmatrix} \begin{pmatrix} J_1 & J_2 & J \\ M_1 & M_2 & M \end{pmatrix} = [1/(2J+1)] \delta_{JJ'} \delta_{MM'} \quad (\text{C.4b})$$

Symmetry properties: The  $3j$  symbol is invariant under cyclic permutations of its columns and multiplied by  $(-1)^{J_1+J_2+J}$  by noncyclic ones. In particular,

$$\begin{pmatrix} J_1 & J_2 & J \\ M_1 & M_2 & M \end{pmatrix} = \begin{pmatrix} J_2 & J & J_1 \\ M_1 & M & M_1 \end{pmatrix} = \begin{pmatrix} J & J_1 & J_2 \\ M & M_1 & M_2 \end{pmatrix} \quad (\text{C.5a})$$

$$\begin{pmatrix} J_1 & J_2 & J \\ M_1 & M_2 & M \end{pmatrix} = (-1)^{J_1+J_2+J} \begin{pmatrix} J_2 & J_1 & J \\ M_2 & M_1 & M \end{pmatrix} \quad (\text{C.5b})$$

$$= (-1)^{J_1+J_2+J} \begin{pmatrix} J_1 & J_2 & J \\ -M_1 & -M_2 & -M \end{pmatrix} \quad (\text{C.5c})$$

Special case:

$$\begin{pmatrix} J_1 & J_2 & 0 \\ M_1 & -M_2 & 0 \end{pmatrix} = \frac{(-1)^{J_1-M_1}}{(2J_1+1)^{1/2}} \delta_{J_1 J_2} \delta_{M_1 M_2} \quad (\text{C.6})$$

*6j Symbols*

Definition:

$$\begin{Bmatrix} J_1 & J_2 & J_3 \\ j_1 & j_2 & j_3 \end{Bmatrix} = \sum_{\text{all } M_i, m_i} (-1)^{\Sigma J_i + \Sigma j_i + \Sigma m_i} \begin{pmatrix} J_1 & J_2 & J_3 \\ -M_1 & -M_2 & -M_3 \end{pmatrix} \begin{pmatrix} J_1 & j_2 & j_3 \\ M_1 & m_2 & -m_3 \end{pmatrix} \times \begin{pmatrix} j_1 & J_2 & j_3 \\ -m_1 & M_2 & m_3 \end{pmatrix} \begin{pmatrix} j_1 & j_2 & J_3 \\ m_1 & -m_2 & M_3 \end{pmatrix} \quad (\text{C.7})$$

Symmetries: The  $6j$  symbol is invariant for interchange of any two columns, and for interchange of the upper and lower arguments in each of any two columns; for example,

$$\begin{Bmatrix} J_1 & J_2 & J_3 \\ j_1 & j_2 & j_3 \end{Bmatrix} = \begin{Bmatrix} J_1 & J_3 & J_2 \\ j_1 & j_3 & j_2 \end{Bmatrix} = \begin{Bmatrix} j_1 & j_2 & J_3 \\ J_1 & J_2 & j_3 \end{Bmatrix} \quad (\text{C.8})$$

Contraction:

$$\begin{aligned} \sum_{M_1 M_2 M_3} (-1)^{J_1+J_2+J_3+M_1+M_2+M_3} & \begin{pmatrix} J_1 & J_2 & j_3 \\ M_1 & -M_2 & m_3 \end{pmatrix} \begin{pmatrix} J_2 & J_3 & j_1 \\ M_2 & -M_3 & m_1 \end{pmatrix} \\ & \times \begin{pmatrix} J_3 & J_1 & j_2 \\ M_3 & -M_1 & m_2 \end{pmatrix} = \begin{pmatrix} j_1 & j_2 & j_3 \\ m_1 & m_2 & m_3 \end{pmatrix} \begin{Bmatrix} j_1 & j_2 & j_3 \\ J_1 & J_2 & J_3 \end{Bmatrix} \end{aligned} \quad (\text{C.9})$$

Orthogonality:

$$\sum_J (2J+1)(2J''+1) \begin{Bmatrix} J_1 & J_2 & J' \\ J_3 & J_4 & J \end{Bmatrix} \begin{Bmatrix} J_3 & J_2 & J \\ J_1 & J_2 & J'' \end{Bmatrix} = \delta_{J'J''} \quad (\text{C.10})$$

Special value:

$$\begin{Bmatrix} J_1 & J_2 & J_3 \\ 0 & J_3 & J_2 \end{Bmatrix} = \frac{(-1)^{J_1+J_2+J_3}}{[(2J_2+1)(2J_3+1)]^{1/2}} \quad (\text{C.11})$$

### C.1.1 Rotation Matrix Elements

Definition:

$$D(\gamma\beta\alpha)_{M'M}^{(J)} = \exp(iM'\gamma) d(\beta)_{M'M}^{(J)} \exp(iM\alpha) \quad (\text{C.12})$$

Symmetries:

$$\begin{aligned} d(\beta)_{M'M}^{(J)} &= d(-\beta)_{MM'}^{(J)} \\ &= (-1)^{M'-M} d(\beta)_{MM'}^{(J)} = (-1)^{M'-M} d(\beta)_{-M'-M}^{(J)} \end{aligned} \quad (\text{C.13})$$

$$D(\gamma\beta\alpha)_{M'M}^{(J)*} = (-1)^{M'-M} D(\gamma\beta\alpha)_{-M'-M}^{(J)} \quad (\text{C.14})$$

Special values:

$$d(\pi)_{M'M}^{(J)} = (-1)^{J+M} \delta_{M'M}, \quad d(0)_{M'M}^{(J)} = \delta_{M'M} \quad (\text{C.15})$$

Relation to the spherical harmonics  $Y_{JM}$  and Legendre polynomials  $P_J$ :

$$D(\gamma\beta\alpha)_{MO}^{(J)} = (-1)^M [4\pi/(2J+1)]^{1/2} Y(\beta\gamma)_{JM} \quad (\text{C.16a})$$

$$D(\gamma\beta\alpha)_{0M}^{(J)} = [4\pi/(2J+1)]^{1/2} Y(\beta\alpha)_{JM} \quad (\text{C.16b})$$

$$D(\gamma\beta\alpha)_{00}^{(J)} = P(\cos\beta)_J \quad (\text{C.16c})$$

Contraction ( $\omega = \gamma\beta\alpha$ ):

$$D(\omega)_{M'_1 M_1}^{(J_1)} D(\omega)_{M'_2 M_2}^{(J_2)} = \sum_{JMM'} (2J+I) \begin{pmatrix} J_1 & J_2 & J \\ M'_1 & M'_2 & M' \end{pmatrix} \begin{pmatrix} J_1 & J_2 & J \\ M_1 & M_2 & M \end{pmatrix} D(\omega)_{M'M}^{(J)*} \quad (\text{C.17})$$

Orthogonality:

$$\int D(\gamma\beta\alpha)_{mm'}^{(j)*} D(\gamma\beta\alpha)_{MM'}^{(J)} \sin\beta d\beta da d\gamma = (8\pi^2/(2J+1)) \delta_{Jj} \delta_{mM} \delta_{m'M'} \quad (\text{C.18})$$

### C.1.2 Matrix Elements of Irreducible Tensor Operators

Wigner–Eckart theorem:

$$\langle J'M'|T_{KQ}|JM\rangle = (-1)^{J'-M'} \begin{pmatrix} J' & K & J \\ -M' & Q & M \end{pmatrix} \langle J'||T_K||J\rangle \quad (\text{C.19})$$

Reduction for composite systems ( $L + S = J$ ,  $L' + S' = J'$ ): If the tensor operator  $T_{KQ}$  acts only on the system with angular momenta  $L$ ,  $L'$  then

$$\begin{aligned} \langle (L'S')J'||T_K||(LS)J\rangle &= (-1)^{L'+S+J+K} [(2J'+1)(2J+1)]^{1/2} \\ &\times \begin{pmatrix} L' & J' & S \\ J & L & K \end{pmatrix} \langle L'||T_K||L\rangle \delta_{SS'} \end{aligned} \quad (\text{C.20})$$

### C.1.3 Spherical Harmonics

Symmetry properties:

$$Y(\beta\alpha)_{KQ}^* = (-1)^Q Y(\beta\alpha)_{K-Q} \quad (\text{C.21})$$

Addition theorem:

$$\begin{aligned} Y(\beta\alpha)_{K_1Q_1} Y(\beta\alpha)_{K_2Q_2} &= \sum_{KQ} \left( \frac{(2K_1+1)(2K_2+1)(2K+1)}{4\pi} \right)^{1/2} \\ &\times \begin{pmatrix} K_1 & K_2 & K \\ 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} K_1 & K_2 & K \\ Q_1 & Q_2 & Q \end{pmatrix} Y(\beta\alpha)_{KQ}^* \end{aligned} \quad (\text{C.22})$$

Orthogonality:

$$\int_0^{2\pi} d\alpha \int_0^\pi d\beta \sin \beta Y(\beta\alpha)_{K'Q'}^* Y(\beta\alpha)_{KQ} = \delta_{K'K} \delta_{Q'Q} \quad (\text{C.23})$$

## D.1 Appendix D: The Efficiency of a Measuring Device

The diagonal elements  $\langle n|\rho|n\rangle$  of the density matrix are the probabilities that the pure state  $|n\rangle$  will be observed in an experimental observation. However, most experimental situations which can be devised will not respond to only one particular pure state and, in general, the detector responds to several states  $|n\rangle$  with the relative probabilities (“efficiencies”)  $\epsilon_n$ . The total probability of the response of the apparatus will then be given by

$$W = \sum_n \epsilon_n \langle n | \rho | n \rangle \quad (\text{D.1})$$

in the representation with basis vectors  $|n\rangle$ . We introduce the operator

$$\epsilon = \sum_n \epsilon_n |n\rangle \langle n| \quad (\text{D.2})$$

which is analogous to the density operator (2.8), and (D.1) can then be written in the form

$$W = \text{tr } \rho \epsilon \quad (\text{D.3})$$

$\epsilon$  is called the “efficiency matrix” of the measuring device which completely describes the response of the apparatus. If the apparatus responds only to a single state  $|n\rangle$  with certainty (that is, it is a perfect filter), then  $\epsilon = |n\rangle \langle n|$ . In this case we can project out of the mixture the definite pure state  $|n\rangle$  and (D.1) reduces to

$$W = W_n = \langle n | \rho | n \rangle \quad (\text{D.4})$$

As an example we will consider the measurement of polarization of spin-1/2 particles. The efficiency matrix  $\epsilon$  of the polarization filter is a  $2 \times 2$  matrix which can be expanded in terms of the two-dimensional unit matrix  $\mathbf{1}$  and the Pauli matrices in a similar way as the density matrix in Sect. 1.1.5:

$$\epsilon = (1/2) \left( \mathbf{1} + \sum_i Q_i \sigma_i \right) = (1/2)(\mathbf{1} + \mathbf{Q}\sigma) \quad (\text{D.5})$$

Transforming to a representation with basis states  $|\pm 1/2, z'\rangle$  where  $\epsilon$  is diagonal we find

$$\epsilon = \frac{1}{2} \begin{pmatrix} 1 + Q & 0 \\ 0 & 1 - Q \end{pmatrix} \quad (\text{D.6})$$

where  $Q = |\mathbf{Q}|$ . Hence, in this system,  $\epsilon$  can be written in the form

$$\epsilon = (1/2)(1 + Q)|1/2, z'\rangle \langle 1/2, z'| + (1/2)(1 - Q)|-1/2, z'\rangle \langle -1/2, z'| \quad (\text{D.7})$$

which relates the parameters  $Q$  to the efficiencies with which the filter responds to the states  $|\pm 1/2, z'\rangle$ .

Furthermore, it follows from (1.49) and (D.5) that

$$W = \text{tr } \rho \epsilon = (1/2)(1 + \mathbf{P}\mathbf{Q}) \quad (\text{D.8})$$

and hence  $W$  has its maximum value  $W_{\uparrow\uparrow}$  if  $\mathbf{P}$  and  $\mathbf{Q}$  are parallel and its minimum value  $W_{\downarrow\downarrow}$  if  $\mathbf{P}$  and  $\mathbf{Q}$  are antiparallel. It follows that the direction of  $\mathbf{Q}$  is that

direction in which the polarization filter must be oriented in order to get maximum response.

Thus, in order to determine  $\mathbf{P}$  for a given beam with a polarization filter with a known  $Q$ , the orientation of the filter must first be altered until  $W$  is a maximum. This direction is then the direction of  $P$ . The magnitude  $|\mathbf{P}|$  of the polarization vector is then found from a measurement of the values  $W_{\uparrow\uparrow}$  and  $W_{\downarrow\downarrow}$  at maximum and minimum response and the known value of  $Q$ :

$$P = \frac{W_{\uparrow\uparrow} - W_{\downarrow\downarrow}}{Q(W_{\uparrow\uparrow} + W_{\downarrow\downarrow})} \quad (\text{D.9})$$

## E.1 Appendix E: The Scattering and Transition Operators

In scattering theory it is convenient to consider the incoming state of the particles as the state vector  $|\psi_{\text{in}}\rangle$  at an infinitely remote past when the interaction between the particles can be neglected, and the outgoing state as the state vector  $|\psi_{\text{out}}\rangle$  at an infinitely late future instant corresponding to such a large distance between the particles for the interaction between them to be neglected again. The  $S$  matrix can then be defined by the relation

$$|\psi_{\text{out}}\rangle = S|\psi_{\text{in}}\rangle \quad (\text{E.1})$$

that is, the collision is thought of as a “black box,” mathematically represented by  $S$ , which transforms the “in” states into the “out” states. When the initial state is represented by the density matrix

$$\rho_{\text{in}} = \sum_i W_i |\psi_{\text{in}}^{(i)}\rangle \langle \psi_{\text{in}}^{(i)}|$$

the density matrix  $\rho'_{\text{out}}$  describing the final particles, is obtained by operating on  $\rho_{\text{in}}$  by  $S$  and  $S^\dagger$ :

$$\begin{aligned} S \rho_{\text{in}} S^\dagger &= \sum_i W_i S |\psi_{\text{in}}^{(i)}\rangle \langle \psi_{\text{in}}^{(i)}| S^\dagger \\ &= \sum_i W_i |\psi_{\text{out}}^{(i)}\rangle \langle \psi_{\text{out}}^{(i)}| \\ &\equiv \rho'_{\text{out}} \end{aligned} \quad (\text{E.2})$$

Since one is usually only interested in transitions between different states it is convenient to extract from  $S$  the unit operator  $\mathbf{1}$  and to define the *transition operator*  $T$  by

$$T = S - \mathbf{1} \quad (\text{E.3})$$

From (E.1) and (E.2) it follows

$$T|\Psi_{\text{in}}\rangle = |\Psi_{\text{out}}\rangle - |\Psi_{\text{in}}\rangle \quad (\text{E.4})$$

All possible transitions (scattering, reactions) in the system will be connected with the dissimilarity between initial and final state, that is,  $T$  transforms the “in” state into the scattered state. The interesting part of the density matrix (E.2) is then that one which contains the information on the scattered states alone, which is given by

$$\rho_{\text{out}} = T\rho_{\text{in}}T^\dagger \quad (\text{E.5})$$

The central problem of scattering theory is then the determination of  $T$ , that is, the determination of all elements of  $T$  (see Sect. 3.5).

## F.1 Appendix F: Some Consequences of Density Matrix Theory for Polarization Vectors and Tensors

In Sect. 3.6.3 we have considered the  $4 \times 4$  density matrix describing systems of two spin-1/2 particles. We have seen that the most general density matrix is characterized by 16 real parameters (15 if the normalization is taken into account). On the other hand, we have another set of 15 independent elements, namely the six components of the two individual polarization vectors  $\mathbf{P}^{(1)}$  and  $\mathbf{P}^{(2)}$ , and the nine components  $P_i^{(1)} \times P_j^{(2)}$  of the correlation tensor. It is convenient to expand the density matrix  $\rho$  in terms of this set.<sup>1</sup>

In order to achieve this we generalize the procedure leading to (1.48), where the  $2 \times 2$ -density matrix has been expanded in terms of the three Pauli matrices and the identity matrices. Similarly, we expand the  $4 \times 4$  density matrix  $\rho$  in terms of the unit matrix, the operators  $\sigma_i \times \mathbf{1}$  and  $\mathbf{1} \times \sigma_j$ , and the nine direct products  $\sigma_i \times \sigma_j$  ( $i, j = x, y, z$ ).

The components of the polarization vectors are defined by the relations

$$P_i^{(1)} = \text{tr } \rho (\sigma_i \times \mathbf{1}) = \text{tr } \rho^{(1)} \sigma_i , \quad (\text{F.1a})$$

and

$$P_j^{(2)} = \text{tr } \rho (\mathbf{1} \times \sigma_j) = \text{tr } \rho^{(2)} \sigma_j , \quad (\text{F.1b})$$

where  $\mathbf{1}$  denotes the  $2 \times 2$  identity matrix, and where  $\rho$  is now the full  $4 \times 4$  matrix.  $\rho^{(1)}$  and  $\rho^{(2)}$  denote the reduced density matrices of the first and second system,

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<sup>1</sup>The derivations are a bit lengthy, and readers not interested in the mathematical details may directly proceed to (F.6).

respectively. The components of the correlation tensor are given by (3.58):

$$P_i^{(1)} \times P_j^{(2)} = \text{tr} \rho (\sigma_i \times \sigma_j) . \quad (\text{F.1c})$$

We make the *ansatz*

$$\rho = \frac{1}{4} \left( \mathbf{1} \times \mathbf{1} + \sum_i a_i (\sigma_i \times \mathbf{1}) + \sum_j b_j (\mathbf{1} \times \sigma_j) + \sum_{ij} c_{ij} (\sigma_i \times \sigma_j) \right) . \quad (\text{F.2})$$

Here,  $\mathbf{1}$  denotes the  $2 \times 2$  identity matrix and the direct product  $\mathbf{1} \times \mathbf{1}$  gives the  $4 \times 4$  unit matrix (see (A.1), Appendix A.1). In order to determine the coefficients  $a_i, b_j, c_{ij}$  we have to calculate certain traces by using (1.44), (1.44), and (A.2) of Appendix A.1. Applying the relations we obtain

$$\begin{aligned} \text{tr} ((\sigma_i \times \sigma_j)(\sigma_k \times \sigma_\ell)) &= \text{tr} (\sigma_i \sigma_k \times \sigma_j \sigma_\ell) \\ &= \text{tr} (\sigma_i \sigma_k) \text{tr} (\sigma_j \sigma_\ell) \\ &= 4 \delta_{ik} \delta_{j\ell} , \end{aligned} \quad (\text{F.3a})$$

and the special cases

$$\text{tr} (\sigma_i \times \sigma_j) = \text{tr} \sigma_i \text{tr} \sigma_j = 0 , \quad (\text{F.3b})$$

and

$$\text{tr} ((\sigma_i \times \sigma_j)(\sigma_k \times \mathbf{1})) = \text{tr} (\sigma_i \sigma_k) \text{tr} \sigma_j = 0 . \quad (\text{F.3c})$$

Taking the trace of (F.2), and using (F.3), we can verify the normalization

$$\text{tr} \rho = 1 . \quad (\text{F.4})$$

In order to determine the coefficients  $a_i$  we multiply (F.2) by the operator  $\sigma_k \times \mathbf{1}$  and take the trace by applying (F.3). Only the second term in (F.2) survives and we obtain

$$\begin{aligned} \text{tr} \rho (\sigma_k \times \mathbf{1}) &= \frac{1}{4} \sum_i a_i \text{tr} ((\sigma_i \times \mathbf{1})(\sigma_k \times \mathbf{1})) \\ &= a_k , \end{aligned}$$

and with the definition (F.1a) we have

$$a_k = P_k^{(1)} . \quad (\text{F.5a})$$

Similarly, we obtain

$$b_j = P_j^{(2)}, \quad (\text{F.5b})$$

and

$$c_{ij} = P_i^{(1)} \times P_j^{(2)}. \quad (\text{F.5c})$$

Substitution of (F.5) into (F.2) yields

$$\begin{aligned} \rho = \frac{1}{4} & \left( \mathbf{1} \times \mathbf{1} + \sum_i P_i^{(1)} (\sigma_i \times \mathbf{1}) + \sum_j P_j^{(2)} (\mathbf{1} \times \sigma_j) \right. \\ & \left. + \sum_{ij} (P_i^{(1)} \times P_j^{(2)}) (\sigma_i \times \sigma_j) \right); \end{aligned} \quad (\text{F.6})$$

see also [Burke and Schey \(1962\)](#). This relation generalizes (1.48) for the one-particle case, and shows that the density matrix  $\rho$  is completely determined in terms of the observables (F.1). These 15 parameters must be measured in order to determine completely the polarization properties of an unknown two-particle spin-1/2 system. Of course, in special cases several of these parameters may be zero, as discussed in Sect. 3.6.3.

The great potential of tensor expansions like (F.6) will become apparent in chapters four to seven, where also more powerful methods will be employed. Here we will only use (F.6) to derive some relations between the polarization vector and the tensor components.

Throughout the rest of this appendix we will assume that  $\rho$  describes a pure state. According to (1.40) (or more generally (2.21)) this requires that the condition

$$\text{tr}(\rho^2) = 1 \quad (\text{F.7})$$

is satisfied (taking the normalization (F.2) into account).

Calculating  $\rho^2$ , taking the trace with the help of relations (F.3), and requiring that condition (F.7) is satisfied, we obtain after some algebra the expression

$$\text{tr}(\rho^2) = 1 = \frac{1}{4} \left[ 1 + \sum_i (P_i^{(1)})^2 + \sum_j (P_j^{(2)})^2 + \sum_{ij} (P_i^{(1)} \times P_j^{(2)})^2 \right]. \quad (\text{F.8})$$

Let us specialize to the pure state (3.49), or alternatively (3.54). The non-vanishing components of polarization vector and correlation tensor are given by (3.57) and (3.66). Equation F.8 reduces then to the expression

$$\frac{1}{4} \left[ 1 + \left( P_z^{(1)} \right)^2 + \left( P_z^{(2)} \right)^2 + \left( P_x^{(1)} \times P_x^{(2)} \right)^2 + \left( P_y^{(1)} \times P_y^{(2)} \right)^2 + \left( P_z^{(1)} \times P_z^{(2)} \right)^2 + \left( P_x^{(1)} \times P_y^{(2)} \right)^2 + \left( P_y^{(1)} \times P_x^{(2)} \right)^2 \right] = 1 . \quad (\text{F.9})$$

By using (3.81c) it can readily be seen that the values (3.57) and (3.66) satisfy condition (F.9).

Assume now that the individual polarization vectors vanish (as is the case for the maximally entangled state (3.80), resulting in the expression

$$\sum_{ij} \left( P_i^{(1)} \times P_j^{(2)} \right)^2 = 3 , \quad (\text{F.10})$$

as follows from (F.8). Comparing with (F.9) one can conclude that the vanishing of  $P_z^{(1)}$  and  $P_z^{(2)}$  must be compensated by larger absolute values of at least some of the correlation tensor components.

Finally, for the Bell states (3.84), also the correlation parameters with  $i \neq j$  vanish, and we are left with the expression

$$\sum_i \left( P_i^{(1)} \times P_i^{(2)} \right)^2 = 3 . \quad (\text{F.11})$$

Hence, the remaining components are each required to assume their maximal possible value

$$\left( P_i^{(1)} \times P_i^{(2)} \right)^2 = 1 .$$

Let us consider (F.8) for the other extreme case where the individually observed polarization vectors take on their maximal possible values. This is the case when both systems are completely polarized, say, along the  $z$ - and  $x$ -directions, respectively

$$P_z^{(1)} = P_x^{(2)} = 1 . \quad (\text{F.12a})$$

In this case both systems are necessarily in pure states, represented by the state vectors  $|z(+)\rangle$  and  $|x(+)\rangle$ , respectively, and the combined state is separable:

$$|\psi\rangle = |z(+)\rangle|x(+)\rangle .$$

The only non-vanishing component of the correlation tensor is the *trivial* one:

$$P_z^{(1)} \times P_x^{(2)} = P_z^{(1)} \cdot P_x^{(2)} = 1 , \quad (\text{F.12b})$$

which means that the two systems are completely uncorrelated according to (3.59b). The values (F.12a) and (F.12b) exhaust condition (F.8).

Combining the results (F.10) and (F.12) we obtain that the tensor components are constrained by the condition

$$1 \leq \sum_{ij} \left( P_i^{(1)} \times P_j^{(2)} \right)^2 \leq 3. \quad (\text{F.13})$$

Equations F.8–F.12 hold only for pure states. For mixtures we have only the inequality

$$\text{tr}(\rho^2) < 1$$

at our disposal, so that only inequalities can be derived.

## G.1 Appendix G: Derivation of Equation (3.66b)

The tensor components are defined by (3.58):

$$P_i^{(1)} \times P_j^{(2)} = \text{tr} \rho (\sigma_i \times \sigma_j). \quad (\text{G.1})$$

The system under consideration is defined by the state vector (3.49), or equivalently by the density operator (3.53)

$$\rho = |\psi\rangle\langle\psi|. \quad (\text{G.2})$$

Applying the trace relation

$$\text{tr} |\psi\rangle\langle\psi| (\sigma_i \times \sigma_j) = \langle\psi|\sigma_i \times \sigma_j|\psi\rangle, \quad (\text{G.3})$$

we insert (3.49) for  $|\psi\rangle$  and use (A.8) with the operators  $Q(R) \times Q(r)$  replaced by  $\sigma_i \times \sigma_j$ . We obtain for example for  $i = j = x$ :

$$\begin{aligned} P_x^{(1)} \times P_x^{(2)} &= |f|^2 \langle + - | \sigma_x \times \sigma_x | + - \rangle + f^* g \langle + - | \sigma_x \times \sigma_x | - + \rangle \\ &\quad + f g^* \langle - + | \sigma_x \times \sigma_x | + - \rangle + |g|^2 \langle - + | \sigma_x \times \sigma_x | - + \rangle \\ &= |f|^2 \langle + | \sigma_x | + \rangle \langle - | \sigma_x | - \rangle + f^* g \langle + | \sigma_x | - \rangle \langle - | \sigma_x | + \rangle \\ &\quad + f g^* \langle - | \sigma_x | + \rangle \langle + | \sigma_x | - \rangle + |g|^2 \langle - | \sigma_x | - \rangle \langle + | \sigma_x | + \rangle. \end{aligned} \quad (\text{G.4})$$

The explicit matrix representations (1.1) and (1.7) may be condensed to:

$$\begin{aligned} \sigma_x |+\rangle &= |-\rangle, & \sigma_x |-\rangle &= |+\rangle, \\ \sigma_y |+\rangle &= i|-\rangle, & \sigma_y |-\rangle &= -i|+\rangle, \\ \sigma_z |+\rangle &= |+\rangle, & \sigma_z |-\rangle &= -|-\rangle. \end{aligned} \quad (\text{G.5})$$

Using these relations and the orthogonality of the basis states we obtain that the first and the last term in (G.4) vanish, and that the remaining matrix elements are equal to one. Hence,

$$P_x^{(1)} \times P_x^{(2)} = f^*g + fg^* .$$

The other correlation parameters can be obtained similarly.

## H.1 Appendix H: Conditions for Maximal Entanglement

In this appendix we will derive (3.75) and (3.76) of the main text. There are several possibilities how these relations can be proved. We will choose the following standard mathematical method.

Equation 3.64 shows that the maximal and minimal values of  $P_a^{(1)} \times P_b^{(2)}$  are  $+1$  and  $-1$ , respectively. In order to find out under which conditions the correlation parameters can assume these extrema, we consider  $P_a^{(1)} \times P_b^{(2)}$  as a function of the four variables  $\beta, \beta', \alpha$  and  $\alpha'$ . A necessary criterion for a maximum or minimum to occur is that the corresponding four partial derivatives of  $P_a^{(1)} \times P_b^{(2)}$  vanish *simultaneously* at these points.

We start with (3.68):

$$P_a^{(1)} \times P_b^{(2)} = 2|f||g| \sin \beta \sin \beta' \cos(\alpha' - \alpha + \delta) - \cos \beta \cos \beta' . \quad (\text{H.1})$$

We will assume that both angles,  $\beta$  and  $\beta'$ , are different from zero and different from  $\pi$  since this case would bring us back to Sect. 3.6.4.

Taking the partial derivative of the function (H.1) with respect to  $\alpha'$  we obtain

$$\frac{\partial (P_a^{(1)} \times P_b^{(2)})}{\partial \alpha'} = -2|f||g| \sin \beta \sin \beta' \sin(\alpha' - \alpha + \delta) .$$

This equation vanishes if condition

$$\sin(\alpha' - \alpha + \delta) = 0$$

is satisfied, or alternatively conditions (H.2a) or (H.2b):

$$\cos(\alpha' - \alpha + \delta) = 1 , \quad (\text{H.2a})$$

$$\cos(\alpha' - \alpha + \delta) = -1 , \quad (\text{H.2b})$$

so that we have arrived at (3.76). The partial derivative with respect to  $\alpha$  gives the same result.

In order to proceed assume that (H.2a) is valid. Substitution of this expression into (H.1) yields

$$P_a^{(1)} \times P_b^{(2)} = 2|f||g| \sin \beta \sin \beta' - \cos \beta \cos \beta' . \quad (\text{H.3})$$

We calculate the partial derivations with respect to  $\beta$  and  $\beta'$ , respectively, set the obtained equations equal to zero, and derive the conditions under which a *simultaneous* solution is possible.

We obtain

$$\frac{\partial (P_a^{(1)} \times P_b^{(2)})}{\partial \beta} = 2|f||g| \cos \beta \sin \beta' + \sin \beta \cos \beta' = 0 , \quad (\text{H.4a})$$

and

$$\frac{\partial (P_a^{(1)} \times P_b^{(2)})}{\partial \beta'} = 2|f||g| \sin \beta \cos \beta' + \cos \beta \sin \beta' = 0 . \quad (\text{H.4b})$$

Dividing these equations by  $\cos \beta \cos \beta'$  (excluding the value  $\pi/2$  which can easily be treated separately) we obtain

$$2|f||g| \tan \beta' = -\tan \beta , \quad (\text{H.5a})$$

from (H.4a), and

$$2|f||g| \tan \beta = -\tan \beta' \quad (\text{H.5b})$$

from (H.4b). Both equations must hold simultaneously which is only possible if

$$2|f||g| = 1 \quad (\text{H.6})$$

is satisfied. Starting with (H.2b) instead of (H.2a) gives the same requirement. Equation H.6 is the basic condition (3.75). The further discussion of the obtained equations will be given in Sect. 3.6.5.

## I.1 Appendix I: Properties of Maximally Entangled States

In this appendix we will rederive some of the results of Sect. 3.6.5, following a different path, which will also allow to illustrate our former discussions. We will consider maximally entangled states of the form (3.80):

$$|\psi\rangle = \frac{1}{\sqrt{2}} (|+-\rangle + e^{i\delta} |--\rangle) . \quad (\text{I.1})$$

Although this state is not easily accessible by experiment, we will consider it because of its theoretical simplicity. We will discuss measurements where the

detector – analyzer assembly of the first beam is oriented along an arbitrary but fixed direction  $\mathbf{a}$  (3.51a). We will however restrict  $\mathbf{a}$  to lie within the  $x - z$ -plane ( $\alpha = 0$ ). States with spin up and spin down with respect to  $\mathbf{a}$  will be denoted by  $|a(+)\rangle$  and  $|a(-)\rangle$ , respectively. An expression in terms of the basis states  $|+\rangle$  and  $|-\rangle$  is given by (3.86) or (1.10):

$$|a(+)\rangle = |+\rangle \cos \frac{\beta}{2} + |-\rangle \sin \frac{\beta}{2}, \quad (\text{I.2a})$$

$$|a(-)\rangle = |+\rangle \sin \frac{\beta}{2} - |-\rangle \cos \frac{\beta}{2}, \quad (\text{I.2b})$$

where  $\beta$  is the angle between  $\mathbf{a}$  and the  $z$ -axis.

Assume now that the first beam is sent through an analyzer aligned along the unit vector  $\mathbf{a}$ . Any particle will then be projected into one of the two eigenstates of the analyzer, either  $|a(+)\rangle$  or  $|a(-)\rangle$ . The combined system will then undergo a change of state which is described by applying the respective projectors  $|a(+)\rangle\langle a(+)|$  or  $|a(-)\rangle\langle a(-)|$  to  $|\psi\rangle$ . As a result *both* systems will acquire a definite state vector after the measurement on the first beam, either

$$|\psi\rangle \longrightarrow |a(-)\rangle\langle a(-)|\psi\rangle, \quad (\text{I.3a})$$

or

$$|\psi\rangle \longrightarrow |a(+)\rangle\langle a(+)|\psi\rangle. \quad (\text{I.3b})$$

That is, any time a particle has been recorded in state  $|a(-)\rangle$  ( $|a(+)\rangle$ ), its collision partner in the second beam is automatically projected into the (unnormalized) state  $\langle a(-)|\psi\rangle$  ( $\langle a(+)|\psi\rangle$ ). Here,  $\langle a(-)|\psi\rangle$  and  $\langle a(+)|\psi\rangle$  denote partial scalar products where  $\langle a(-)|$  and  $\langle a(+)|$  act only on the state of the first particle in the combined state  $|\psi\rangle$ . Explicitly, we obtain by substituting (I.1) and (I.2b) into the scalar product  $\langle a(-)|\psi\rangle$

$$\begin{aligned} \langle a(-)|\psi\rangle &= \frac{1}{\sqrt{2}} \left( \langle a(-)|+|-\rangle + e^{i\delta} \langle a(-)|-|+\rangle \right) \\ &= \frac{1}{\sqrt{2}} \left( |-\rangle \sin \frac{\beta}{2} - e^{i\delta} |+\rangle \cos \frac{\beta}{2} \right) \\ &= -\frac{1}{\sqrt{2}} e^{i\delta} \left( |+\rangle \cos \frac{\beta}{2} + e^{i(\pi-\delta)} |-\rangle \sin \frac{\beta}{2} \right). \end{aligned} \quad (\text{I.4})$$

Renormalizing and neglecting the overall phase factor in (I.4), we represent the state of the second system by the expression in the bracket. Introducing the notation  $|b_0(+)\rangle$  for the bracket, we write

$$|b_0(+)\rangle = |+\rangle \cos \frac{\beta'_0}{2} + e^{i\alpha'_0} |-\rangle \sin \frac{\beta'_0}{2}, \quad (I.5)$$

where we have introduced the angles

$$\beta'_0 = \beta, \quad \alpha'_0 = \pi - \delta, \quad (I.6)$$

which corresponds to (3.78). In (I.5) we have written the state in the standard form (1.1.9) from which we can read off that  $|b_0(+)\rangle$  describes a state with spin up with respect to a special direction  $\mathbf{b}_0$  defined by the angles (I.6).

Similarly, for the scalar product in (I.3b) we obtain

$$\langle a(+)|\psi\rangle = \frac{1}{\sqrt{2}} e^{i\delta} \left( |+\rangle \sin \frac{\beta}{2} + e^{-i\delta} |-\rangle \cos \frac{\beta}{2} \right).$$

Renormalizing and ignoring the overall phase factor and denoting the bracket by  $|b_0(-)\rangle$ , we write

$$|b_0(-)\rangle = |+\rangle \sin \frac{\beta'_0}{2} - e^{i\alpha'_0} |-\rangle \cos \frac{\beta'_0}{2}, \quad (I.7)$$

where the angles (I.6) have been inserted. This state vector describes a state of the second beam with spin down with respect to the direction  $\mathbf{b}_0$  defined above.

We note that  $|b_0(+)\rangle$  and  $|b_0(-)\rangle$  are mutually orthogonal. It can be shown that this is an essential requirement for maximal entanglement, which however does in general not hold if condition (3.75) is violated.

It can readily be verified that (I.1) can be written in the equivalent form

$$|\psi\rangle = \frac{1}{\sqrt{2}} \left( |a(+)\rangle |b_0(-)\rangle - |a(-)\rangle |b_0(+)\rangle \right), \quad (I.8)$$

where  $|b_0(+)\rangle$  and  $|b_0(-)\rangle$  are the special states defined by (I.5) and (I.7), respectively. Equation (I.8) is our main result.

In conclusion, we have arrived at these results by a straightforward application of quantum mechanics. Equation I.8 makes the correlation between the two beams evident. Given that the total system is represented by the state vector  $|\psi\rangle$ , and that a particle in the first beam has been found in state  $|a(+)\rangle$ , then there is a unique state  $|b_0(-)\rangle$  associated with the second member of the collision pair in the second beam (up to normalization and overall phase factors) and vice versa. Similarly, if a particle in the first beam has been found and recorded in state  $|a(-)\rangle$ , its collision partner in the second beam is projected in the well-defined state  $|b_0(+)\rangle$ . This happens immediately at the end of the first measurement, before the second beam has been in contact with a measuring device. If the second beam passes subsequently through an analyzer – detector assembly oriented along direction  $\mathbf{b}_0$ , then the state vector (I.8) predicts a strict anticorrelation between the measurement results for the spin

components with respect to  $\mathbf{a}$  and  $\mathbf{b}_0$ . If the second analyzer direction is reversed into direction  $-\mathbf{b}_0$  (corresponding to (3.79)), then one obtains perfect correlation with respect to  $\mathbf{a}$  and  $-\mathbf{b}_0$ . For all other directions of the second analyzer the degree of correlation is reduced. We refer to Sect. 3.6.6 where a specific example is analyzed in detail.

## J.1 Appendix J: Eigenvalues of Density Matrices Condition for Separability Schmidt–Decomposition

In this appendix we will derive a set of related formulas useful for the discussions in Sect. 3.6. Consider a  $2 \times 2$  density matrix with elements  $\rho_{ij}$ , satisfying the Hermiticity condition  $\rho_{ij} = \rho_{ji}^*$ , and normalized according to

$$\rho_{11} + \rho_{22} = 1. \quad (\text{J.1})$$

The eigenvalues  $\lambda_1$  and  $\lambda_2$  of  $\rho$  are the solutions of the equation

$$\det \begin{pmatrix} \rho_{11} - \lambda & \rho_{12} \\ \rho_{12}^* & \rho_{22} - \lambda \end{pmatrix} = 0, \quad (\text{J.2})$$

where “det” denotes the determinant of the matrix. The resulting quadratic equation has the standard solutions

$$\begin{aligned} \lambda_{1,2} &= \frac{1}{2} \pm \frac{1}{2} \sqrt{1 - 4(\rho_{11}\rho_{22} - |\rho_{12}|^2)} \\ &= \frac{1}{2} \pm \frac{1}{2} \sqrt{1 - 4 \det \rho}, \end{aligned} \quad (\text{J.3})$$

where the normalization (J.1) has been taken into account, and where  $\lambda_1(\lambda_2)$  corresponds to the plus-sign (minus-sign) in (J.3).

Let us specialize to spin-1/2 particles. Polarization vector  $\mathbf{P}$  and density matrix elements are related by (1.36) which yields

$$P_z = \rho_{11} - \rho_{22}, \quad P_x = \rho_{12} + \rho_{12}^*, \quad P_y = i(\rho_{12} - \rho_{12}^*).$$

Calculating the square we obtain

$$\begin{aligned} \mathbf{P}^2 &= (\rho_{11} - \rho_{22})^2 + 4|\rho_{12}|^2 \\ &= \rho_{11}^2 + \rho_{22}^2 - 2\rho_{11}\rho_{22} + 4|\rho_{12}|^2. \end{aligned} \quad (\text{J.4})$$

The normalization condition (J.1) yields

$$1 = (\rho_{11} + \rho_{22})^2 = \rho_{11}^2 + \rho_{22}^2 + 2\rho_{11}\rho_{22} ,$$

or

$$\rho_{11}^2 + \rho_{22}^2 = 1 - 2\rho_{11}\rho_{22} . \quad (\text{J.5})$$

By combining (J.4) and (J.5) we arrive at the expression

$$\begin{aligned} \mathbf{P}^2 &= 1 - 4\rho_{11}\rho_{22} + 4|\rho_{12}|^2 \\ &= 1 - 4 \det \rho , \end{aligned} \quad (\text{J.6})$$

from which follows  $0 \leq \det \rho \leq 1/4$ . Equations (J.3) and (J.6) expresses the eigenvalues and the magnitude of  $\mathbf{P}$  in terms of the determinant and the trace of  $\rho$  which are those properties of the density matrix which remain invariant under unitary transformations.

In Sect. 1.1.5 it has been shown that ensembles in pure states are characterized by  $|\mathbf{P}| = 1$ . This condition can now be reformulated: A given spin-1/2 density matrix describes a pure state if and only if the condition

$$\det \rho = 0 \quad (\text{J.7})$$

is satisfied. If this is the case the eigenvalues assume the values  $\lambda_1 = 1$  and  $\lambda_2 = 0$ .

Furthermore, by combining (J.3) and (J.6) we can express the eigenvalues in terms of the magnitude  $|\mathbf{P}|$  of the polarization vector

$$\lambda_{1,2} = \frac{1}{2} \pm \frac{1}{2}|\mathbf{P}| , \quad (\text{J.8a})$$

or

$$|\mathbf{P}| = \lambda_1 - \lambda_2 . \quad (\text{J.8b})$$

After these preliminaries we will derive some consequences of entanglement for pure bipartite states. The most general pure state describing two spin-1/2 particles can be expressed in the form

$$|\psi\rangle = a|++\rangle + b|+-\rangle + c| -+\rangle + d|--\rangle , \quad (\text{J.9})$$

where the only restriction on the complex numbers  $a, b, c, d$  is that their absolute squares add up to unity. The corresponding density operator is given by  $\rho = |\psi\rangle\langle\psi|$  and the reduced density matrices of the two subsystems are obtained similar to (3.56):

$$\rho_1 = \begin{pmatrix} |a|^2 + |b|^2 & ac^* + bd^* \\ a^*c + b^*d & |c|^2 + |d|^2 \end{pmatrix} \quad (\text{J.10})$$

and a similar expression for  $\rho_2$  which is obtained by interchanging the coefficients  $b$  and  $c$  in  $\rho_1$ . The determinant is given by the expression

$$\begin{aligned}\det \rho_1 &= (|a|^2 + |b|^2)(|c|^2 + |d|^2) - |ac^* + bd^*|^2 \\ &= |a|^2|d|^2 + |b|^2|c|^2 - ab^*c^*d - a^*bcd^* \\ &= |ad - bc|^2.\end{aligned}\quad (\text{J.11})$$

The same result follows for  $\rho_2$ . Hence, the two reduced density matrices have always the same value of their determinants:

$$\det \rho_1 = \det \rho_2. \quad (\text{J.12a})$$

From (J.6) follows that both subsystems have polarization vectors with the same magnitude

$$|\mathbf{P}_1| = |\mathbf{P}_2|, \quad (\text{J.12b})$$

(see for example (3.56)). The relations (J.12) express remarkable consequences of the quantum correlations, that exist between two beams of spin-1/2 particles which have been interacted in the past.

Equation J.12a combined with (J.3) yields the result *that  $\rho_1$  and  $\rho_2$  have necessarily the same set of eigenvalues*. This result is of key relevance for the discussion of the *entropy of entanglement*, outlined in Subsect. 3.6.5.

Assume now, that the state (J.9) is separable and can be written in product form

$$|\psi\rangle = |\psi_1\rangle|\psi_2\rangle. \quad (\text{J.13})$$

The two subsystems are then in pure states,  $|\psi_1\rangle$  and  $|\psi_2\rangle$ , respectively, which requires that the corresponding reduced density matrices  $\rho_1$  and  $\rho_2$  have vanishing determinants according to condition (J.7). By combining this result with the explicit form (J.11), we arrive at the following simple criterion for separability: A given pure bipartite state  $|\psi\rangle$ , written in the basis (J.9), is factorizable if and only if the condition

$$ad = bc \quad (\text{J.14})$$

is satisfied. Otherwise the state is entangled. An example has been given at the end of Subsect. 3.6.2.

Finally, we note that the general state (J.9) can always be written in the form

$$|\psi\rangle = f|\varphi_1\rangle|\chi_1\rangle + g|\varphi_2\rangle|\chi_2\rangle, \quad (\text{J.15})$$

where  $|\varphi_1\rangle$  and  $|\varphi_2\rangle$  are mutually orthogonal, as well as  $|\chi_1\rangle$  and  $|\chi_2\rangle$ . The  $\varphi$ -states ( $\chi$ -states) describe the first (second) subsystem and are linear superpositions of the basis  $|+\rangle$  and  $|-\rangle$ . For a proof of this so-called *Schmidt-decomposition*, (J.15), we refer for example to Nielsen and Chuang (2000).

The corresponding reduced density matrices of the two subsystems are easily obtained:

$$\rho_1 = \rho_2 = \begin{pmatrix} |f|^2 & 0 \\ 0 & |g|^2 \end{pmatrix}, \quad (\text{J.16})$$

where  $\rho_1$  ( $\rho_2$ ) is written using the states  $|\varphi_1\rangle$  and  $|\varphi_2\rangle$  ( $|\chi_1\rangle$  and  $|\chi_2\rangle$ ) as basis. Since the magnitude of the polarization vector is an invariant independent of the choice of the basis, we obtain

$$|\mathbf{P}_1| = |\mathbf{P}_2| = |f|^2 - |g|^2. \quad (\text{J.17})$$

Taking the normalization

$$1 = |f|^2 + |g|^2, \quad (\text{J.18})$$

into account and combining (J.17) and (J.18) we get the expression

$$\mathbf{P}_1^2 = \mathbf{P}_2^2 = 1 - (2|f||g|)^2, \quad (\text{J.19})$$

which generalizes (3.81c).

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