Lecture Notes in Chemistry 90

Richard D. Harcourt

Bonding in Electron-Rich Molecules

Qualitative Valence-Bond Approach via Increased-Valence Structures

Second Edition

Springer

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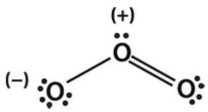
Preface for the Second Edition

Both editions of this book provide qualitative molecular orbital and valence-bond descriptions of the electronic structures for primarily electron-rich molecules. Strong emphasis is given to the valence-bond approach.

Electron-rich molecules form a very large class of molecules, and the results of quantum mechanical studies from different laboratories indicate that qualitative valence-bond descriptions for many of these molecules are incomplete in so far as they usually omit “long-bond” Lewis structures from elementary descriptions of bonding. For example, the usual valence-bond representation for the electronic structure of the ground-state for O_3 involves resonance between the standard, (or Kekulé-type) Lewis structures



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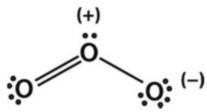
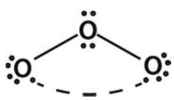


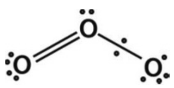
At least until the early 1980s, any significant contribution to the ground-state resonance of the “long-bond” (or spin-paired/singlet diradical or Dewar-type) Lewis structure



had been mostly ignored in elementary descriptions of chemical bonding.[i]

[i] As discussed in both volumes, singlet diradical structures help the standard Kekulé-type structures to interact. Resonance between these two types of Lewis structures generates electronic hypervalence – for example a possible valence greater than four for the central nitrogen atom of N_2O – and is needed to ensure that valence-bond formulations of mechanisms for S_N2 and 1,3-dipolar cycloaddition reactions are those for concerted reactions. Also, as will be shown in Chapter 25, Pauling “3-electron bonds” are components of increased-valence structures for (non electron-rich) 3-electron 3-centre bonding units.

For the ground-states of other electron-rich molecules, the results of valence-bond calculations from different laboratories – see for example references 24-29 of Chapter 2 – also indicate also indicate that “long-bond” structures are more important than is usually supposed, and therefore they need to be included in qualitative valence-bond descriptions of their electronic structure. This book describes how this can be done, and some of the resulting consequences for the interpretation of the electronic structure, bond properties and reaction mechanisms for various electron-rich molecules. When appropriate, molecular orbital and valence-bond descriptions of bonding are compared, and relationships that exist between them are derived. Considerable attention is given to the use of Pauling “3-electron bonds” ($\mathbf{A}\cdots\mathbf{B}$ as $\dot{\mathbf{A}}\cdot\dot{\mathbf{B}}$) for providing qualitative valence-bond descriptions of electronic structure. The “increased-valence” structures for electron-rich molecules – for example



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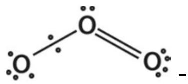


– are equivalent to resonance between standard and “long-bond” Lewis structures (to give singlet diradical character), and usually involve Pauling “3-electron bonds” as diatomic components. Because “increased-valence” structures include both types of Lewis structures, they must provide lower-energy representations of electronic structure than do the more familiar qualitative descriptions that utilize only the standard Lewis structures.

To provide the necessary background for readers who are familiar only with the elements of qualitative valence-bond and molecular orbital theory, extensive use is made of an elementary, even pedagogical, approach. Some familiar, relevant valence-bond and molecular orbital concepts are reviewed briefly in Chapter 1. After a discussion in Chapter 2 of the need for an “increased-valence” theory, Chapters 3 to 9 are concerned primarily with qualitative descriptions of the electronic structures for numerous paramagnetic molecules that may have Pauling “3-electron bonds” as diatomic components in their primary valence-bond structures. The bonding and magnetic behaviour for the dimers of some of these molecules are also discussed in Chapters 7 and 8, using both Lewis valence-bond and molecular orbital theory. It is shown that if the monomer has a well-developed Pauling “3-electron bond”, then the dimer may require “long-bond” as well as standard Lewis structures to contribute significantly to the ground-state, Lewis structure resonance. An “increased-valence” description of the bonding for one of these dimers, namely N_2O_4, is developed in Chapter 10; this provides a convenient connection between the Pauling “3-electron bond” theory for paramagnetic molecules, and the “increased-valence” theory of the remaining Chapters for (mostly) diamagnetic molecules.

In the 1st edition of this volume, I have acknowledged those people who had helped with its production. I continue to recognize that the late Professor Ronald D. Brown AM, FAA (Monash University) influenced and inspired me during my Ph.D. years. This book developed from the research project that he had suggested, namely to explain why the N-N bond of N_2O_4 is long and weak. (Of course, since that time, much progress has been made!) I also appreciate greatly the regular valence-bond interactions that I have with Professors Thomas M. Klapötke (LMU Munich) and Brian J. Duke (Monash Pharmacy). I am indebted to and thank the School of Chemistry at the University of Melbourne for its continuous support. I also thank Springer for inviting me to prepare a 2nd edition, Dr. Steffen Pauly and Beate Siek for editorial assistance, and Dr. Angelika Schulz for her patience and help with the printing of this 2nd edition, using a now difficult-to-handle 1st edition. Dr. Walter P. Roso provided us with his *ab initio* valence-bond program.

For this 2nd edition, I have made only minor modifications to the text for the 1st edition, and essentially not up-dated its content and references. However I have included an addendum with a number of the chapters. These addenda, together with a new chapter, present some of the post-1982 applications of increased-valence theory. Michael Whitehead drew some of the additional valence-bond structures. Although other valence-bond researchers almost never use increased-valence descriptions of electronic structure, I appreciate the significant alternative contributions to valence-bond theory that these researchers have made. However because I am presenting essentially the increased-valence approach to electronic structure, in this volume I refer rarely to their contributions.

Texts on alternative types of valence-bond theory include those of references 1 and 2. Reference 3 provides a review of modern *ab initio* methods and classical valence-bond approaches to electronic structure. References 4 and 5 provide reviews of generalised and spin-coupled valence-bond theory. Both of these theories can use delocalised orbitals that involve more than two atomic centres to accommodate the active-space electrons. In references 6-8, overviews are presented of aspects of increased-valence theory.

1) N.D. Epiotis, "Unified Valence-bond Theory of Electronic Structure", Lecture Notes in Chemistry, (Springer-Verlag Berlin Heidelberg New York) Volume 29 (1982) and Volume 34 (1983).

2) S.S. Shaik and P.C. Hiberty, "A Chemist's Guide to Valence-bond Theory", (Wiley-Interscience & Sons, Inc. Hoboken, New Jersey) (2008).

3) W. Wu, P. Su, S. Shaik and P.C. Hiberty, Chem. Revs. **111**, 7557-7593 (2011).

4) W.A. Goddard III, T.H. Dunning Jr., W.J. Hunt and P.J. Hay, Acc. Chem. Res. **6**, 368-376 (1973).

5) D.L. Cooper, J. Gerratt and M. Raimondi, Chem. Rev. **91**, 929 (1991). See also the spin-coupled valence-bond chapters in each of Refs. 6(a), (b) and (c) below.

6) R.D. Harcourt, (a) in "Valence-bond Theory and Chemical Structure" (Delete H_2^- postscript) (Elsevier Science BV; editors D. Klein and N. Trinajstić) pp. 251-285 (1990). (b) in "Pauling's Legacy: Modern Modelling of the Chemical Bond" (Elsevier Science B.V.; editors Z.B. Maksić and W.J. Orville-Thomas) pp. 449-480 (1999). (c) in "Quantum Chemical Methods in

Main-Group Chemistry” (Wiley; authors T.M. Klapötke and A. Schulz), pp. 217-250 (1998)). (d) Eur. J. Inorg. Chem. 1901-1916 (2000). (e) in “Valence-bond Theory” (Elsevier Science B.V.; editor D.L. Cooper) pp. 349-378 (2002).

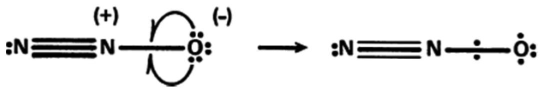
7) R.D. Harcourt and T.M. Klapötke, Pauling three-electron bonds and increased-valence structures as components of the "intellectual heritage" of qualitative valence-bond theory. Trends Inorg. Chem. 9, 11-22 (2006).

8) T.M. Klapötke in “Moderne Anorganische Chemie” (de Gruyter, Berlin: editor, E. Riedel) 3rd edition (2007).

9) The Chemical Bond (Wiley-VCH; editors G. Frenking and S. Shaik) (a) Fundamental Aspects of Chemical Bonding, pp. 1-411 (2014); (b) Chemical Bonding Across the Periodic Table, pp. 1-544 (2014).

For readers who wish to give primary consideration to the “increased-valence” theory, Sections 3-6, 3-9, 4-1 to 4-7, 6-1, 7-1 and 7-2 are the main components of the earlier chapters that are required as background for chapters 10 to 25. A reading of chapter 2 might also be appropriate in order to obtain a rationalization of the need for an “increased-valence” theory.

The “increased-valence” theory represents a natural extension of the more familiar Lewis-Pauling valence-bond theory. Therefore an understanding of it may be useful for all chemists who have an interest in qualitative valence-bond descriptions of electronic structure. It will be shown that all Lewis-type valence-bond structures with lone-pairs of electrons can be stabilized easily via one-electron delocalizations from doubly-occupied atomic orbitals into diatomic bonding molecular orbitals when the relevant atomic orbitals overlap, as is shown here for the two sets of oxygen π electrons of N_2O.



1 I

Finally, as indicated previously[1], I agree with Shaik and Hiberty that qualitative valence-bond theory can provide “insight, and the ability to think, reason and predict chemical patterns”[2].

1) 1. R.D. Harcourt, J. Biol. Inorg. Chem. **19**, 113 (2014)
2) 2. S. Shaik and P.C. Hiberty, WIREs Comput. Mol. Sci. **1**, 18 (2011)

Table of Contents

Chapter 1 Atomic Orbitals, Electron Spin, Linear Combinations

We shall provide here a brief survey of the relevant background quantum mechanics that is required for the chemical bonding treatment presented in this book. In general, we shall state only the main results, without any derivation of them. Much, if not all of this material could be familiar to many readers. For fuller treatments, the reader should consult some of the numerous standard texts[1] on quantum mechanics and valence.

1-1 Atomic Orbitals

For any atom, there are n^2 atomic orbitals with principal quantum number n (= 1, 2, 3, ...). These orbitals may be classified as ns, np, nd, nf, ... according to the value of the total orbital angular momentum quantum number l (≡ 0, 1, 2, ... n - 1) for an electron. For each value of l, there are $2l$ + 1 orbitals. Thus, there are one 3s, three 3p ($3p_x$, $3p_y$ and $3p_z$) and five 3d ($3d_{xy}$, $3d_{xz}$, $3d_{yz}$, $3d_{x^2-y^2}$ and $3d_{z^2}$) orbitals for l = 0, 1 and 2; here we have assumed that the np and nd orbitals are all real orbitals[i]. For certain purposes, the nd_{xy}, nd_{xz} and nd_{yz} orbitals are designated as t_{2g} orbitals, and the corresponding designation for the remaining pair of nd orbitals is e_g. Schematic contours for 1s, 2p and 3d orbitals are displayed in Figure 1-1.

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[i] The hydrogenic atomic orbitals have the general form $\psi(r,\theta,\phi) = R(r)\theta(\theta)\Phi(\phi)$, in which r, θ and φ are the polar coordinates for the electron. For complex atomic orbitals, $\Phi(\phi) = \exp(im_z\phi)$ with i= √(-1) and $m_z = 0$, ±1, ±2, ... ±l. The np_{+1}, np_0 and np_{-1} orbitals have $m_z = +1$, 0 and -1. The real np orbitals are related to the complex orbitals as follows: $np_x = (np_{+1} + np_{-1}) / 2$, $np_y = (np_{+1} - np_{-1}) / 2i$, $np_z = np_0$. In the absence of a magnetic field, orbitals with the same n and l values are *degenerate,* i.e. they have the same energies. For given n and l values, the number of degenerate orbitals is $2l$ + 1.

R.D. Harcourt, *Bonding in Electron-Rich Molecules*,
Lecture Notes in Chemistry 90, DOI 10.1007/978-3-319-16676-6_1

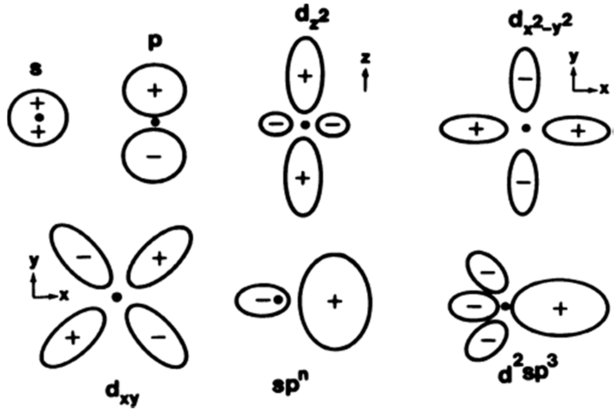

Figure 1-1: Schematic contours for 1s, 2p, 3d, sp^n and d^2sp^3 atomic orbitals.

When the atomic orbitals are located on the same atomic centre, it is often useful to consider the *hybridization* of some of them, i.e., to construct linear combinations of them. This may be done either by requiring that the energy of the linear combination in the molecule be a minimum, or that the bond-angles determine the nature of the hybridization[ii]. The latter is usually used for elementary discussions of (approximate) hybridization of orbitals in valence-bond structures, and is therefore appropriate for the valence bond treatments that we shall present in this book. For our purposes, the most relevant of the hybrid orbitals are the following, in which we have indicated the explicit forms of the linear combinations for only the first two, for the special cases of equivalent hybrids.

i) Digonal: $sp\ (h_1 = (s+p)/2^{\frac{1}{2}},\ h_2 = (s-p)/2^{\frac{1}{2}})$

ii) Trigonal: $sp^2(h_1 = (s+2^{\frac{1}{2}}p_x)/3^{\frac{1}{2}},\ h_2 = (2^{\frac{1}{2}}s - p_x + 3^{\frac{1}{2}}p_y)/6^{\frac{1}{2}},$
$h_3 = (2^{\frac{1}{2}}s - p_x - 3^{\frac{1}{2}}p_y)/6^{\frac{1}{2}})$

iii) Tetrahedral: sp^3.

iv) Square planar: sp^2d (ns, np_x, np_y and $nd_{x^2-y^2}$) and dsp^2 ($nd_{x^2-y^2}$, $(n+1)$ s, $(n+1)$ p_x and $(n+1)p_y$) for atoms of main-group elements and transition metals.

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ii If λ_1 and λ_2 are the hybridization parameters for two orthogonal hybrid atomic orbitals $h_1 = s + \lambda_1 p_1$ and $h_2 = s + \lambda_2 p_2$, then the angle θ between the hybrid orbitals is given by the Coulson formula[2] $\cos\theta = -1/\lambda_1\lambda_2$. If the hybrid orbitals are assumed to be oriented along the bond axes for two σ-bonds that emanate from the atomic centre, then this angle is the bond angle. The "orbital following" which is then concomitant with this approach has been questioned (see Ref. 3 for details). The results of STO-6G valence bond calculations[6,7] for *cis* N_2O_2, FNO and O_2NNO shows that "orbital following" does not occur for the nitrogen atoms of the NO substituent, cf. Figure 1-5 at end of this Chapter.

shape	σ-bond hybridization	σ-bonds	number of lone pairs	π-bonds	valence-bond structure
linear	sp	2	0	0	
		2	0	1	
		2	0	2	
trigonal planar	sp^2	3	0	0	
		3	0	1	
trigonal pyramidal	sp^2	4	0	0	
angular	sp^2	2	1	1	
tetrahedral	sp^3	4	0	0	
		4	0	2	
pyramidal	sp^3	3	1	0	
		3	1	1	
angular	sp^3	2	2	0	
square planar	dsp^2	4	4	0	
trigonal bipyramidal	sp^3d	5	0	0	
distorted tetrahedral	sp^3d	4	1	0	
		4	1	1	
"T-shaped"	sp^3d	3	2	0	
octahedral	sp^3d^2	6	0	0	
square-pyramidal	sp^3d^2	5	1	0	
		5	1	1	
planar	sp^3d^2	4	2	0	
pentagonal-bipyramidal	sp^3d^3	7	0	0	

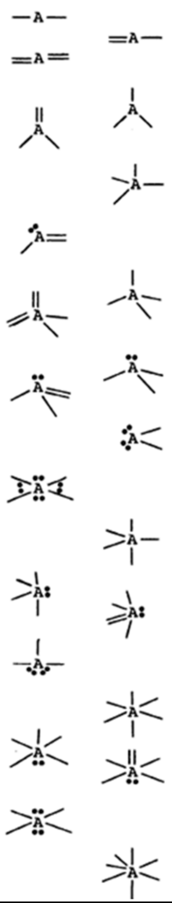

Figure 1-2: Lewis valence-bond structures for different σ-bond hybridization schemes. (Adapted from E. Carmell and G.W.A. Fowles, Valency and Molecular Structure (4th ed. Butterworths, 1977).

v) Trigonal bipyramid: sp^3d (ns, three np and $nd_{x^2-y^2}$ or nd_{z^2}) and dsp^3 ($nd_{x^2-y^2}$ or nd_{z^2}, $(n+1)$ s and three $(n+1)$ p) for atoms of main-group elements and transition metals. For each of sp^3d and dsp^3 an infinite number of linear combinations of $d_{x^2-y^2}$ and d_{z^2} is possible to form the appropriate d orbital for the hybridization scheme.

vi) Octahedral: sp^3d^2 (ns, three np, $nd_{x^2-y^2}$, nd_{z^2}) and d^2sp^3 ($nd_{x^2-y^2}$, nd_{z^2}, $(n+1)$ s and three $(n+1)$ p) for atoms of main-group elements and transition metals.

Schematic contours for some of these hybrid atomic orbitals are displayed in Figure 1-1. In Figure 1-2, we show the number of bonds and lone-pairs at a given atom when these hybridization schemes are appropriate for the formation of σ-bonds.

Any real orbital ψ is *normalized*[iii] if $\int \psi^2 \mathrm{d}v = 1$; if $\int \psi_i \psi_j \mathrm{d}v = 0$ for a pair of real orbitals, then the orbitals are *orthogonal.* The square of a real orbital, (ψ^2) gives the charge density, or probability density for an electron when it occupies the orbital. The integral $\int \psi^2 \mathrm{d}v = 1$ gives the total charge when one electron occupies a normalized orbital.

1-2 Electron Spin

The spin quantum number s = 1/2 for an electron determines the magnitude of the total spin angular momentum according to the formula $\sqrt{s(s+1)}\,(h/2\pi)$ (with h = Planck's constant). When an external magnetic field is applied, the spin angular momentum vector orients in two different directions so that the z-component of spin angular momentum (i.e. the component parallel to the direction of the magnetic field) takes values of $s_Z(h/2\pi)$ with $s_Z = \pm 1/2$. These orientations are displayed in Figure 1-3.

For two electrons, the same types of spin angular momentum expressions pertain, with the two-electron spin quantum numbers S and $S_z (\equiv s_z(1) + s_z(2))$ replacing s and s_z. The allowed values for S and S_z are: (i) S = 0, $S_z = 0$; (ii) S = 1, $S_z = +1$, 0, –1, and the orientations of the spin angular momentum vectors for these quantum numbers are also displayed in Figure 1-3. The spin angular momentum vectors are parallel (↑↑) for S = 1, and antiparallel (↑ ↓) for S = 0.

In general, if the total spin quantum number for an atom or a molecule is S, there are $2S + 1$ values for the S_z spin quantum number, namely S, $S - 1$, $S - 2$, ... $-S$.

If an atom or molecule has n singly-occupied orthogonal (i.e. non-overlapping) orbitals, the lowest-energy arrangement of the spins for the n electrons is that for which the spins are all parallel. This is a statement of Hund's rule of maximum spin multiplicity. The total spin quantum number is then $S = n/2$.

If an orbital is doubly-occupied, the Pauli exclusion principle does not allow the two electrons to have the same values for their s_z quantum numbers. Therefore, not more than two electrons may occupy the same orbital.[iv]

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iii For a real atomic orbital in an atom, $\int \psi^2\, \mathrm{d}v = \int_0^\infty \int_0^\pi \int_0^{2\pi} \psi^2 r^2 \sin\theta\, \mathrm{d}r\, \mathrm{d}\theta\, \mathrm{d}\varphi$. Later, $\mathrm{d}\tau \equiv \mathrm{d}v_1 \mathrm{d}v_2 \mathrm{d}v_3 \mathrm{d}s_1 \mathrm{d}s_2 \mathrm{d}s_3$ ..., with s_i = "spin coordinate" for electron i.

iv Without reference to electron spin, this result may also be deduced for atoms from Bohr circular orbit theory + Heisenberg uncertainty relationship[4a-c,-5]. For principal quantum

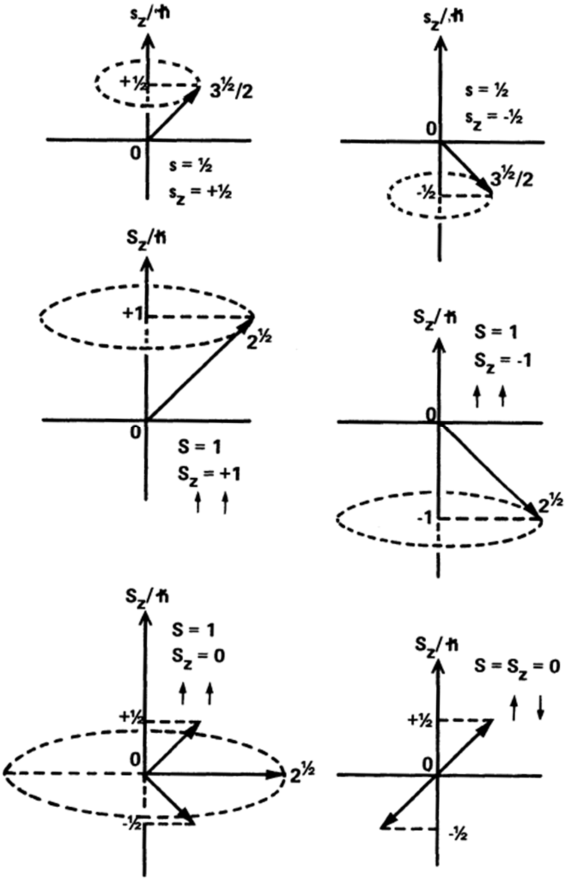


Figure 1-3: Orientations of spin angular momentum vectors for one and two electrons relative to an external magnetic field directed along the z-axis. $\hbar = h/2\pi$.

Diamagnetic and paramagnetic substances develop magnetic moments that are respectively opposed to, and in the direction of an external magnetic field. The magnetic moments for the paramagnetic molecules that we shall discuss in this book arise either primarily or almost entirely from the presence of one or more unpaired-electron spins, i.e. the total spin quantum number S is non-zero for such a molecule. For a molecule with spin quantum number S, the spin angular

number n, it may be deduced that a maximum of $2n$ electrons may occupy each of n independent circular orbits around the nucleus. There are n^2 atomic orbitals with principal quantum number n. Therefore $2n \times n/n^2 = 2$. The $2 \times n^2 = 2n \times n$ factorizations of $2n^2$ give the human identity[4f] Pauli + Schrödinger = Heisenberg + Bohr!

momentum generates a magnetic moment of $\sqrt{n(n+2)}$ Bohr magneton for which $n \equiv 2S$ is the number of unpaired-electron spins.

1-3 Linear Combinations of Wave Functions

If ψ_1 and ψ_2 are two (real) wave-functions, then linear combinations of the form $\psi = c_1\psi_1 + c_2\psi_2$ (or $\psi = \psi_1 + k\psi_2$) may be constructed, in which the coefficients c_1 and c_2 (or *k*) are constants. If the coefficients c_1 and c_2 are determined so that the energy of ψ (i.e. $E = \int \psi_1 \hat{H} \psi_2 d\tau / \int \psi^2 d\tau$ with $\hat{H}$ =Hamiltonian operator) is a minimum, then provided that ψ_1 and ψ_2 interact (i.e. $H_{12} \equiv \int \psi_1 \hat{H} \psi_2 \mathrm{d}\tau \neq 0$), two (orthogonal) linear combinations are generated that have respectively *lower* and *higher* energies than have either of ψ_1 and ψ_2 alone. The resulting energy-level diagrams are displayed in Figure 1-4.

In the absence of magnetic fields, the Hamiltonian operator $\hat{H}$ for a system of electrons in an atom or molecule involves the sum of kinetic and electrostatic potential energy operators (designated as $\hat{T}$ and $\hat{V}$) for the electrons, i.e. $\hat{H}=\hat{T}+\hat{V}$. The kinetic energy $\hat{T}$ operator is given by $\sum_i (-h^2/8\pi^2 \mathrm{m})\nabla_i^2$, and $\hat{V}$ is the sum of the terms that involve the classical electrostatic attractions between the electrons and the atomic nuclei, and repulsions between the electrons. The

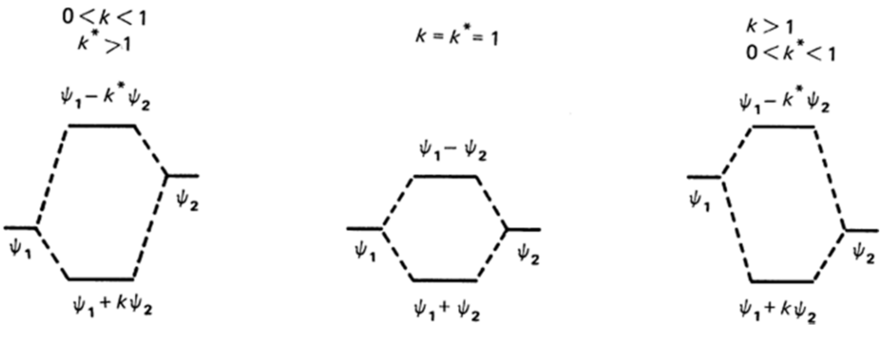


Figure 1-4: Energy level diagrams for the linear combinations of two interacting wave-functions ψ_1 and ψ_2 assuming that $\int \psi_1 \hat{H} \psi_2 \mathrm{d}\tau < 0$. When $H_{12} = ES_{12}$ and $H_{22} \geq H_{11}$, no linear combination is stabilized relative to ψ_1 . When ψ_1 and ψ_2 overlap, with $\int \psi_1 \hat{H} \psi_2 \mathrm{d}\tau < 0$, the destabilizations of $k^* \psi_1 - \psi_2$ and $\psi_1 - \psi_2$ is greater than the stabilizations of $\psi_1 + k\psi_2$ and $\psi_1 + \psi_2$ relative to the ψ_1 or ψ_2 .

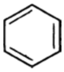
requirement that $\partial E / \partial c_1 = \partial E / \partial c_2 = 0$ as a necessary condition that E is a minimum gives the *secular equations*

$$(H_{11} - E)c_1 + (H_{12} - ES_{12})c_2 = 0$$
$$(H_{21} - ES_{21})c_1 + (H_{22} - E)c_2 = 0$$

for normalized ψ_1 and ψ_2, with $H_{ij} = \int \psi_i \hat{H} \psi_j \mathrm{d}\tau$ and $S_{ij} = \int \psi_i \psi_j \mathrm{d}\tau$. In this book, the wave-functions ψ_1 and ψ_2 are of two main types:

a) *Atomic and molecular orbitals:* If ψ_1 and ψ_2 are a pair of (real) atomic orbitals centred on two atomic nuclei, the interaction integral (or resonance integral) $\int \psi_1 \hat{H} \psi_2 \, \mathrm{d}v$ is non-zero if these atomic orbitals *overlap*, i.e. the overlap integral $S_{12} = \int \psi_1 \psi_2 \mathrm{d}v \neq 0$. The lower and higher energy linear combinations of ψ_1 and ψ_2 are designated as *bonding* and *antibonding* molecular orbitals, respectively. If the atomic orbitals are located on the same atomic centre, then usually they are orthogonal (i.e. $\int \psi_1 \psi_2 \mathrm{d}v = 0$). When this is the case, no lower-energy linear combination may be constructed. *Hybrid* atomic orbitals, examples of which were provided in Section 1-1, are linear combinations of atomic orbitals located on the same atomic centre.

b) *Two-electron and many-electron configurations of electrons:* An electron configuration designates the orbital occupancies and spins for the electrons. The following two-electron or many-electron configurations need to be considered here:

i) *Valence-bond structure functions (bond-eigenfunctions)*: These wave-functions describe the configurations of electrons that are associated with valence-bond structures. If a pair of valence-bond structures (for example, Li—H and $\mathrm{Li}^+ : \mathrm{H}^-$ for LiH, or  and  for C_6H_6) have configuration wave-functions (or structure wavefunctions or bond-eigenfunctions) designated as ψ_1 and ψ_2 for their electrons, then the construction of linear combinations of these wave functions is equivalent to invoking resonance between the valence-bond structures. The valence-bond structures are said to be *stabilized by resonance* if one of the linear combinations has a lower energy than has either ψ_1 and ψ_2 alone. Resonance stabilization can only occur if $\int \psi_1 \hat{H} \psi_2 \mathrm{d}\tau$ (the *exchange* integral) is non-zero. A necessary (but not necessarily sufficient) condition for this to occur is that the bond-eigenfunctions ψ_1 and ψ_2 must have the same sets of values for their S and S_z spin quantum numbers.

ii) *Molecular orbital configurations*: If ψ_1 and ψ_2 are two different molecular orbital configurations with the same spatial symmetry and sets of spin quantum numbers (for example, ψ_1 and ψ_2 involve two electrons that doubly-occupy bonding and antibonding molecular orbitals, respectively), then lower-energy (and higher-energy) linear combinations of these two configurations can be constructed. This procedure is referred to as *configuration interaction.* Because the molecular orbitals are orthogonal, a lower-energy linear-combination may only be constructed if the configurations ψ_1 and ψ_2 do not differ in the orbital and spin designations of more than two electrons[v]. (This limitation does not necessarily apply to the bond-eigenfunctions of (i), because at least some of the atomic orbitals for these valence-bond configurations must overlap.)

If for any of (a) and (b), the functions ψ_1 and ψ_2 can also interact with a third wave-function ψ_3, then the linear combination $\psi = c_1\psi_1 + c_2\psi_2 + c_3\psi_3$ (with c_1, c_2 and c_3 chosen so that the energy of ψ is minimized) will have a lower energy than has either $\psi = c_1\psi_1 + c_2\psi_2$ or ψ_3 alone. If ψ is a molecular orbital formed from a linear combination of three overlapping atomic orbitals χ_1, χ_2 and χ_3 centred on three atomic nuclei, this molecular orbital is referred to as a *delocalized* or *3-centre* molecular orbital. We shall often encounter 3-centre molecular orbitals, and usually use the symbols y, a and b to designate the atomic orbitals χ_1, χ_2 and χ_3.

Diatomic molecular orbitals which are either symmetric or antisymmetric with respect to rotation around the bond-axis are designated as σ and π. Alternatively, these orbitals have, respectively, 0 and 1 nodal planes (i.e. planes on which the orbital wave-function is zero at all points) that pass through the atomic nuclei and include the bond axis. There are two sets of degenerate π-type molecular orbitals. With the z-axis as the bond axis, these orbitals are labelled here as either π_x and π_y or π and $\overline{\pi}$, and have, respectively, the *xz* and *yz* planes as nodal planes. Bonding and antibonding diatomic molecular orbitals have 0 and 1 nodal planes passing through the bond axis parallel to the *xy* planes. Their energies are respectively less than, and greater than the atomic orbitals from which they are constructed. The same theory is appropriate for the delocalized molecular orbitals of linear triatomic and linear polyatomic molecules. For non-linear planar molecules, the delocalized molecular orbitals may be either of σ or π or $\sigma + \overline{\pi}$ type, with π non-degenerate. The $\sigma + \overline{\pi}$ molecular orbitals have σ-symmetry with respect to at least one pair of adjacent atoms, and $\overline{\pi}$ symmetry with respect to at least another pair of adjacent atoms. In Figure 1-5, atomic orbitals that may be used to construct $\sigma + \overline{\pi}$ molecular orbitals for N_2O_2, FNO and N_2O_3 are displayed.

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[v] With self-consistent field molecular orbital theory, no direct interaction can occur between the lowest-energy configuration with doubly-occupied molecular orbitals and singly-excited $S = 0$ spin configurations with the same symmetry as that of the lowest-energy configuration, if the orbitals used to construct all configurations are the "best" orbitals for the lowest-energy configuration.

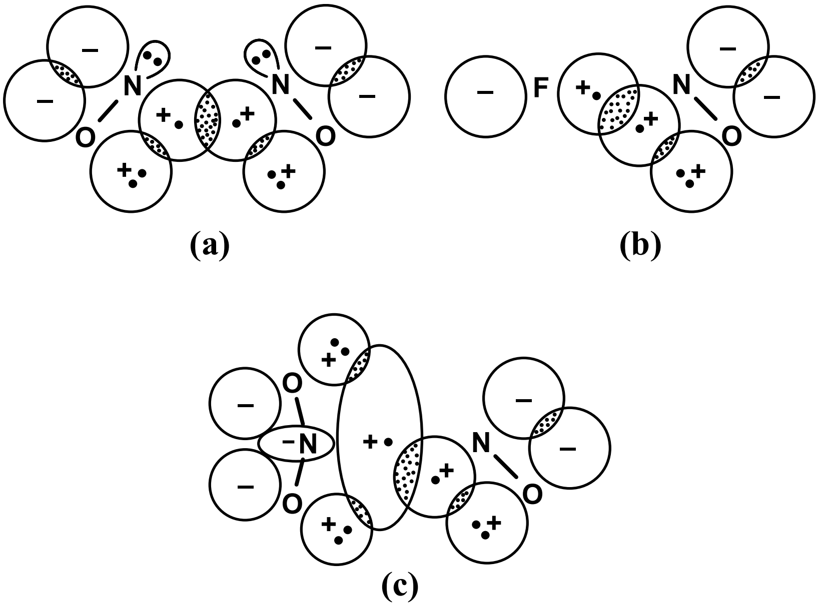

Figure 1-5: Calculated[6,7] atomic orbitals for $\sigma + \bar{\pi}$ molecular orbitals of N_2O_2, FNO and N_2O_3.

References

1. See for example (a) R.W. McWeeny "Coulson's Valence" (Oxford, 1979); (b) J.N. Murrell, S.F.A. Kettle and J.M. Tedder "The Chemical Bond" (John Wiley, 1978).
2. Ref. 1(a), p. 196.
3. M.C.R. Symons, Chem. Soc. Specialist Reports: Electron Spin Resonance. (a) 5, 146 (1979); (b) **6**, 108 (1981).
4. R.D. Harcourt, (a) Naturwiss. **64**, 485 (1977); (b) Specul. Sci. Techn. **1**, 338 (1978). (c) J. Mol. Struct. (Theochem) **338**, 195 (1995); corrections **369**, 217 (1996). (d) Foundations Chem. **1**, 295 (1999). For applications of Bohr circular orbit theory to chemical bonding, see also Refs. (b), (c) above, (d) Spec. Sci. Techn., **2**, 527 (1979); **3**, 77, 628 (1980); **4**, 367 (1981) (e) J. Chem. Educ. **64**, 1070 (1987) and Ref. 5 below.(f) Trends. Phys. Chem. **15**, 45 (2014) and Ref. 9 therein.
5. R.D. Harcourt and T.M. Klapötke, J. Fluor. Chem. **127**, 712 (2006).
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Chapter 2 Pauling "3-Electron Bonds", 4-Electron 3-Centre Bonding, and the Need for an "Increased-Valence" Theory

2-1 Introduction

In elementary chemical bonding theory, a rather neglected concept is a type of chemical bond that Pauling has designated as the "3-electron bond". This type of bond is usually represented as $\mathbf{A} \cdots \mathbf{B}$ and it involves three electrons distributed amongst two overlapping atomic orbitals centred on the atoms **A** and **B**. Alternative designations[2] are either "3-electron 2-centre" bond or "3-electron 2-orbital" bond.

In 1931, Pauling[1] introduced the "3-electron bond", to help describe the electronic structures for a number of molecules and ions, such as NO, He_2^+, O_2, NO_2 and ClO_2, whose ground-states are paramagnetic at room temperature. Pauling's valence-bond structures for these systems are displayed in Figure 2-1. It is mostly considered that the occurrence of the Pauling "3-electron bond" was restricted to paramagnetic molecules of this type. If we exclude transition metal compounds, there is only a small number of molecular systems whose ground-states are paramagnetic and stable. Therefore, the Pauling "3-electron bond" usually does not feature prominently in discussions on valence theory.

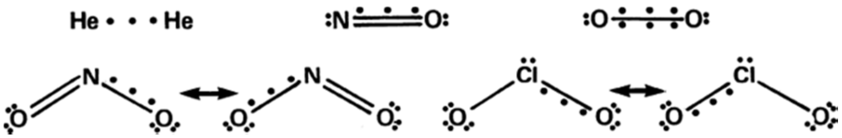

Figure 2-1: Pauling "3-electron bond" valence-bond structures for He_2^+, NO, O_2, NO_2, and ClO_2

In this book, we shall demonstrate that, in contrast to what is usually thought the Pauling "3-electron bond" is an extremely useful construct, and that its occurrence is not restricted to paramagnetic molecules. However, to make effective use of the Pauling "3-electron bond" for descriptions of the bonding for diamagnetic molecules, it is necessary to introduce a modification to its representation, namely that proposed by Green and Linnett[3] in 1960. For reasons that we shall discuss more fully in Chapter 3, Green and Linnett have shown that the $\mathbf{A} \cdots \mathbf{B}$ valence-bond structure for the "3-electron bond" is better written as $\dot{\mathbf{A}} \cdot \dot{\mathbf{B}}$, with one bonding electron and two electrons (with spins opposed to that of the bonding electron)

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Lecture Notes in Chemistry 90, DOI 10.1007/978-3-319-16676-6_2

located in atomic orbitals centred on the **A** and **B** nuclei. This modification enables emphasis to be put on Pauling's earlier conclusion that the strength of a "3-electron bond" is approximately equal to that of a 1-electron bond, and that some unpaired-electron charge is associated with each of the two atoms. This unpaired-electron charge is available for (fractional or partial) sharing with unpaired electron charges on other atoms, and it provides the basis for the development of an "increased-valence" theory.

In Chapters 3–9, we shall examine the electronic structures of numerous paramagnetic molecules, for which Pauling's "3-electron bonds" may be utilized in their valence-bond structures. Lewis-type valence-bond descriptions for the dimers of some of these molecules will also be considered. In Chapters 10–25, the incorporation of Pauling's "3-electron bonds" into the valence-bond structures for diamagnetic molecules will be described. The resulting valence-bond structures for diamagnetic systems are designated as "increased-valence" structures, to stress the point that they involve more electrons in nearest-neighbour and non-neighbour bonding than do Lewis-type valence-bond structures, which have electron-pair bonds and lone-pairs of electrons.

The remainder of this chapter provides a discussion of the need for an "increased-valence" theory. A reading of it is not required in order to follow the Pauling "3-electron bond" and Lewis theory of Chapters 3–9.

2-2 Electron Deficient and Electron Excess Bonding Units

Nearly all molecules that involve atoms of main-group elements and an even number of electrons have diamagnetic ground-states. (Molecular O_2 is one important exception, to which we have referred in Section 2-1.) For these molecules, the familiar Lewis valence-bond structures, with electron-pair bonds and lone-pairs of electrons, are mostly used to provide qualitative valence-bond descriptions of their electronic structures. Sometimes, as is the case for H_2, N_2, H_2O, C_2H_6, C_2H_4 and butadiene of Figure 2-2, one Lewis structure alone can give a fairly adequate description of the bonding. If necessary, bond polarity can be indicated in these structures, either by arrowheads or by fractional net charges δ^+ and δ^-, as is shown for H_2O. The bond line represents a pair of shared electrons with opposite spins, the sharing (in orbital theory) arising from atomic orbital overlap. Each lone-pair of electrons also involves two electrons with opposite spins, as is shown for N_2 and H_2O. (The crosses and circles (**x** and **o**) represent electrons with s_z spin quantum numbers of +½ and -½, respectively). For each of the molecules of Figure 2-2, the Lewis structure has the maximum number of electron-pair bonds linking pairs of adjacent atoms. Any other Lewis structure for these molecules, such as the "long-bond" and ionic or polar structures displayed for H_2O and butadiene, have fewer covalent bonds between adjacent atoms, but of course they can participate in resonance with the primary valence-bond structure.

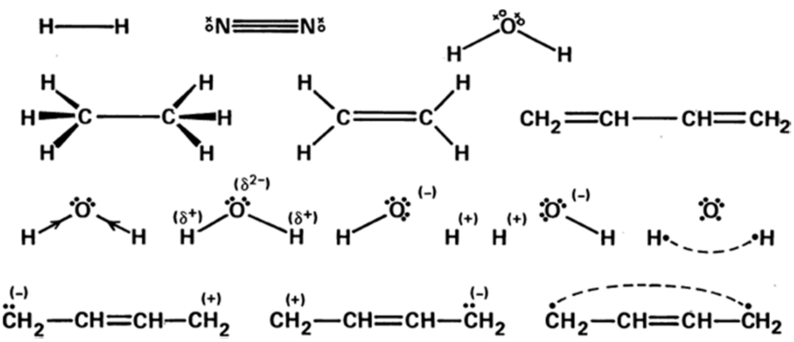
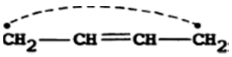
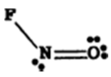
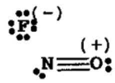


Figure 2-2: Lewis valence-bond structures for H_2, N_2, H_2O, C_2H_6, C_2H_4 and C_4H_6. "Long-bonds" between pairs of non-adjacent atoms are indicated by pecked (-----) bond lines.

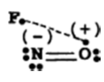
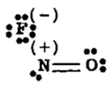
Frequently throughout this volume, we shall use the expression "standard valence-bond structure" or "standard Lewis structure"[i], which we define to be a Lewis structure that

a) has the maximum number of electron-pair bonds permitted by the rules of valence for a given atomic orbital basis set (e.g. the Lewis-Langmuir octet rule for atoms of first-row elements), and
b) locates electron-pair bonds between pairs of adjacent atoms only.

Thus, for butadiene, $\mathbf{CH_2 = CH - CH = CH_2}$ is a standard valence-bond structure, whereas the polar and "long-bond" structures $\overset{(+)}{\mathbf{C}}\mathbf{H_2 - CH = CH} - \overset{(-)}{\ddot{\mathbf{C}}}\mathbf{H_2}$ and  are not. Similarly, both

 and 

are standard Lewis structures for FNO, whereas

 and 

are not.

For a large number of molecules, it is possible to construct two or more Lewis structures that have the same number of electron-pair bonds between adjacent atoms. Familiar examples of these molecules (or ions) are C_6H_6, H_3^+, B_2H_6,

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[i] Standard and long-bond Lewis structures are also designated as Kekulé and Dewar/formal bond/singlet diradical Lewis structures, respectively.

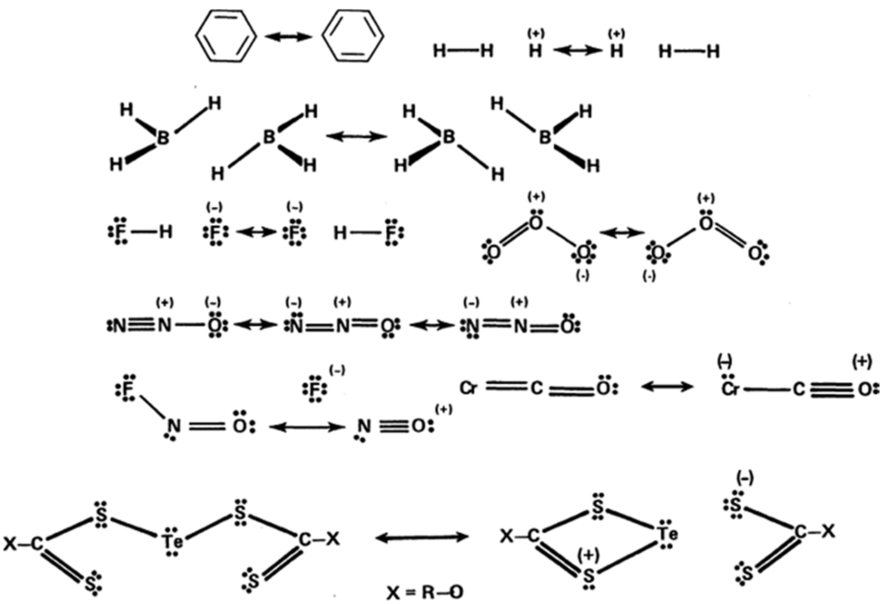


Figure 2-3: Standard Lewis structures for C_6H_6, and some electron-deficient and electron-excess systems.

HF_2^-, O_3, N_2O, FNO and the Cr-CO linkages of $Cr(CO)_6$, whose standard Lewis structures (together with those for $Te(ROCS_2)_2$)[4] are displayed in Figure 2-3.

To describe simply the electronic structures of these molecules and ions, it is usual to invoke resonance between these structures if they are either degenerate (symmetrically equivalent structures such as those displayed for C_6H_6 then contribute equally to the resonance) or considered to have fairly similar energies.

It may be noted that instead of invoking resonance between the standard Lewis structures of Figure 2-3, it is also possible to use the Linnett non-paired spatial orbital structures[3b, c] displayed in Figure 2-4 for some of them.

Although the wave-functions for the two types of valence-bond structures differ (see for example Chapter 23), on inspection, the structures provide the same type of qualitative information concerning bond-properties (in particular, bond-lengths). In contrast, the "increased-valence" structures that are the subject of Chapters 10-24 can provide different information than what can be obtained by inspection of the standard Lewis structures.

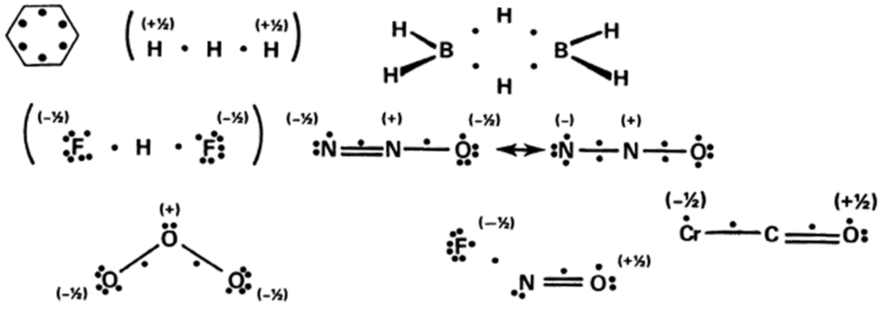


Figure 2-4: Linnett non-paired spatial orbital structures, with pseudo[22] one-electron bonds.

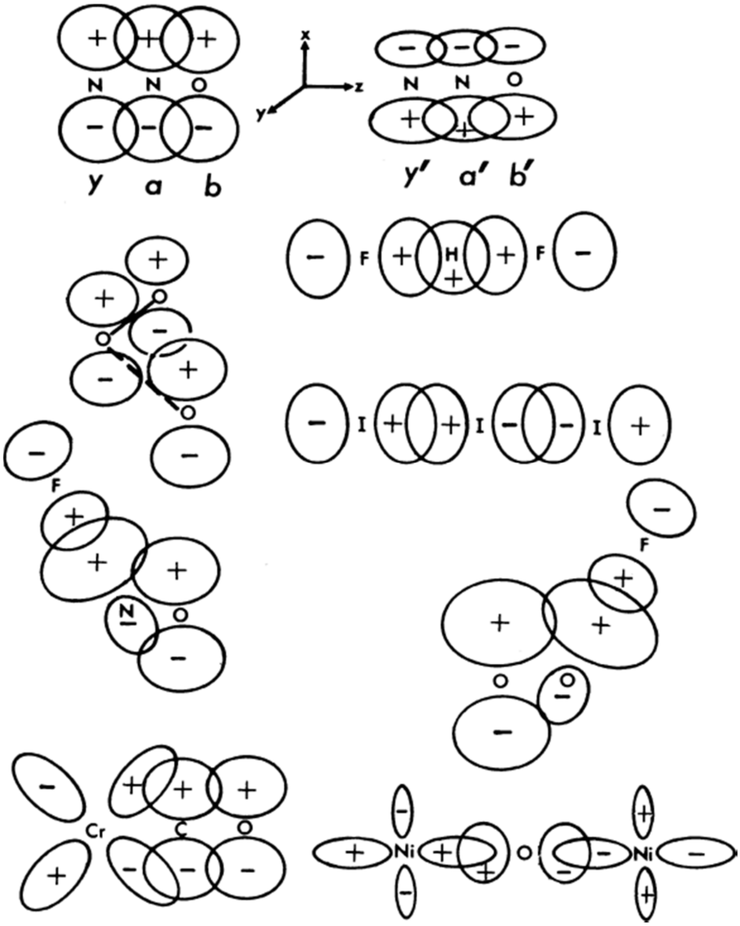


Figure 2-5: Sets of overlapping atomic orbitals used for 4-electron 3-centre bonding units for N_2O , O_3 , HF_2^- , I_3^- , FNO, F_2O_2 , Cr-CO linkage for $Cr(CO)_6$ and Ni-O-Ni linkage for solid NiO.

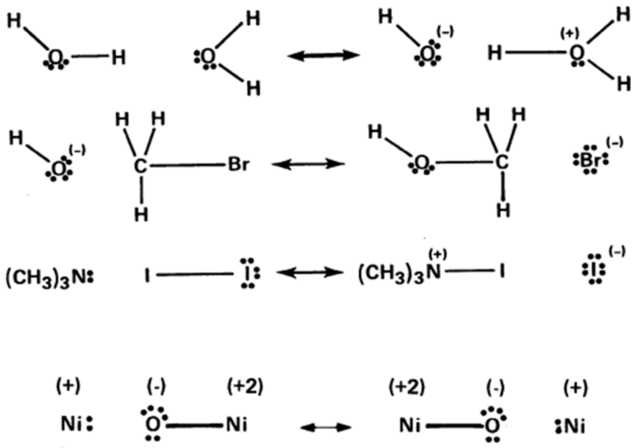


Figure 2-6: Standard Lewis structures for $(H_2O)_2$, the transition state for the S_N2 reaction of $OH^- + CH_3Br$, the complex $Me_3N....I_2$, and an Ni-O-Ni linkage of solid $Ni^{2+}O^{2-}$.

Molecules and ions such as B_2H_6 and H_3^+ are examples of *electron deficient* systems. For them, the number of valence-shell electrons is less than $2(N\text{-}1)$, with N = number of atoms. However, it is with molecules and ions such as N_2O, O_3, FNO, and HF_2^- that we shall be concerned in Chapters 10-24. Each of these latter systems has one or more sets of four electrons distributed amongst three atoms with three overlapping atomic orbitals located around the atomic centres, i.e. they are *electron-rich.* The atomic orbitals are shown in Figure 2-5.

See Figure 1-5 for the calculated orientation of the nitrogen orbital of FNO, which could also pertain for the oxygen orbital of the O-F bond of FO_2.

In Figure 2-3, the standard valence-bond arrangements for sets of four electrons that participate in resonance are of the general types (**1**) and (**2**),

(**1**) (**2**)

in which **Y**, **A**, and **B** are three atoms with overlapping atomic orbitals y, a, and b. Each of the structures **1** and **2** has an electron pair-bond and a lone-pair of electrons, and because they have more electrons than overlapping (valence-shell) atomic orbitals, structures (**1**) and (**2**) are examples of standard valence-bond or standard Lewis structures for electron-rich bonding units.

Valence-bond structures of type (**1**) or (**2**) can occur as components of Lewis-type structures for a large number of intra- and inter-molecular systems, i.e. for any system in which a Lewis structure has an atom with a lone-pair of electrons occupying an atomic orbital that overlaps with the orbitals for the electron-pair

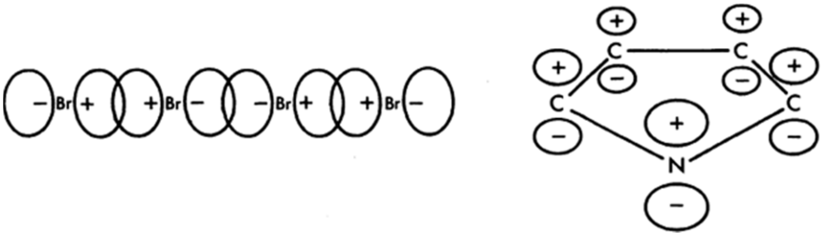


Figure 2-7: Atomic orbitals for a 6-electron 4-centre σ and a 6-electron 5-centre π bonding unit. (In Figure 1-5, a 6-electron 4-centre bonding unit of the $\sigma + \bar{\pi} -$type is displayed.)

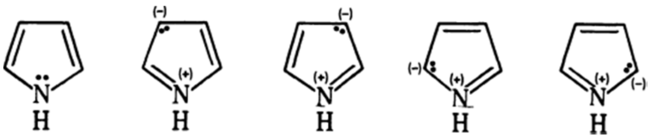
bond between two adjacent atoms. Resonance between structures (**1**) and (**2**) is then possible; the relative weights for these structures depend on the nature of the particular system. Some intermolecular examples, namely $(H_2O)_2$, $Me_3N....I_2$, the transition state for the S_N2 reaction $HO^- + CH_3Br$, and an O-Ni-O linkage for solid $Ni^{2+}O^{2-}$ are shown in Figure 2-6. In Chapters 11-14, we shall show that any electron-excess bonding unit of types (**1**) or (**2**) can be modified and stabilized by developing a Pauling "3-electron bond" structure as a component of it. The consequences of doing this for elementary valence-bond theory and chemical insight are very considerable.

Other types of electron-excess bonding units are also possible. For example, Br_4^{2-} with standard Lewis structures

$$\overset{(-)}{:\ddot{\underset{\cdot\cdot}{\mathrm{Br}}}:}\ \mathrm{Br}—\mathrm{Br}\ \overset{(-)}{:\ddot{\underset{\cdot\cdot}{\mathrm{Br}}}:},\quad \mathrm{Br}—\mathrm{Br}\ \overset{(-)}{:\ddot{\underset{\cdot\cdot}{\mathrm{Br}}}:}\ \overset{(-)}{:\ddot{\underset{\cdot\cdot}{\mathrm{Br}}}:}\ \text{and}\ \overset{(-)}{:\ddot{\underset{\cdot\cdot}{\mathrm{Br}}}:}\ \overset{(-)}{:\ddot{\underset{\cdot\cdot}{\mathrm{Br}}}:}\ \mathrm{Br}—\mathrm{Br}$$

has a 6-electron 4-centre σ bonding unit for a set of six electrons distributed amongst the four overlapping 4pσ atomic orbitals of Figure 2.7.

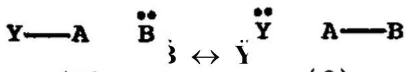
A cyclic 6-electron 5-centre bonding unit obtains for the π-electrons of pyrrole (Figure 2-7), for which the standard Lewis structures are



These longer *N*-centre bonding units of the general types $\ddot{\mathrm{A}}$ **B—C** $\ddot{\mathrm{D}}$ and **Y—A** $\ddot{\mathrm{B}}$ **C—D** represent elaborations of the 4-electron 3-centre bonding unit that we have already described. When appropriate, they will be introduced again later.

2-3 Delocalized Molecular Orbital Theory for 4-Electron 3-Centre Bonding Units

In Section 2-2, we have indicated that the standard Lewis representation for a 4-electron 3-centre bonding unit involves resonance between valence-bond structures of the general types (**1**) and (**2**), i.e.



(1) (2)

A delocalized molecular orbital description of 4-electron 3-centre bonding is also widely used[5,6], and we shall describe three examples of the molecular orbital theory here.

2-3(a) Symmetrical 4-electron 3-centre bonding: H_3^-

The linear triatomic anion H_3^- with four electrons and three overlapping 1s atomic orbitals is the simplest electron-excess system that may be used to describe the molecular orbital procedure. The atomic orbitals y, a and b are displayed in Figure 2-8, and linear combinations of these orbitals may be constructed.

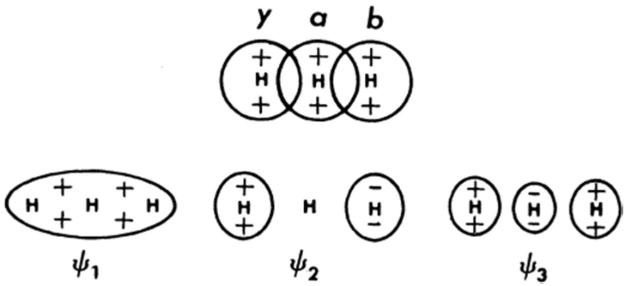


Figure 2-8: Atomic and molecular orbitals for 4-electron 3-centre bonding unit of H_3^- .

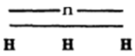
Because y and b are symmetrically-equivalent atomic orbitals, the delocalized molecular orbitals have the forms given by Eqn. (1),

$$\psi_1 = y + b + k_1 a\,,\ \psi_2 = y - b\,,\ \psi_3 = y + b - k_3 a \qquad (1)$$

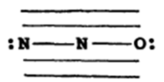
for which k_1 and k_3 are constants, both greater than zero. (Orthogonality of ψ_1 and ψ_3 relates k_3 to k_1.)

Approximate contours for these molecular orbitals are displayed in Figure 2-7 and examination of them shows that ψ_1, ψ_2 and ψ_3 are respectively bonding, non-bonding and antibonding with respect to each pair of adjacent hydrogen atoms.

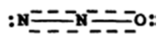
The lowest-energy molecular orbital configuration for the 4-electron 3-centre bonding unit is therefore $(\psi_1)^2(\psi_2)^2$, with the antibonding ψ_3 molecular orbital vacant. Structure (**3**), in which n is the node for the non-bonding molecular orbital, is the molecular orbital valence structure with 3-centre molecular orbitals to accommodate the four electrons.



(3)



(4)



(5)

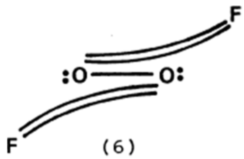
2-3(b) Non-symmetrical 4-electron 3-centre bonding: N_2O and F_2O_2

A large number of electron-excess molecular systems have non-symmetrical 4-electron 3-centre bonding units. For example, N_2O has two sets of four π-electrons, each of which forms a non-symmetrical 4-electron 3-centre bonding unit. The π-electron atomic orbitals y, a, b, y′, a′, and b′ are displayed in Figure 2-5 and the 3-centre molecular orbitals are those of Eqn. (2).

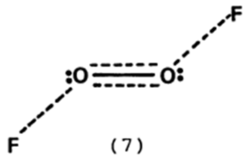
$$\psi_i = c_{i1}\mathrm{y} + c_{i2}\mathrm{a} + c_{i3}\mathrm{b} \text{ and } \psi'_i = c_{i1}\mathrm{y}' + c_{i2}\mathrm{a}' + c_{i3}\mathrm{b}' \text{ for } i = 1, 2, 3 \qquad (2)$$

The lowest-energy molecular orbital configuration is $(\psi_1)^2(\psi_2)^2(\psi'_1)^2(\psi'_2)^2$. Because the terminal nitrogen and oxygen atoms are not symmetrically-equivalent, the molecular orbitals ψ_2 and ψ'_2 are not necessarily non-bonding orbitals with respect to either or both pairs of adjacent atoms. The molecular orbital valence structure for N_2O now corresponds to that of structure (**4**). Sometimes, it is represented as (**5**), for which each broken line represents a set of four delocalized π-electrons.

F_2O_2 provides another example of a molecule in which non-symmetrical 4-electron 3-centre bonding units occur. This molecule has two important sets of 4-electron 3-centre bonding units, which involve the atomic orbitals of the type displayed in Figure 2.5 for one FOO component. The 3-centre molecular orbitals are also given by Eqn. (2), and the resulting molecular orbital configuration of lowest energy is of the same form as that for N_2O, namely $(\psi_1)^2(\psi_2)^2(\psi'_1)^2(\psi'_2)^2$. The valence-bond structure that corresponds to this configuration is either (**6**) or (7), which are similar to structures (**4**) and (**5**) for N_2O. With respect to the O-O bonds, the 3-centre molecular orbitals have $\overline{\pi}$ – and π-character, respectively.



(6)



(7)

The molecular orbital description of 4-electron 3-centre bonding is easy to construct, and the molecular orbital procedure is probably the most suitable to use to calculate the electron distributions in a polyatomic molecule. But, it has the disadvantage that one cannot see *by inspection* what the properties of the individual bonds for many electron-excess molecules should be when they are compared with those for molecules that have essentially localized 2-centre bonds. For example, the N-N and N-O bond-lengths[i] of 1.129 Å and 1.188 Å for N_2O are similar to the triple and double bond[7, 8] lengths of 1.098 Å and 1.214 Å for $\mathbf{:N \equiv N:}$ and $\mathbf{CH_3N = O}$. But inspection of the molecular orbital valence structures (**4**) and (**5**) for N_2O does not make this similarity obvious. For F_2O_2, the O-O bond-length of 1.217 Å is almost identical[9] to the double-bond length of 1.207 Å for free O_2, but neither of the molecular orbital valence structures (**6**) or (**7**) gives any hint as to why this is so. The inability to provide much bond-length information without calculation is true of all delocalized molecular orbital descriptions of the bonding for 4-electron 3-centre (and larger) bonding units.

For qualitative molecular orbital descriptions of the bonding for a large number of triatomic and polyatomic molecules, we refer the reader to Gimarc's text[10].

To compare by inspection the bond-properties of related molecules, it is necessary to use valence-bond structures that have *localized* or *two-centre* bonds, i.e. bonds that link together *pairs* of atoms only. In Section 2-4, we shall examine how this is normally done for electron-excess molecules, using N_2O and F_2O_2 as examples again.

2-4 Standard Valence-Bond Theory for N_2O and F_2O_2

2-4(a) The octet rule and the electroneutrality principle

The basis of the modern electronic theory of valence was established by Lewis[11] in 1916, who suggested that the chemical bond between two similar atoms in a covalent molecule consists of one or more pairs of shared electrons. In 1919, Langmuir[12] elaborated the Lewis theory, and gave the name of *covalent bond* to

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[i] Unless stated otherwise, all bond-lengths have been taken from reference 7. Differences in the operational definitions of bond-lengths (i.e r_s, r_o, r_g, r_e), and uncertainties in bond-lengths have been ignored.

any bond that arises from electron sharing by two atoms. The concept of an energy stabilization through resonance between two or more Lewis structures was developed by Pauling and Slater in the early 1930s. For references to this period, the reader is referred to Ref. (1b), p.184.

Lewis also suggested that when carbon, nitrogen, oxygen and fluorine atoms are bonded to other atoms in a molecule, they tend to acquire the electron configuration of the inert gas neon. With a $1s^2 2s^2 2p^6$ ground-state configuration, the neon atom has eight electrons in its valence shell. When they form covalent bonds, atoms of the other elements above acquire this neon configuraton, by sharing their unpaired electrons with the unpaired electrons of other atoms. According to Lewis, stable (or low energy) valence-bond structures have eight valence-shell electrons disposed around the atomic kernels (atomic nuclei + inner-shell electrons) for any of these first-row elements. Lewis and Langmuir respectively gave the names of “rule of eight” and “octet rule” to this requirement. One quantum mechanical justification for this rule is provided by the existence of four $n = 2$ atomic orbitals (namely 2s, $2p_x$, $2p_y$, and $2p_z$), and a maximum occupancy of two electrons per orbital is permitted by the Pauli exclusion principle.

2-4(b) Standard Valence-Bond Theory and N_2O

We shall now use the covalent molecule N_2O to consider how the octet rule is usually applied. For this molecule, there are nine Lewis structures (namely structures (**1**)-(**9**) of Figure 2-9) that have different π-electron distributions, and which satisfy the octet rule. Each of these structures will contribute to the ground state resonance description of the electronic structure[ii]. To provide a simple qualitative discussion of the bonding, it is usual to select those valence-bond structures that are considered to be the most important, and to make deductions about molecular properties by consideration of them. For N_2O, none of the nine Lewis structures of Figure 2-8 alone can account for the similarity of the N-N and N-O bond-lengths (1.13 and 1.19 Å) to those of triple and double bonds (1.10 and 1.20 Å – see Section 2-3(b)). It is therefore hoped that resonance between the most stable of these structures (i.e. those of lowest energy) will account for the observation. Two

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[ii] Altogether, there are 27 other Lewis-type valence-bond structures that differ in the distributions of the four π- and four $\overline{\pi}$-electrons, and which participate in resonance with the octet structures of Figure 2.9. These structures have fewer covalent bonds than have the octet structures. Here, we are restricting our attention to a consideraton of the octet structures because these are usually the most useful for qualitative discussions of bonding. In Chapter 23, we shall describe how to take account of the non-octet structures when constructing wavefunctions. See also Refs. 13a-d.

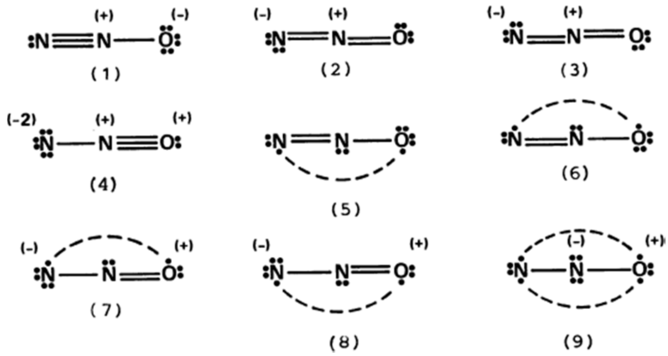


Figure 2-9: Lewis-Langmuir octet structures for N_2O. "Long-bonds" between pairs of non-adjacent atoms are indicated by pecked bond lines.

simple rules are usually invoked to help decide which structures these should be. They are:

a) For a covalent molecule, the low-energy Lewis structures should be those that have the maximum number of covalent bonds between pairs of adjacent atoms.
b) The low-energy structures are those whose atomic formal charges are compatible with those that are required by the *electroneutrality principle* for the molecule. This principle states that for a neutral covalent molecule, the atomic formal charges should be essentially zero, and not greater than ½ or ½.

The order in which these rules is usually applied is (a) before (b). Thus for N_2O, rule (a) suggests that the standard Lewis structures (**1**)-(**4**) should be the most important structures. Each of them has four covalent bonds between pairs of adjacent atoms. Having selected these four structures, rule (b) is then invoked. For structure (**4**), the atomic formal charges (–2, +1, +1) are larger than they are for any of the structures (**1**)-(**3**), namely (0, +1, –1) and (–1, +1, 0). Therefore, structure (**4**) should be a higher energy structure, and its contribution to the ground-state resonance should be smaller than are those of structures (**1**)-(**3**). The bond properties of N_2O are then discussed in terms of resonance between the structures (**1**)-(**3**), and the observed bond-lengths are assumed to be those expected as a consequence of this resonance[15]. Thus, if it is assumed that each of these structures has an approximately equal weight, then we would deduce that the N-N and N-O bonds (with bond-numbers[iii] of 2.67 and 1.67) have lengths that are longer than triple and double bonds, respectively. With respect to the N-N bond, this deduction is valid, but as we have seen, the N-O bond is slightly shorter than the double

[iii] Two different bonding indices will be used in this book, namely bond-number and bond-order. The bond number refers to the number of pairs of electrons that form a covalent bond. It may be calculated from the weights of the valence-bond structures that are used to describe the electronic structure of the molecule, as is demonstrated above for N_2O. The bond-order is a molecular orbital index of bonding. For the purpose of qualitative discussion of diatomic bonding, we shall define the bond-order to be ½{(No. of bonding electrons) – (No. of antibonding electrons)}. Another definition of bond-order will be introduced in Chapter 14.

bond for $CH_3N{=}O$. No matter how we vary the contributions of structures (**1**), (**2**) and (**3**) to the resonance, it is not possible to account for both bond-length observations simultaneously. However, often a "resonance shortening correction" is invoked, which may increase the theoretical N-N and N-O bond-numbers to values closer to 3 and 2 respectively. This type of correction may have a valid basis in theory (see for example Ref. 13a), but we contend that better valence-bond structures may be constructed, which can also rationalize the observations. We shall postpone consideration of this matter until Section 2-5(b).

2-4(c) Standard Valence-Bond Theory and F_2O_2

We shall use F_2O_2 to provide a second example that illustrates some unsatisfactory features of the standard Lewis descriptions for many electron-excess systems.

In Section 2-3(b) we have indicated that the O-O bond-length[9] of 1.217 Å for F_2O_2 is similar to the double-bond length of 1.207 Å for the O_2 ground state. The O-F bond-lengths of 1.575 Å are appreciably longer than the 1.42 Å for the O-F single-bonds of F_2O. A set of nine valence-bond structures that conform to the Lewis-Langmuir octet rule is displayed in Figure 2-10.

If rule (a) of Section 2-4(a) is invoked, we would select the standard Lewis structures (**1**)-(**4**) to be the important valence-bond structures for the F_2O_2 ground state. If we then invoke rule (b) (the electroneutrality principle), we would deduce the order of importance for these Lewis structures to be (**1**) > (**2**) = (**3**) > (**4**). If we assume that structure (**1**) alone represents the electronic structure of F_2O_2, then we cannot account for the observed bond-lengths of this molecule. (By contrast it may be noted that for hydrogen peroxide H_2O_2, the valence-bond structure which is the same as structure (**1**), with H replacing F, is in accord with the observations that O-O and O-H bond-lengths of 1.464 Å and 0.965 Å are essentially those of O-O and O-H single bonds[16].) For F_2O_2, it is necessary to assume that structures (**2**) and (**3**) at least make substantial contributions to the ground-state resonance scheme. A justification for this assumption is also provided by electronegativity considerations, which allow fluorine atoms to acquire formal negative charges (as they do in structures (**2**) and (**3**)). If as is sometimes done, we assume that resonance between structures (**2**) and (**3**) alone can be used to describe the electronic structure of F_2O_2, then we can account for the similarity of the O-O bond-length to that of an O-O double-bond, and also for the lengthening of the O-F bonds relative to those of O-F single-bonds. However, such a description ignores the contribution of Lewis structure (**1**) to the resonance. The absence of formal charges for this structure would suggest that it is also important. If we include structure (**1**), together with structures (**2**) and (**3**), then the O-O bond-length would be predicted to be rather longer than a double bond. To restore agreement between theory and experiment, it is then necessary to assume that valence-bond structure (**4**) (with an O-O triple bond) also contributes to the resonance, and that its contribution to the resonance scheme is equal to that of structure (**1**). The very different sets of formal charges (and bond-arrangements) would not permit structures (**1**) and (**4**) to have

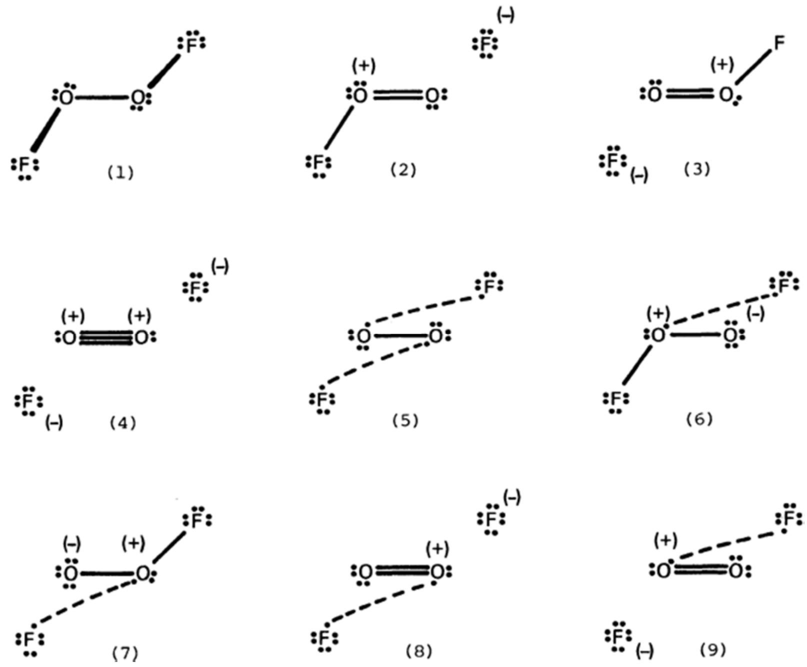


Figure 2-10: Lewis-Langmuir octet structures for F_2O_2. “Long-bonds” between non-adjacent atoms are indicated by pecked bond lines.

similar weights. These considerations suggest that use of the standard Lewis structures (**1**)-(**4**) alone does not provide a satisfactory qualitative valence-bond description of the electronic structure for F_2O_2.

2-5 “Long-Bond” Lewis Structures and a Need for an “Increased-Valence” Theory

2-5(a) The Electroneutrality Principle and “Long-Bond” Valence-Bond Structures

For N_2O, let us now suppose that rule (b) of Section 2-4(a) is given precedence over rule (a). Because Lewis structures (**5**) and (**6**) of Figure 2-9 carry zero formal charges on all atoms, we would now choose them to be the most important of the valence-bond structures displayed in Figure 2-9. Each of the structures (**5**) and (**6**) has a “long” π or $\bar{\pi}$ bond between the terminal nitrogen and oxygen atoms. The atomic orbitals for these “long” bonds are displayed in Figure 2-5, namely orbitals y and b for the long π-bond, and orbitals y′ and b′ for the long $\bar{\pi}$-bond. Because the orbitals y and b are located on non-adjacent atoms, as are y′ and b′, their overlap integrals ($S_{\mathrm{yb}} \equiv \int \mathrm{yb}\,\mathrm{d}v$ etc.,) are much smaller than are those that pertain for pairs of atomic orbitals located on adjacent atomic centres. Thus, we have calculated $S_{\mathrm{yb}} \equiv S_{\mathrm{y'b'}} = 0.01$. For the N-N and N-O π- or $\overline{\pi}$-bonds of structures (**1**)-(**3**), which utilize atomic orbitals on adjacent atoms, the overlap integrals are $S_{\mathrm{ya}} \equiv S_{\mathrm{y'a'}} = 0.26$, and $S_{\mathrm{ab}} \equiv S_{\mathrm{a'b'}} = 0.19$. Consequently, if we assume that the magnitude of the overlap integral provides a qualitative guide to the extent of covalent bonding, then there is less covalent bonding for structures (**5**) and (**6**) than there is for structures (**1**)-(**4**).

It is conceivable that the reduction in nearest-neighbour covalent bonding that occurs in the "long-bond" structures (**5**) and (**6**) may be either partially or completely compensated by the absence of atomic formal charges in these structures. Should this be the case, then consideration of both rules (a) and (b) together on a more equal footing would lead us to conclude that Lewis structures (**1**), (**2**) (**3**), (**5**) and (**6**) could all make important contributions to the ground-state resonance description of the electronic structure of N_2O. For F_2O_2, Lewis structures (**1**), (**2**), (**3**) and (**5**) of Figure 2-10 might also be selected as important structures. If we extend these types of considerations to other molecules, then according to the electroneutrality principle, we have no right to assume that "long-bond" Lewis structures make minor contributions to the ground-state resonance description for many molecules. The results for a number of calculations of valence-bond wavefunctions[13,17] indicate that this assumption is especially not valid when the standard Lewis structures (for example, structures (**1**)-(**4**) of Figure 2-9 for N_2O) carry non-zero atomic formal charges and one or more of the "long-bond" structures do not. The generalized valence-bond calculations of Goddard and his co-workers[18], and the valence-bond calculations of Hiberty and Le-Forestier[19], provide further support for this conclusion.

Although perhaps it is very much concealed, the wavefunctions (or bond-eigenfunctions) for valence-bond structures with "long bonds" also contribute to the molecular orbital description for 4-electron 3-centre bonding[13,17]. We shall demonstrate this here for a symmetrical 4-electron 3-centre bonding unit, with the molecular orbitals of Eqn. (1). These molecular orbitals may be used to express the lowest-energy molecular orbital configuration $(\psi_1)^2(\psi_2)^2$ as a linear combination of the bond-eigenfunctions for six valence-bond structures, namely

$$(\psi_1)^2(\psi_2)^2 = 2k_1\{\Psi_1(\mathrm{Y{-}A}\quad \ddot{\mathrm{B}}) + \Psi_2(\ddot{\mathrm{Y}}\quad \mathrm{A{-}B})\} + k_1^2\Psi_3(\dot{\mathrm{Y}}\quad \ddot{\mathrm{A}}\quad \dot{\mathrm{B}})$$
$$+\,4\Psi_4(\ddot{\mathrm{Y}}\quad \mathrm{A}\quad \ddot{\mathrm{B}}) + k_1^2\{\Psi_5(\ddot{\mathrm{Y}}\quad \ddot{\mathrm{A}}\quad \mathrm{B}) + \Psi_6(\mathrm{Y}\quad \ddot{\mathrm{A}}\quad \ddot{\mathrm{B}})\}$$

thereby showing that the bond-eigenfunction for the "long-bond" structure $\dot{\mathrm{Y}}\ \ddot{\mathrm{A}}\ \dot{\mathrm{B}}$ contributes to the linear combination. It may be noted that because this linear combination contains only one parameter (k_1) whose value may be determined so that the total energy is a minimum, the molecular orbital configuration does not represent the "best" (i.e., lowest-energy) linear combination of the six bond-eigenfunctions. For the "best" linear combination, the coefficient for

 differs from those for $\Psi(\ddot{Y}\ \ddot{A}\ B)$ and $\Psi(Y\ \ddot{A}\ \ddot{B})$ (whereas they are the same in the linear combination above). Thus for O_3, Gould and Linnett have calculated the "best" linear combination to be[17a]

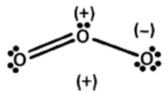
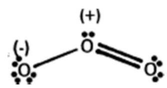
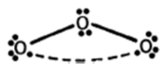
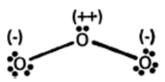
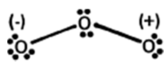
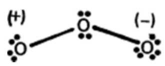
$$\Psi(\text{best}) = 0.351(\Psi_1 + \Psi_2) + 0.390\Psi_3 + 0.124\Psi_4 + 0.028(\Psi_5 + \Psi_6)$$

thereby demonstrating the importance of the bond-eigenfunction for the "long-bond" structure with zero formal charges on all atoms. Similar results for O_3 obtained by other workers[13b, d, 19] are reported in Table 2-1.

We therefore suggest that satisfactory qualitative valence-bond descriptions for many molecular systems with 4-electron 3-centre bonding units often require the inclusion of certain "long-bond" structures as well as the standard Lewis-structures, all of which obey the Lewis-Langmuir octet rule. Whether or not the weights of the "long-bond" Lewis structures are large, a more-stable (or lower energy) description of the molecular systems must *always* be obtained by include-ing rather than excluding the "long-bond" structures (provided that the coefficients of the bond-eigenfunctions are chosen so that the total energy of the valence-bond wave-function is minimized).

In the Appendix, a further justification for the inclusion of "long-bond" structures is provided. It is based on consideration of the magnitudes of the overlap and Hamiltonian matrix elements in the secular equations (cf. Section 1-3). The wave-function Ψ_3 for the long-bond structure overlaps better with the wavefunctions Ψ_1 and Ψ_2 for the standard structures than do the latter wavefunctions with each other.

Table 2-1: Bond-eigenfunction coefficients (C_i)[13b, d] and weights $(W_i = C_i^2\ S_{ii} + \frac{1}{2}\sum_{j\neq i} C_iC_jS_{ij})$[19] for the O_3 ground-state. (N.B. The C_i in the text are for non-normalized bond-eigenfunctions for Ref. 17a.) See Refs. 24-29 for some post-1982 estimates of the C_i or W_i.

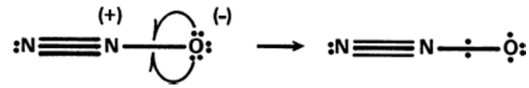
		C_i	C_i	W_i
	Ψ_1	0.337	0.308	0.184
	Ψ_2	0.337	0.308	0.184
	Ψ_3	0.859	0.793	0.593
	Ψ_4	0.110	0.0670	0.023
	Ψ_5	0.108	0.0674	0.008
	Ψ_6	0.108	0.0674	0.008

2-5(b) The Need for "Increased-Valence" Structures

If a number of "long-bond" Lewis structures are included together with the standard Lewis structures in a qualitative resonance description of electronic structure, the resonance description may become rather cumbersome. We may also lose quick insight into the expected properties of the bonds. For example, if we include the "long-bond" structures (**5**) and (**6**) together with (**1**), (**2**) and (**3**) to represent the ground-state electronic structure for N_2O, we might be led to deduce that the contributions from structures (**5**) and (**6**) would reduce the N-N and (nearest neighbour) N-O bond-numbers below the values of 2.67 and 1.67 obtained from resonance between (**1**), (**2**) and (**3**) (with each of these latter structures contributing equally). However, this need not be the case, because this deduction ignores the effect of resonance on bonding[i]. This suggests that we require a technique for using all of the important Lewis octet structures (both standard and "long-bond") together with some indication of the effect on bonding of resonance between these valence-bond structures. One technique involves the incorporation of 1-electron bonds (via the Pauling "3-electron bonds") as well as electron-pair bonds into the valence-bond structures. In Chapters 10-14, we shall describe in some detail how this may be done. Here, we shall only display these types of structures for N_2O and F_2O_2 and make some obvious comments about them.

2-5(c) "Increased-Valence" Structures for N_2O and F_2O_2

In Section 13-1, we shall generate valence-bond structures (**I**)-(**IV**) of Figure 2-10 for N_2O, each of which has two 1-electron bonds as well as electron-pair bonds. In Section 13-1, we shall demonstrate in more detail that we can easily generate these structures from the standard Lewis structures (**1**)-(**4**) of Figure 2.9 by delocalizing non-bonding π- and $\bar{\pi}$-electrons into the adjacent N-O or N-N bond regions, for example as is shown here for structure (**1**) $\rightarrow$ structure (**I**).



(**1**) (**I**)

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i To illustrate this point, we may refer to the valence-bond structures $(\overset{(+)}{\mathrm{H}}\ \dot{\mathrm{H}})$ and $(\dot{\mathrm{H}}\ \overset{(+)}{\mathrm{H}})$ for the 1-electron molecule ion H_2^+ Each of these structures alone does not have a bonding electron. However, resonance between them generates a 1-electron bond, i.e. $(\overset{(+)}{\mathrm{H}}\ \dot{\mathrm{H}}) \leftrightarrow (\dot{\mathrm{H}}\ \overset{(+)}{\mathrm{H}}) \equiv (\mathrm{H}\ \cdot \mathrm{H})^+$. Orbital theory for this resonance is developed in Section 3-2.

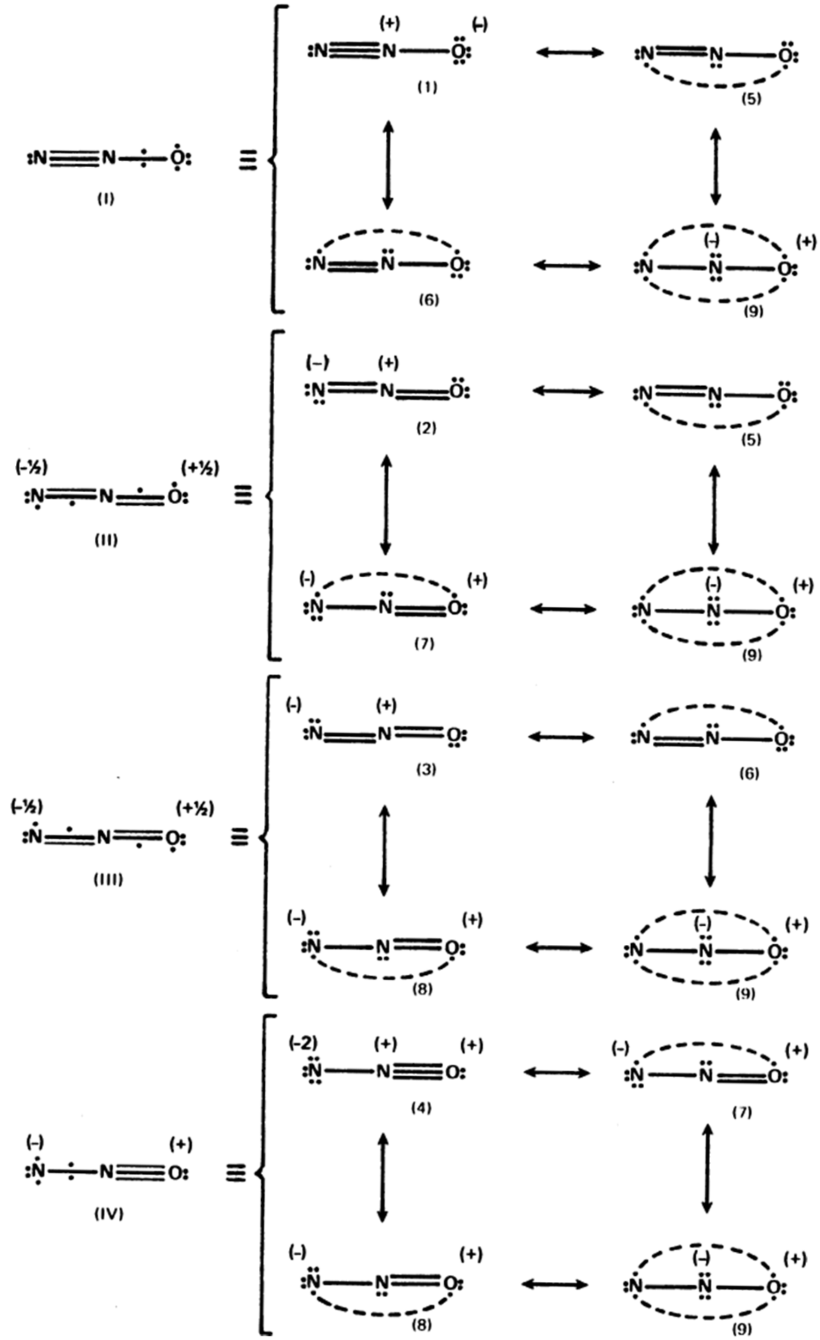

Figure 2-11: "Increased-Valence" structures and component Lewis octet structures.

If we use the result that a 1-electron bond between a pair of atoms **A** and **B** summarizes resonance between valence-bond structures $(\dot{\mathbf{A}}\ \ \mathbf{B})$ and $(\mathbf{A}\ \ \dot{\mathbf{B}})$ (i.e. $\mathbf{A} \cdot \mathbf{B} \equiv (\dot{\mathbf{A}}\ \ \mathbf{B}) \longleftrightarrow (\mathbf{A}\ \ \dot{\mathbf{B}})$), it is easy to demonstrate that each of the structures (**I**)-(**IV**) summarizes resonance between one standard *and* three of the "long-bond" Lewis structures of Figure 2-9. Thus,

(**I**) ≡ (**1**) ↔ (**5**) ↔ (**6**) ↔ (**9**),
(**II**) ≡ (**2**) ↔ (**5**) ↔ (**7**) ↔ (**9**),
(**III**) ≡ (**3**) ↔ (**6**) ↔ (**8**) ↔ (**9**) and
(**IV**) ≡ (**4**) ↔ (**7**) ↔ (**8**) ↔ (**9**),

as is shown in Figure 2-11. Therefore by invoking resonance between structures (**I**)-(**IV**), we are able to summarize resonance between *all* of the Lewis octet structures of Figure 2-9. It may be noted also that each of (**I**)-(**IV**) seems to have two more bonding electrons than has any of the octet structures (**1**)-(**9**). Therefore (for reasons that will be developed further in Section 11-1), structures (**I**)-(**IV**) are examples of a class of valence-bond structures, which have been designated as "increased-valence" structures[13, 20].

For illustrative purposes only, the formal charges for "increased-valence" structures are usually to be assigned on the assumption[ii] that bonding electrons are shared equally by pairs of adjacent atoms. If we invoke the electroneutrality principle, then the absence of formal charges for structure (**I**) would suggest that this structure is more important than are any of the structures (**II**), (**III**) and (**IV**). By assuming this to be the case, we may conclude that the electronic structure of N_2O more-closely resembles that of (**I**) than that for any of the other increased-valence structures. Indeed, if we select structure (**I**) alone to represent (approximately) the electronic structures of N_2O, we may deduce that the N-O bond-length should be similar to that of a double bond, and that the N-N bond-length should be longer than that of a triple bond, but still resemble a triple bond. Both of these deductions are in accord with the observations reported in Section 2-4 (a). The N-O double-bond character for structure (**I**) is implied by the presence of four bonding electrons located in the N-O bond region. Relative to the N-N triple bond of N_2, the reduction of the N-N bond-number for structure (**I**) arises because this

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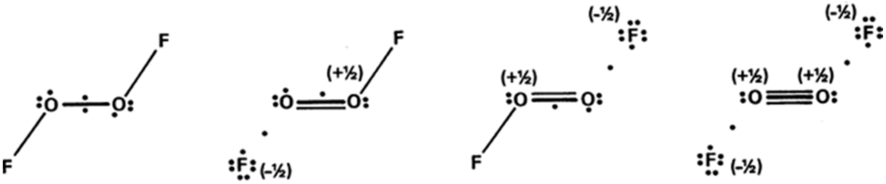
ii This is the normal procedure that is used to assign formal charges to the atoms of valence-bond structures. The actual atomic formal charges for a molecule are then determined (primarily) by the weights of the different valence-bond structures that participate in resonance. However, because an "increased-valence" structure summarizes resonance between a number of Lewis structures, some of which will have different weights, the "best" set of formal charges for an "increased-valence" structure will in general not be integer or $\frac{1}{2}$-integer in magnitude. In the absence of knowledge as to what they are, we shall use the same procedure that Linnett[3] had used to assign atomic formal charges for his non-paired spatial orbital structures, namely to assume that bonding electrons are shared equally by adjacent atoms of the "increased-valence" structures. In generalized valence-bond structures, such as $(\dot{\mathbf{A}}\ \ \mathbf{B})$, $(\mathbf{A}\ \ \dot{\mathbf{B}})$, (**A • B**), **Y—A B:** and **Y⌐⌐A • B•,** atomic formal charges will usually be omitted.

structure is equivalent to resonance between the Lewis structures (**1**), (**5**), (**6**) and (**9**) of Figure 2-9, and only structure (**1**) has an N-N triple bond.

In Chapter 11, we shall generate "increased-valence" structure (**V**) for F_2O_2, which has two more bonding electrons than have any of the Lewis structures displayed in Figure 2-9. This "increased-valence" structure accounts for the similarity of the O-O bond-length to that of free O_2, and the lengthening of the O-F bonds relative to those of O-F single bonds. In structure (**V**), there are four O-O bonding electrons as is required for a double bond. It may also be deduced that structure (**V**) summarizes resonance between the standard Lewis structure (**1**) and the "long-bond" structures (**5**), (**6**) and (**7**) of Figure 2-10. In each of the structures (**5**), (**6**) and (**7**), the absence of either one or two O-F covalent bonds between a pair of adjacent oxygen and fluorine atoms reduces the O-F bond-numbers for structure (**V**) below those of unity for structure (**1**).



(V) (VI) (VII) (VIII)

"Increased-valence" structures (**VI**)-(**VIII**) may also be constructed for F_2O_2, and they may also participate in resonance with "increased-valence" structure (**V**). The electroneutrality principle would suggest that because structure (**V**) carries zero atomic formal charges on all atoms, this structure has the largest weight, i.e. it is the most important of the four "increased-valence" structures. By assuming that this is so, we have been able to account qualitatively for the observed O-O and O-F bond-lengths without giving consideration to the contributions of structures (**VI**), (**VII**) and (**VIII**) to the resonance.

2-6 "Increased-Valence" Structures: Some General Comments

Inspection of the "increased-valence" structures (**I**)-(**VIII**) shows that each of them involves electron distributions of the following types:

$$\mathbf{N{-}N\cdot\dot{O}}\,,\ \mathbf{\dot{N}\cdot N{-}O}\,,\ \mathbf{F{-}O\cdot\dot{O}}\ \text{and}\ \mathbf{\dot{F}\cdot O{-}O}$$

We may generalize these structures to write them as $\mathbf{Y{-}A\cdot\dot{B}}$. All "increased-valence" structures have this type of electron distribution for each set of electrons that is involved in 4-electron 3-centre bonding. As we shall demonstrate further in Chapter 11, we may generate this "increased-valence" electron distribution by bonding a Pauling "3-electron bond" structure $\mathbf{\dot{A}\cdot\dot{B}}$ to a third atom $\mathbf{\dot{Y}}$ which has an odd-electron. Thus, using the Green and Linnett representation for the Pauling "3-electron bond" (i.e. $\dot{\mathbf{A}} \cdot \dot{\mathbf{B}}$ rather than $\mathbf{A}\cdots\mathbf{B}$ – see Section 2-1), we may write

$$\dot{\mathbf{Y}} + \dot{\mathbf{A}} \cdot \dot{\mathbf{B}} \rightarrow \mathbf{Y}—\mathbf{A} \cdot \dot{\mathbf{B}}$$

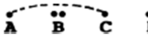
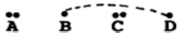
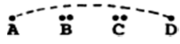
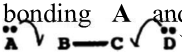
We are therefore led to conclude that all "increased-valence" structures for 4-electron 3-centre bonding units can have Pauling "3-electron bonds" as components of their valence-bond structures. And because the phenomenon of 4-electron 3-centre bonding occurs extremely frequently, it follows that the relevance of Pauling "3-electron bond" and "increased-valence" theory for qualitative valence-bond descriptions of electronic structure is very great. The need for an "increased-valence" theory has also been implied by Bent[21] in his review on inter- and intramolecular donor and acceptor complexes.

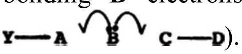
The discussion above shows that the general "increased-valence" structure $\mathbf{Y}—\mathbf{A} \cdot \dot{\mathbf{B}}$ for 4-electron 3-centre bonding has the following properties. These will be elaborated further in Chapters 11, 12 and 14.

a) It summarizes resonance between the standard and "long-bond" Lewis structures $\mathbf{Y}—\mathbf{A}\ \ \ddot{\mathbf{B}}$ and $\mathbf{Y}\ \ \ \ddot{\mathbf{A}}\ \ \ \mathbf{B}$. Therefore $\mathbf{Y}—\mathbf{A} \cdot \dot{\mathbf{B}}$ is more stable than either of the component structures alone.
b) It can be derived *either* from the standard Lewis structure (**1**) by delocalizing a non-bonding **B** electron into either a bonding molecular orbital located in the adjacent **A-B** bond region (i.e. $\mathbf{Y}—\mathbf{A}\ \ddot{\mathbf{B}} \rightarrow \mathbf{Y}—\mathbf{A} \cdot \dot{\mathbf{B}}$) *or* by spin-pairing the odd electrons of the Pauling "3-electron bond" structure $\dot{\mathbf{A}} \cdot \dot{\mathbf{B}}$ and a $\dot{\mathbf{Y}}$ atom when the odd-electron orbitals overlap. Its $\mathbf{Y}—\mathbf{A}$ bond is a *fractional* electron-pair bond, and therefore it is longer and weaker than the normal $\mathbf{Y}—\mathbf{A}$ electron-pair bond of $\mathbf{Y}—\mathbf{A}\ \ddot{\mathbf{B}}$. (In Chapter 14, it will also be shown that $\mathbf{Y}—\mathbf{A} \cdot \dot{\mathbf{B}}$ can also be derived from the standard Lewis structure (**2**) by delocalizing a non-bonding **Y** electron into an antibonding **A-B** molecular orbital.)

In Chapters 11, 12 and 14, the following additional properties will also be demonstrated.

c) In (b), the odd-electron of $\dot{\mathbf{A}} \cdot \dot{\mathbf{B}}$ that is spin-paired with that of $\dot{\mathbf{Y}}$ occupies an antibonding A-B orbital.
d) A total of three electrons may participate in fractional **Y-A**, **Y-B** and **A-B** bonding in $\mathbf{Y}—\mathbf{A} \cdot \dot{\mathbf{B}}$. Each of $\mathbf{Y}—\mathbf{A}\ \ \ddot{\mathbf{B}}$ and $\mathbf{Y}\ \ \ \ddot{\mathbf{A}}\ \ \ \mathbf{B}$ has two bonding electrons, and therefore the "increased-valence" designation for $\mathbf{Y}—\mathbf{A} \cdot \dot{\mathbf{B}}$ is a consequence of this property.
e) The **A** atom valence for the "increased-valence" structure can exceed the value of unity that exists for the standard Lewis structure $\mathbf{Y}—\mathbf{A}\ \ \ddot{\mathbf{B}}$.

For 6-electron 4-centre (and longer *N*-centre) bonding units, similar types of properties exist for most of the "increased-valence" structures. For example, by spin-pairing the odd-electrons of the Pauling "3-electron bond" structures $\dot{\mathbf{A}} \cdot \dot{\mathbf{B}}$ and $\dot{\mathbf{C}} \cdot \dot{\mathbf{D}}$, "increased-valence" structure $\dot{\mathbf{A}} \cdot \mathbf{B} — \mathbf{C} \cdot \dot{\mathbf{D}}$ for 6-electron 4-centre bonding units is obtained. This structure summarizes resonance between the Lewis structures $\ddot{\mathbf{A}}\ \ \mathbf{B} —— \mathbf{C}\ \ \ddot{\mathbf{D}}$, ,  and  and may also be generated from the standard Lewis structure by delocalizing non-bonding **A** and **D** electrons into the **A-B** and **C-D** bond regions (i.e ).

Some of the longer *N*-centre bonding units do not have Pauling "3-electron bonds" as components in their "increased-valence" structures. Thus, for 6-electron 5-centre bonding, no Pauling "3-electron bond" is present visually in the "increased-valence" structure $\mathbf{Y} — \mathbf{A} \cdot \mathbf{B} \cdot \mathbf{C} — \mathbf{D}$ which is derived from the standard Lewis structure $\mathbf{Y} —— \mathbf{A}\ \ \ddot{\mathbf{B}}\ \ \mathbf{C} —— \mathbf{D}$ by delocalizing the two non-bonding **B** electrons into the adjacent **B-A** and **B-C** bond regions, (i.e. ). However it is equivalent to resonance between two other increased-valence structures, each of which possesses a Pauling "3-electron bond".

Other approaches to "increased-valence" are possible for molecules that involve atoms of first-row elements. For example, the valence-bond structure $\mathbf{:N \equiv N = \ddot{\underset{\cdot\cdot}{O}}}$ with an apparent valence of five for the central nitrogen atom, is sometimes used to represent the electronic structure of N_2O. In Chapter 16, we shall discuss why this type of structure is less useful for qualitative purposes than are those (such as $\mathbf{:N \equiv N \div \dot{\underset{\cdot}{O}}:}$) that involve one-electron and fractional electron-pair bonds as well as normal electron-pair bonds.

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Addendum Chapter 2

Unless stated otherwise, throughout this volume, the same atomic orbital is used to accommodate electrons when the atomic orbital is both singly-occupied and doubly-occupied. For example, for the valence-bond structures $\ddot{\mathbf{A}}\ \dot{\mathbf{B}}$ and $\dot{\mathbf{A}}\ \ddot{\mathbf{B}}$, the atomic orbital configurations are $(a)^2(b)^1$ and $(a)^1(b)^2$), respectively. This gives the simplest form of theory that is needed to develop the increased-valence theory. Procedures that can be used to go beyond this "minimal basis set" approach, both by using four atomic orbitals, as in $(a_1)^2(b_1)^1$ and $(a_2)^1(b_2)^2$, and six atomic orbitals as in $(a_1)^1(a_2)^1(b)^1$ and $(a)^1(b_1)^1(b_2)^1$, with a_1-a_2 and b_1-b_2 electron-spin pairings, are described in ref. 30. The "breathing orbital" valence-bond procedure[31] uses a different atomic orbital in a valence bond structure according to the nature of the atomic formal charge, and as to whether the orbital is singly- or doubly-occupied.

30. R.D. Harcourt, (a) J. Phys. Chem. A, **101**, 2496, 5962 (1997). (b) in "Increased-valence Structures in Quantum Chemical Methods in Main-Group Chemistry" (T.M. Klapötke and A. Schulz, Wiley 1998), pp. 217-253. (c) in "Pauling's Legacy: Modern Modelling of the Chemical Bond", Theoretical and Computational Chemistry, Vol. 6 (Elsevier Science B.V., Z.B. Maksić and W.J. Orville-Thomas editors, 1999) pp. 449-480.
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Chapter 3 Wave-Functions and Valence-Bond Structures for 1-Electron Bonds, Electron-Pair Bonds, Pauling "3-Electron Bonds" and "no Bonds"

For diatomic systems, an elementary survey will be presented here of types of valence-bond structures and simple orbital wave-functions that may be used to describe 1-electron bonds, electron-pair bonds, Pauling "3-electron bonds" and "no-bonds".

3-1 Diatomic Bonding and Antibonding Molecular Orbitals

If **A** and **B** are two atoms with overlapping atomic orbitals a and b, whose overlap integral $S_{ab} \equiv \int ab dv$ is greater than zero, we may construct the bonding and antibonding molecular orbitals $\psi_+ \equiv \psi_{ab} = a + kb$ and $\psi_- = \psi^*_{ab} = k^* a - b$. The parameters k and k^* are constants (both greater than zero) that are related through the requirement that the two molecular orbitals be orthogonal (i.e. $\int \psi_{ab}\psi_{ab^*}\, dv = 0$. If k is chosen so that the energy of ψ_{ab} is a minimum, then the bonding molecular orbital has an energy which is lower than that of the orthogonal antibonding molecular orbital. For H_2^+, H_2, He_2^+ and He_2, approximate contours for these orbitals, which are constructed from overlapping 1s atomic orbitals, are displayed in Figure 3-1.

R.D. Harcourt, *Bonding in Electron-Rich Molecules*,
Lecture Notes in Chemistry 90, DOI 10.1007/978-3-319-16676-6_3

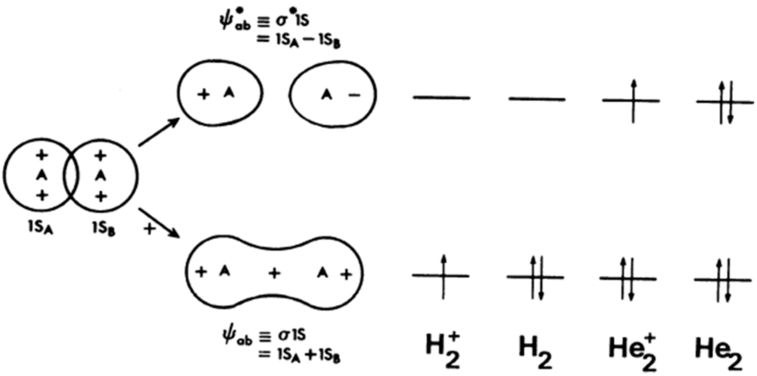


Figure 3-1: σ1s and σ*1s bonding and antibonding molecular orbitals, and orbital occupations for the ground-state configurations of H_2^+, H_2, He_2^+ and He_2.

The symmetry for each of these systems requires that $k = k^* = 1$. If **A** and **B** are non-equivalent atoms (or more particularly, a and b are non-equivalent atomic orbitals), then in general $k \neq k^* \neq 1$. The parameter k is then either > 1 or < 1 according to whether **B** is more or less electronegative than **A** with respect to the electron(s) that occupy the molecular orbital.

For the special case that a and b are equivalent atomic orbitals (i.e. $k = k^* = 1$), the energies for molecular orbitals ψ_{ab} and ψ^*_{ab} may be expressed according to Eqs. (1) and (2)

$$\varepsilon_+ = (H_{aa} + H_{ab})/(1 + S_{ab}) \quad (1)$$
$$\varepsilon_- = (H_{aa} - H_{ab})/(1 - S_{ab}) \quad (2)$$
$$H_{aa} \equiv \int a\hat{H}a \, dv \equiv \int b\hat{H}b \, dv \quad (3)$$
$$H_{ab} \equiv \int a\hat{H}b \, dv \equiv \int b\hat{H}a \, dv \quad (4)$$

if the atomic orbitals are normalized (i.e. $\int a^2 dv = \int b^2 dv = 1$). The H_{aa} and H_{ab} are the coulomb and resonance integrals defined according to Eqs. (3) and (4); $\hat{H}$ is the Hamiltonian operator for an electron. When $S_{ab} > 0$, it may be deduced that $H_{ab} < 0$ and that $\varepsilon_- > \varepsilon_+$, i.e. that $H_{ab} - S_{ab}H_{aa} < 0$.

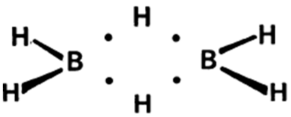
3-2 One-Electron Bonds

For the 1-electron bond of the valence-bond structure $\mathbf{A} \cdot \mathbf{B}$, the electron is accommodated in the bonding molecular orbital $\psi_{ab} = a + kb$. This orbital wave-function shows immediately that $\mathbf{A} \cdot \mathbf{B}$ summarizes resonance between the valence-bond structures ($\dot{\mathbf{A}}\ \ \mathbf{B}$) and ($\mathbf{A}\ \ \dot{\mathbf{B}}$) whose wave-functions are the atomic orbitals a and b respectively, i.e. we may write

$$\mathbf{A \cdot B \equiv (\dot{A}\ \ B) \longleftrightarrow (A\ \ \dot{B})}$$

$$\psi_{ab} = a + kb \equiv a + kb$$

For the 1-electron bond of the hydrogen molecule ion H_2^+, with 1s atomic orbitals, the bonding molecular orbital wave-function and corresponding valence-bond structures are $\psi_{ab} = 1s_A + 1s_B \equiv \sigma 1s$ and $\mathbf{(H \cdot H)^+ \equiv (\dot{H}\ \ H^+) \longleftrightarrow (H^+\ \ \dot{H})}$. In the Linnett valence-bond structures (**1**) and (**2**) for B_2H_6 and C_6H_6, the bridging B-H bonds and the C-C π-bonds are 1-electron bonds[1]. For each of these bonds, the a and b atomic orbitals are a pair of boron sp^3 and hydrogen 1s orbitals, and a pair of 2pπ-orbitals located on adjacent carbon atoms.



(1)

(2)

For H_2^+, the bonding molecular orbital $\sigma 1s = 1s_A + 1s_B$ has the energy given by Eqn.(1). If no overlap occurs between the atomic orbitals, then H_{ab} as well as S_{ab} equals zero. The energy for σ1s is then equal to H_{aa}. The energy difference between H_{aa} and $(H_{aa} + H_{ab})/(1 + S_{ab})$ namely $(H_{ab} - S_{ab} H_{aa})/(1 + S_{ab})$ is designated as the "constructive interference energy"[2] and corresponds to the drop in energy that occurs for H_2^+ when the atomic orbitals overlap. (This energy is also equal to the resonance stabilization energy). An analysis[2-5] of the kinetic and potential energy contributions to this energy shows that the kinetic energy is reduced appreciably and the potential energy rises slightly when the atomic orbitals overlap, i.e. the stabilization of the σ1s bonding molecular orbital relative to a 1s atomic orbital is due to a *net drop in kinetic energy* when atomic orbital overlap occurs.

3-3 Electron-Pair Bonds

For the electron-pair bond of the valence-bond structure **A—B**, two simple types (with $S_{ab} > 0$) of wave-functions can be used to describe the electron configuration.

i) *Molecular orbital:* The Pauli exclusion principle allows any orbital to have a maximum occupancy of two electrons. Consequently the two electrons of the

A—B bond can both occupy the bonding molecular orbital $\psi_{ab} = a + kb$. Therefore, the lowest-energy molecular orbital configuration is $\psi_{ab}(1)\psi_{ab}(2) \equiv (\psi_{ab})^2$. For H_2, a and b are the 1s atomic orbitals and k = 1. The resulting molecular orbital configuration is $\sigma 1s(1)\sigma 1s(2) \equiv (\sigma 1s)^2$ with $\sigma 1s = 1s_A + 1s_B$.

ii) *Heitler-London valence-bond:* Instead of forming the 2-electron wave-function as a product of 1-electron molecular orbitals, we may also construct products of the singly-occupied overlapping atomic orbitals a and b. The resulting 2-electron wave-functions, a(1)b(2) and b(1)a(2) differ only in the labelling (1 or 2) of the electrons, and are equally-acceptable wave-functions. The linear combinations $a(1)b(2) \pm b(1)a(2)$ can therefore be constructed. The lower-energy linear combination is $a(1)b(2) + b(1)a(2)$, and this is the Heitler-London (valence-bond) wave-function for the electron-pair covalent bond **A—B**. With overlapping 1s atomic orbitals, the Heitler-London wave-function for H_2 is written as $1s_A(1)1s_B(2) + 1s_B(1)1s_A(2)$ with a normalization constant of $1/(2+2S_{ab}^2)^{\frac{1}{2}}$.

For either of the above wave functions, the Pauli exclusion principle requires that the two electrons have opposite spins (Section 3-4), i.e. the total spin quantum number (S) = 0. If we use crosses and circles (x and o) to represent electrons with s_z spin quantum numbers of +½ and –½ (or α and β spin wave-functions), then we may write

$$\mathbf{A} — \mathbf{B} = \mathbf{A} \overset{\mathrm{x}}{\underset{\mathrm{o}}{}} \mathbf{B} \text{ for } \Psi(\mathrm{MO}) = \psi_{ab}(1)\psi_{ab}(2) \tag{5}$$

$$\text{and } \mathbf{A} — \mathbf{B} \equiv \overset{\mathrm{x}}{\mathbf{A}}\ \overset{\mathrm{o}}{\mathbf{B}} \leftrightarrow \overset{\mathrm{o}}{\mathbf{A}}\ \overset{\mathrm{x}}{\mathbf{B}} \text{ for } \Psi(\mathrm{HLVB}) = a(1)b(2) + b(1)a(2) \tag{6}$$

For H_2, both the molecular orbital and the Heitler-London wave-functions give appreciable electronic dissociation energies (D_e), namely 2.69 eV and 3.16 eV respectively, when hydrogen-atom 1s atomic orbitals (exp(-ζr) with ζ = 1) are used in the energy calculations. If the orbital exponent ζ is chosen so that the total energy is minimized, these dissociation energies increase to 3.49 eV and 3.78 eV. The exact dissociation energy is $D_e = 4.75$ eV.

To improve further the molecular orbital wave-function, we may invoke "configuration interaction" (C.I.), i.e. linearly combine the bonding configuration $\psi_{ab}(1)\psi_{ab}(2)$ with the antibonding configuration $\psi^*_{ab}(1)\psi^*_{ab}(2)$. "Covalent-ionic" resonance improves the Heitler-London valence-bond function, This resonance involves linearly combining the covalent wave-function $a(1)b(2) + b(1)a(2)$ with the wave-functions a(1)a(2) and b(1)b(2) for the ionic valence-bond structures $\mathbf{A}{:}^-\ \mathbf{B}^+$ and $\mathbf{A}^+\ {:}\mathbf{B}^-$. For H_2, the appropriate ionic wave-function is $1s_A(1)1s_A(2) + 1s_B(1)1s_B(2)$ with both ionic structures $\mathbf{H}{:}^-\ \mathbf{H}^+$ and $\mathbf{H}^+\ {:}\mathbf{H}^-$

Table 3-1: Simple wave-functions, dissociation energies and equilibrium internuclear distances for the H_2 ground-state. (Adapted from Table 5-12 of "Atoms and Molecules", by M. Karplus and R.N. Porter, (Benjamin, N.Y., 1970).)

Wave-function	**Parameters**	D_e(eV)	$R_e(a_o)$
$\{1s_A(1)+1s_B(1)\}\{1s_A(2)+1s_B(2)\}$	$\zeta=1.0$	2.695	1.61
"	$\zeta=1.197$	3.488	1.38
$1s_A(1)1s_B(2)+1s_B(1)1s_A(2)$	$\zeta=1.0$	3.156	1.64
"	$\zeta=1.166$	3.782	1.41
$\phi_A(1)\phi_B+\phi_B(1)\phi_A(2)$	$\zeta_{1s}=\zeta_{2p}=1.19$	4.04	1.416
$\phi=1s+\mu 2p_z$	$\mu=0.105$		
$1s_A(1)1s_B(2)+1s_B(1)1s_A(2)$	$\zeta=1$	3.230	1.67
$+\lambda\{1s_A(1)1s_A(2)+1s_B(1)1s_B(2)\}$	$\lambda=0.105$		
"	$\zeta=1.194$	4.025	1.43
	$\lambda=0.265$		
$\phi_A(1)\phi_B(2)+\phi_B(1)\phi_A(2)$	$\zeta=1.190$	4.122	1.41
$+\lambda\{1s_A(1)1s_A(2)+1s_B(1)1s_B(2)\}$	$\lambda=0.175$		
	$\mu=0.07$		
Experimental		4.74759	1.4006

contributing equally to the resonance. Alternatively we may replace the a and b atomic orbitals of the Heitler-London wave-function with the semi-localized orbitals a + κb and b + κ′a in which κ and κ′ are parameters. If the parameters that arise in each of these three "improved" wave-functions are chosen so that the total energy for each wave-function is minimized, it can be shown that the three wave-functions are equivalent and will generate the same dissociation energy.

For H_2, the three improved wave-functions of the previous paragraph are given by Eqs. (7)-(9)

$$\Psi(\text{MO, CI})=\{a(1)+b(1)\}\{a(2)+b(2)\}+K\{a(1)-b(1)\}\{a(2)-b(2)\} \tag{7}$$

$$\Psi(\text{VB, resonance})=a(1)b(2)+b(1)a(2)+\lambda\{a(1)a(2)+b(1)b(2)\} \tag{8}$$

$$\Psi(\text{VB, semi-localized})=\{a(1)+\kappa b(1)\}\{b(2)+\kappa a(2)\}+\{b(1)+\kappa a(1)\}\{a(2)+\kappa b(2)\} \tag{9}$$

with $a=1s_A$ and $b=1s_B$. Equality is obtained when

$$\lambda=(1+K)/(1-K)=2\kappa/(1+\kappa^2).$$

In Table 3-1, we report the results of calculations of the dissociation energy for H_2, which use the above types of orbital wave-functions for H_2. Because $|\lambda|$ for Eqn. (8) is calculated to be << 1 (for example, 0.105 or 0.265), the primary component for the H_2 ground-state wave-function must be the Heitler-London covalent wave-function.

3-4 Electron Spin Wave-Functions for One-Electron and Two-Electron Systems

In Section 1-2, we have referred to the s and s_z spin quantum numbers for two electrons. For $s_z = +1/2$ and $s_z = -1/2$, the spin wave-functions are designated as α and β, respectively. A *spin-orbital* involves the product of a spatial orbital (for example, ψ_{ab} for the H_2^+ ground-state) with one of these spin wave-functions. Thus for the bonding electron of the H_2^+, there are two spin-orbitals, namely $\psi_{ab}(1)\alpha(1)$ and $\psi_{ab}(1)\beta(1)$. In the absence of a magnetic field, these spin-orbitals are degenerate.

The 2-electron spin wave-functions are $\alpha(1)\alpha(2)$, $\beta(1)\beta(2)$, $\{\alpha(1)\beta(2)+\beta(1)\alpha(2)\}/2^{\frac{1}{2}}$ and $\{\alpha(1)\beta(2)-\beta(1)\alpha(2)\}/2^{\frac{1}{2}}$. They have $S_z\,(\equiv s_z(1)+s_z(2))$ spin quantum numbers of +1, –1, 0 and 0 respectively. Their total spin quantum numbers may be shown to have values of S = 1, 1, 1 and 0. For S = 1 spin, the electron spin orientations are *parallel* (i.e. ↑↑ or ↓↓ or ↑↓ + ↓↑) whereas they are *antiparallel* or opposed (i.e ↑↓ – ↓↑) for S = 0 spin (see Figure 1-3). Each of the three S = 1 spin wave-functions is *symmetric* with respect to the interchange of the electrons, whereas the S = 0 spin wave-function is *antisymmetric* (i.e. changes sign) on electron interchange. The Pauli exclusion principle requires that a symmetric spatial wave-function be associated with the antisymmetric spin wave-function, and vice versa.

Each of the **A-B** bond wave-functions of Eqs. (5)–(9) is symmetric with respect to the interchange of electrons. Therefore they must be associated with the antisymmetric spin wave-function $\{a(1)\beta(2)-\beta(1)\alpha(2)\}/2^{\frac{1}{2}}$ for which the electron spins are antiparallel. Thus we may write

$$\psi_{ab}(1)\psi_{ab}(2)\times\{a(1)\beta(2)-\beta(1)\alpha(2)\}/2^{\frac{1}{2}} \tag{10}$$

and

$$\{a(1)b(2)+b(1)a(2)\}\times\{\alpha(1)\beta(2)-\beta(1)\alpha(2)\}/2^{\frac{1}{2}} \tag{11}$$

as the total wave-functions for the molecular orbital and Heitier-London approximations to the S = 0 spin ground-state.

The symmetric S = 1 spin wave-functions must be associated with antisymmetric spatial wave-functions. Using either bonding and antibonding molecular orbitals or atomic orbitals to construct the spatial wavefunctions, we obtain Eqs. (12) and (13) as the total wave-functions.

$$\{\psi_{ab}(1)\psi^*_{ab}(2) - \psi^*_{ab}(1)\psi_{ab}(2)\} \times \begin{cases} \alpha(1)\alpha(2) \\ \{\alpha(1)\beta(2) + \beta(1)\alpha(2)\}/2^{\frac{1}{2}} \\ \beta(1)\beta(2) \end{cases} \tag{12}$$

$$\{a(1)b(2) - b(1)a(2)\} \times \begin{cases} \{\alpha(1)\alpha(2) \\ \{\alpha(1)\beta(2) + \beta(1)\alpha(2)\}/2^{\frac{1}{2}} \\ \beta(1)\beta(2) \end{cases} \tag{13}$$

For these excited-state wave-functions, the two electrons have parallel spins. An S = 0 spin excited state wave-function, with antiparallel spins for the two electrons is given by Eqn. (14).

$$\{\psi_{ab}(1)\psi^*_{ab}(2) + \psi^*_{ab}(1)\psi_{ab}(2)\} \times \{\alpha(1)\beta(2) - \beta(1)\alpha(2)\}/2^{\frac{1}{2}} \tag{14}$$

Further consideration of the electronic structures of excited states is provided in Chapter 9.

3-5 An Important Identity: 1 bonding electron + 1 antibonding electron = 2 "non-bonding" electrons for parallel-spin electrons

We shall now deduce that, except for the presence of a multiplicative constant, the two S = 1 spin wave-functions of Eqs. (12) and (13) are equivalent[6,7]. This identity will be used often in the following sections, and indeed much of the theory of this book is based on it.

Initially we shall assume that the parameters k and k* both equal unity in the bonding and antibonding molecular orbitals ψ_{ab} and ψ^*_{ab} of Eqn. (12). If we then substitute $\psi_{ab} = a + b$ and $\psi^*_{ab} = a - b$ into Eqn. (12), we obtain Eqn. (15),

$$\psi_{ab}(1)\psi^*_{ab}(2) - \psi^*_{ab}(1)\psi_{ab}(2) = -2\{a(1)b(2) - b(1)a(2)\} \tag{15}$$

thereby demonstrating the equivalence between Eqs. (12) and (13). (For convenience only, we have omitted the spin wave-functions from Eqs. (15) and (16).) In Section 3-7, this result and also those of Section 3-6 will be deduced from the properties of *Slater determinantal* wave-functions.

When the ψ_{ab} and ψ^*_{ab} are normalized to give $\psi_{ab} = (a+b)/(2+2S_{ab})^{\frac{1}{2}}$ and $\psi^*_{ab} = (a-b)/(2-2S_{ab})^{\frac{1}{2}}$, the multiplicative constant of –2 in Eqn. (15) is replaced by $-1/(1-S_{ab}^2)^{\frac{1}{2}}$. For the general orthogonal orbitals $\psi_{ab} = a + kb$ and $\psi^*_{ab} = k^*a - b$, we obtain the identity of Eqn. (16).

$$\psi_{ab}(1)\psi^*_{ab}(2) - \psi^*_{ab}(1)\psi_{ab}(2) = -(1+kk^*)\{a(1)b(2) - b(1)a(2)\} \quad (16)$$

With respect to orbital occupancy for a diatomic system, we may therefore conclude that

$$\boxed{\begin{array}{l} \text{one antibonding electron} \\ \qquad + \qquad\qquad \equiv \text{ two “non-bonding” electrons} \\ \text{one bonding electron} \end{array}} \quad (17)$$

provided that the two electrons have parallel spins[i] and the molecular orbitals are constructed from the same set of atomic orbitals. The non-bonding property of Eqn.(17) arises because the a and b electrons have parallel spins. With respect to energy, this configuration is *net antibonding* when the overlap integral is included in the normalization constants for the molecular orbitals; this is because ψ^*_{ab} is more antibonding than ψ_{ab} is bonding relative to the component atomic orbitals (see, for example, Eqs. (1) and (2)).

3-6 The Pauling “3-Electron Bond”

In 1931, Pauling[8] introduced the “3-electron bond” structure **A···B** as a way to summarize resonance between the Lewis valence-bond structures **A: ·B** and **A· :B**, i.e., Pauling wrote **A···B** ≡ **A: ·B** ↔ **A· :B**.

In Figure 3-2, the 1s atomic orbital occupations for **A: ·B** and **A· :B** are displayed for the helium molecule ion, He_2^+. Because each of these valence-bond structures has only one unpaired electron, Pauling deduced that the length and

i If the two electrons have antiparallel spins, then the spatial wave-function of Eqn. (14) for one bonding + one antibonding electron is equivalent to $(kk^*-1)\ \{a(1)b(2)+b(1)a(2)\} + 2\{k^*a(1)a(2) - kb(1)b(2)\}$.

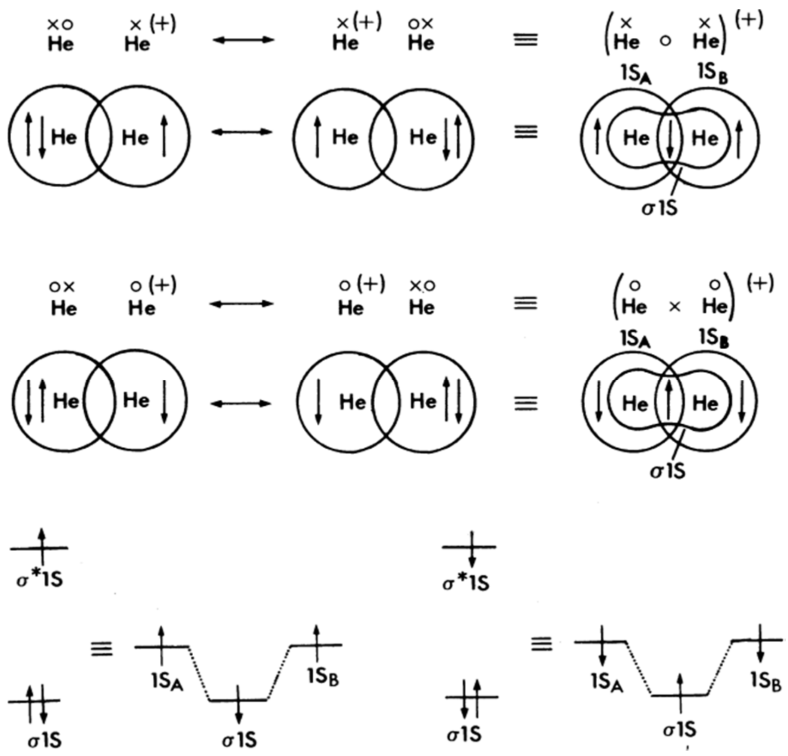


Figure 3-2: Orbital occupations and electron spins for Pauling "3-electron bonds".

strength of a "3-electron bond" should be approximately equal to that of a 1-electron bond. If we indicate the spins of the electrons, as in

$$A^{\times}_{\circ}\ \times B \longleftrightarrow A\times\ \overset{\times}{\circ}B \quad \text{or} \quad \overset{\times\circ}{A}\ \ \overset{\times}{B} \longleftrightarrow \overset{\times}{A}\ \ \overset{\circ\times}{B}$$

then it is obvious that there can only be one bonding electron, because two electrons with the same spin cannot form a bond.

For the three electrons of the Pauling "3-electron bond", a molecular orbital description of them can also be constructed using the bonding and antibonding molecular orbitals $\psi_{ab} = a + kb$ and $\psi^*_{ab} = ka - b$. The Pauli exclusion principle allows only a maximum of two electrons with opposite spins to occupy any orbital. Therefore for the three electrons of the valence-bond structure $\mathbf{A}\cdot\cdot\cdot\mathbf{B}$, the molecular orbital configuration $(\psi_{ab})^2(\psi^*_{ab})^1$ involves two bonding electrons + one antibonding electron. For it, the contribution to bonding by one of the two bonding electrons is cancelled by that of the antibonding electron with the same electron spin (cf. Eqn. (17)), i.e. $(\psi_{ab})^1(\psi^*_{ab})^1 \equiv (a)^1(b)^1$. Therefore for the molecular orbital configuration $(\psi_{ab})^2(\psi^*_{ab})^1$, we can write[ii]

$$(\psi_{ab})^2(\psi^*_{ab})^1 \equiv (\psi_{ab})^1(a)^1(b)^1 \equiv (a+kb)^1(a)^1(b)^1 \equiv (a)^2(b)^1 + k(a)^1(b)^2 \qquad (18)$$

to demonstrate that resonance between the valence-bond structures **A: ·B** and **A· :B** (with atomic orbital configurations $(a)^2(b)^1$ and $(a)^1(b)^2$) is involved, just as it is for the Pauling "3-electron bond" structure **A···B**.

Because the configuration $(\psi_{ab})^1(a)^1(b)^1$ involves only one bonding electron (namely, the electron that occupies ψ_{ab}), and two non-bonding electrons, in 1960, Green and Linnett[9] modified the symbolism for the "3-electron bond" valence-bond structure and wrote it as $\dot{\mathbf{A}} \cdot \dot{\mathbf{B}}$ (or **·A · B·**), which indicates clearly that the Pauling "3-electron bond" involves only one **A-B** bonding electron. Further, because the a and b electrons of this structure are non-bonding electrons with parallel spins, the spin of the bonding ψ_{ab} electron must be opposite to those of the a and b electrons. (This follows because only one of the ψ_{ab} electrons of $(\psi_{ab})^2(\psi^*_{ab})^1$ can have the same spin as that of ψ^*_{ab}.) Therefore, the electron spins of $\dot{\mathbf{A}} \cdot \dot{\mathbf{B}}$ may be those of either $\overset{\times}{\mathbf{A}} \circ \overset{\times}{\mathbf{B}}$ or $\overset{\circ}{\mathbf{A}} \times \overset{\circ}{\mathbf{B}}$, according to whether the antibonding ψ^*_{ab} electron has a $+1/2$ or $-1/2$ (s_z) spin quantum number. In Figure 3-2, the orbitals and electron spin assignments are displayed for these latter valence-bond structures.

The above considerations show that the Green and Linnett structure $\dot{\mathbf{A}} \cdot \dot{\mathbf{B}}$, with one bonding and two non-bonding electrons, provides a "better and clearer diagramatic representation of the electron distribution"[10] than does the Pauling structure **A···B**. Therefore we shall use the $\dot{\mathbf{A}} \cdot \dot{\mathbf{B}}$ representation in the remainder of this book. However, (perhaps misleadingly), we shall continue to refer to this valence-bond structure as a Pauling "3-electron bond" structure.

3-7 Slater Determinants and the Pauling "3-Electron Bond"

Although it is not needed for a reading of much of this book, it is useful here to elaborate further the discussion of the Pauli exclusion principle in order to forma-

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[ii] Our concern here is with orbital occupancies, and therefore this equivalence is appropriate whether or not atomic orbital overlap integrals are included in the normalization constants for the molecular orbitals. See Section 3-10 for a discussion on the inclusion of atomic orbital overlap integrals on the energies of Pauling "3-electron bonds".

lize the derivation of the identity $(\psi_{ab})^2(\psi^*_{ab})^1 \equiv (\psi_{ab})^1(a)^1(b)^1$ for the Pauling "3-electron bond". This is done by utilizing *Slater determinants* to represent *anti-symmetrized-product* wave-functions. We shall do this initially for some 2-electron wave-functions for H_2.

The Pauli exclusion principle (Section 3-4) requires that the total wave-function for an *N*-electron system be antisymmetric with respect to the interchange of the coordinates of any two electrons, i.e.,

$$\Psi(1,2,3,...i,j,...) = -\Psi(1,2,3,...j,i,...) \tag{19}$$

For a two-electron atom or molecule, the total wave-function may be written as the product of a spatial wave-function with a spin wave-function, i.e.

$$\Psi(1,2) = \Psi(1,2)^{\text{space}} \times \Psi(1,2)^{\text{spin}} \tag{20}$$

For the ground-state molecular orbital and Heitler-London valence bond wave-functions of H_2, the antisymmetrized product wave-functions are given by Eqs. (21) and (22) (cf. Eqs. (10) and (11), with $\psi_{ab} \equiv \sigma 1s = s_A + s_B$ and $a \equiv 1s_A \equiv s_A$ etc.).

$$\Psi(\text{MO}) = \sigma 1s(1)\sigma 1s(2)\{\alpha(1)\beta(2) - \beta(1)\alpha(2)\}/2^{1/2} \tag{21}$$

$$\Psi(\text{HLVB}) = \{s_A(1)s_B(2) + s_B(1)s_A(2)\}\{\alpha(1)\beta(2) - \beta(1)\alpha(2)\}/2^{1/2} \tag{22}$$

These wave-functions may be expressed in *determinantal* form. Thus Ψ(MO) of Eqn. (21) may be written as Eqn. (23),

$$\Psi(\text{MO}) = \frac{1}{\sqrt{2}}\begin{vmatrix} \sigma 1s(1)\alpha(1) & \sigma 1s(2)\alpha(2) \\ \sigma 1s(1)\beta(1) & \sigma 1s(2)\beta(2) \end{vmatrix} \tag{23}$$

$$\equiv \left|\sigma 1s(1)\alpha(1)\sigma 1s(2)\beta(2)\right| \equiv \left|\sigma 1s^{\alpha}\sigma 1s^{\beta}\right| \equiv \left|\sigma 1s\overline{\sigma 1s}\right| \tag{24}$$

which is an example of the *Slater determinantal* representation for an antisymmetrized product wave-function. By indicating only the two terms of the leading diagonal, this determinant can be abbreviated to Eqn. (24). Often, the presence or absence of a bar over the spatial orbital indicates that the electron has a β or α spin wave-function.

It is easy to verify that the Heitler-London valence-bond wave-function of Eqn. (22) can be expressed as a sum of two Slater determinants according to Eqn. (25).

$$\Psi(\mathrm{HLVB}) = \left|s_A^\alpha s_B^\beta\right| + \left|s_B^\alpha s_A^\beta\right| \tag{25}$$

One important property of a determinant is that it changes sign if two rows or columns are interchanged. Therefore

$$\left|\sigma 1s^\alpha \sigma 1s^\beta\right| = -\left|\sigma 1s^\beta \sigma 1s^\alpha\right| \tag{26}$$

and $\left|s_A^\alpha s_B^\beta\right| + \left|s_B^\alpha s_A^\beta\right| = \left|s_A^\alpha s_B^\beta\right| - \left|s_A^\beta s_B^\alpha\right|$ (27)

The identity of Eqn. (15) that exists between the $S = 1$ spin configurations of Eqs. (12) and (13) may be written in terms of Slater determinants according to Eqn. (28).

$$\left|\psi_{ab}^\alpha \psi_{ab}^{*\alpha}\right| \equiv -2\left|a^\alpha b^\alpha\right|$$

$$\left|\psi_{ab}^\alpha \psi_{ab}^{*\beta}\right| - \left|\psi_{ab}^{*\alpha} \psi_{ab}^{\beta}\right| \equiv -2(\left|a^\alpha b^\beta\right| - \left|b^\alpha a^\beta\right|) \tag{28}$$

$$\left|\psi_{ab}^\beta \psi_{ab}^{*\beta}\right| \equiv -2\left|a^\beta b^\beta\right|$$

Except for the possible introduction of a multiplicative constant, a determinant is unaltered by adding and subtracting multiples of rows or columns. For example

$$\begin{vmatrix} a & d \\ c & b \end{vmatrix} = -\frac{1}{25}\begin{vmatrix} a+6d & 4a-d \\ c+6b & 4c-b \end{vmatrix}$$

Therefore, for two electrons with parallel spins, the identity of Eqn. (29) obtains.

$$\left|\psi_1^\alpha \psi_2^\alpha\right| = -(1+kk^*)^{-1}\left|(\psi_1 + k\psi_2)^\alpha (k^*\psi_1 - \psi_2)^\alpha\right| \tag{29}$$

Because a determinant has the value of zero if any two rows or columns have identical elements, the Slater determinant form of the antisymmetrized product wave-function indicates immediately that two electrons with parallel spins cannot occupy the same orbital. Thus $\left|\sigma 1s^\alpha \sigma 1s^\alpha\right| = 0$ and $\left|s_A^\alpha s_A^\alpha\right| = 0$.

For a three-electron system, it is not possible to factor out the spatial wave-function from the spin wave-function, as has been done in Eqs. (21) and (22) for a two-electron system. However, we can still construct an antisymmetric total wave-function by using a Slater determinant. To demonstrate this, we shall construct such a wave-function for the $(\sigma 1s)^2(\sigma^* 1s)^1 \equiv (\sigma)^2(\sigma^*)^1$ ground-state configuration of He_2^+ (Section 3-6). If we assume that the antibonding σ* 1s electron has spin wave-function β, the Slater determinantal form of the He_2^+ wave-function is given by Eqn.(30).

$$\left|\sigma^{\alpha}\sigma^{\beta}\sigma^{*\beta}\right| \equiv \frac{1}{\sqrt{3!}}\begin{vmatrix}\sigma(1)\alpha(1) & \sigma(1)\beta(1) & \sigma^*(1)\beta(1)\\ \sigma(2)\alpha(2) & \sigma(2)\beta(2) & \sigma^*(2)\beta(2)\\ \sigma(3)\alpha(3) & \sigma(3)\beta(3) & \sigma^*(3)\beta(3)\end{vmatrix} \tag{30}$$

On expansion of this determinant, we obtain a linear combination of six functions, namely that of Eqn. (31).

$$\begin{aligned}\left|\sigma^{\alpha}\sigma^{\beta}\sigma^{*\beta}\right| = [&\sigma(1)\alpha(1)\ \{\sigma(2)\beta(2)\sigma^*(3)\beta(3) - \sigma(3)\beta(3)\sigma^*(2)\beta(2)\}\\ &+\sigma(2)\alpha(2)\{\sigma(3)\beta(3)\sigma^*(1)\beta(1) - \sigma(1)\beta(1)\sigma^*(3)\beta(3)\}\\ &+\sigma(3)\alpha(3)\{\sigma(1)\beta(1)\sigma^*(2)\beta(2) - \sigma(2)\beta(2)\sigma^*(1)\beta(1)\}]/\sqrt{3!}\end{aligned} \tag{31}$$

$$\begin{aligned}&\equiv \{\sigma(1)\alpha(1)\left|\sigma(2)\beta(2)\sigma^*(3)\beta(3)\right| + \sigma(2)\alpha(2)\left|\sigma(3)\beta(3)\sigma^*(1)\beta(1)\right|\\ &+\ \sigma(3)\alpha(3)\ \left|\sigma(1)\beta(1)\sigma^*(2)\beta\ (2)\right|\}/\sqrt{3!}\end{aligned} \tag{32}$$

By interchanging the coordinates of any two electrons, this linear combination may be shown to be antisymmetric with respect to the interchange of two electrons, and therefore it obeys the Pauli exclusion principle.

For each of the three 2 × 2 Slater determinants of Eqn. (32), the identity of Eqn.(28) pertains i.e. $\left|\sigma^{\beta}\sigma^{*\beta}\right| = -2\left|s_A^{\beta}s_B^{\beta}\right|$. Therefore, an equivalent expression for the Slater determinant of Eqn. (30) is that of Eqn. (33).

$$\left|\sigma^{\alpha}\sigma^{\beta}\sigma^{*\beta}\right| = -2\left|\sigma^{\alpha}s_A^{\beta}s_B^{\beta}\right| = 2\left|s_A^{\beta}\sigma^{\alpha}s_B^{\beta}\right| \tag{33}$$

$$\left|\sigma^{\alpha}\sigma^{\beta}\sigma^{*\alpha}\right| = -\left|\sigma^{\alpha}\sigma^{*\alpha}\sigma^{\beta}\right| = 2\left|s_A^{\alpha}s_B^{\alpha}\sigma^{\beta}\right| = -2\left|s_A^{\alpha}\sigma^{\beta}s_B^{\alpha}\right| \tag{34}$$

If the odd-electron of He_2^+ has spin wave-function α, then the identity of Eqn. (34) is appropriate.

The identities of Eqs. (33) and (34) provide a more complete statement that, except for the presence of a multiplicative constant, the wave-function for two bonding electrons + one antibonding electron is equivalent to the wave-function for two electrons occupying separate atomic orbitals with parallel spins + one electron occupying a bonding molecular orbital with opposite spin. We shall make use of this result on numerous occasions.

This theory is easily extended to the general heteronuclear system **AB** with overlapping atomic orbitals a and b. If **AB** is a three-electron system, with two bonding electrons and one antibonding electron that occupy the orthogonal molecular orbitals $\psi_{\mathrm{ab}} = \mathrm{a} + k\mathrm{b}$ and $\psi^{*}_{\mathrm{ab}} = k^{*}\mathrm{a} - \mathrm{b}$, then by application of Eqn. (29), we obtain Eqs. (35) and (36)

$$|\,\psi^{\alpha}_{\mathrm{ab}}\psi^{\beta}_{\mathrm{ab}}\psi^{*\alpha}_{\mathrm{ab}}\,| = -(1+kk^{*})\left|\mathrm{a}^{\alpha}\psi^{\beta}_{\mathrm{ab}}\mathrm{b}^{\alpha}\right| \quad \overset{\mathrm{x}}{\mathbf{A}}\ \mathrm{o}\ \overset{\mathrm{x}}{\mathbf{B}} \tag{35}$$

$$|\,\psi^{\alpha}_{\mathrm{ab}}\psi^{\beta}_{\mathrm{ab}}\psi^{*\beta}_{\mathrm{ab}}\,| = -(1+kk^{*})\left|\psi^{\alpha}_{\mathrm{ab}}\mathrm{a}^{\beta}\mathrm{b}^{\beta}\right|, \quad \overset{\mathrm{o}}{\mathbf{A}}\ \mathrm{x}\ \overset{\mathrm{o}}{\mathbf{B}} \tag{36}$$

thereby generating the Pauling “3-electron bond” structure $\dot{\mathbf{A}} \cdot \dot{\mathbf{B}}$. The constants k and k^{*} may be related through the requirement that $\psi_{\mathbf{ab}}$ and ψ^{*}_{ab} be orthogonal. (If a and b are real normalized atomic orbitals, with overlap integral S_{ab}, then the orthogonality relationship is $(k^{*}-k)+(kk^{*}-1)S_{\mathrm{ab}}=0)$. We note that if we neglect S_{ab}, then $k^{*}=k$. If **AB** is homopolar, then $k=1=k^{*}$, as is the case for He_2^+.

In Chapters 15 and 23, Slater determinants will be used to construct wave-functions for 4-electron 3-centre, 6-electron 4-centre and larger *N*-centre bonding units.

3-8 “No Bonds”

If we add another electron to the molecular orbital confguration $(\psi_{\mathrm{ab}})^2(\psi^{*}_{\mathrm{ab}})^1$, we obtain the four-electron configuration $(\psi_{\mathrm{ab}})^2(\psi^{*}_{\mathrm{ab}})^2$. It is then easy to show that with respect to orbital occupations, 2 bonding electrons + 2 antibonding electrons is equivalent to 4 non-bonding electrons, i.e., $(\psi_{\mathrm{ab}})^2(\psi^{*}_{\mathrm{ab}}) \equiv (\mathrm{a})^2(\mathrm{b})^2$, and therefore no bond can be formed between atoms **A** and **B** for this four-electron configuration. The valence-bond structure for the four electrons is that for two atoms, each carrying a pair of non-bonding or lone-pair electrons with their electron spins opposed, i.e., $\overset{\mathbf{xo}}{\mathbf{A}}\ \ \overset{\mathbf{xo}}{\mathbf{B}} = \ddot{\mathbf{A}}\ \ \ddot{\mathbf{B}}$ or ${}^{\mathbf{x}}_{\mathbf{o}}\mathbf{A}\ \mathbf{B}^{\mathbf{x}}_{\mathbf{o}} \equiv :\!\mathbf{A}\ \ \mathbf{B}\!:$.

3-9 Valence-Bond Structures and Bond Properties for H_2^+, H_2, He_2^+ and He_2

The four simplest molecular system with ground-state valence-bond structures of the types $\mathbf{A \cdot B}$, $\mathbf{A—B}$, $\dot{\mathbf{A}} \cdot \dot{\mathbf{B}}$ and $\ddot{\mathbf{A}}\ \ddot{\mathbf{B}}$ are H_2^+, H_2, He_2^+ and He_2. For each of them, we may use the 1s atomic orbitals to construct the bonding σ 1s and antibonding σ* 1s molecular orbitals of Figure 3-1. The resulting molecular orbital configurations for the ground-states are reported in Table 3-2, together with their valence-bond structures. From the molecular orbital configurations, we may calculate the bond-orders for these four systems using the formula n = (No. of bonding electrons – No. of antibonding electrons)/2.

Table 3-2: Molecular orbital configurations, valence-bond structures, bond-orders, dissociation energies (eV; $1\ \text{eV} = 96.4\ \text{kJ mol}^{-1}$) and bond-lengths (Å, $1\ \text{Å} = 10^{-10}\ \text{m}$) for H_2^+, H_2, He_2^+ and He_2.

			n	D_e	R_e
H_2^+	$(\sigma 1s)^1$	$(\mathbf{H \cdot H})^+$	1/2	2.79	1.06
H_2	$(\sigma 1s)^2$	$\mathbf{H : H}$	1	4.75	0.75
He_2^+	$(\sigma 1s)^2\ (\sigma^* 1s)^1$	$(\dot{\mathbf{He}} \bullet \dot{\mathbf{He}})^+$	1/2	2.60	1.08
He_2	$(\sigma 1s)^2\ (\sigma^* 1s)^2$	$\ddot{\mathbf{He}}\ \ddot{\mathbf{He}}$	0	0	∞

The bond-orders are reported in Table 3-2, together with the dissociation energies (D_e) and bond-lengths (R_e). Inspection of the valence-bond structures shows that the number of bonding electrons in each of them reflects the trends found for the molecular properties.

3-10 Inclusion of Overlap Integrals in Normalization Constants for Molecular Orbitals; Non-Bonded Repulsions

In Section 3-5, we have indicated that inclusion of the atomic orbital overlap integral S_{ab} in the normalization constants for the bonding and antibonding orbitals of Eqn. (37)

$$\psi_{ab} = (a+b)/(2+2S_{ab})^{\frac{1}{2}},\ \psi^*_{ab} = (a-b)/(2-2S_{ab})^{\frac{1}{2}} \tag{37}$$

leads to a greater destabilization for ψ^*_{ab} than stabilization for ψ_{ab}. The energies for these molecular orbitals are given by Eqs. (1) and (2), in which the coulomb and resonance integrals H_{aa} and H_{ab} are defined in Section 3-2 with $H_{ab} < 0$ when $S_{ab} > 0$.

When electrostatic interactions between the electrons are neglected, the total electronic energies for the Pauling "3-electron bond" and the "no-bond" configurations $(\psi_{ab})^2(\psi^*_{ab})^1$ and $(\psi_{ab})^2(\psi^*_{ab})^2$ are given by Eqs. (38) and (39).

$$2\varepsilon_+ + \varepsilon_- = \{(3 - S_{ab})H_{aa} + (1 - 3S_{ab})H_{ab}\}/(1 - S_{ab}^2) \tag{38}$$

$$2\varepsilon_+ + 2\varepsilon_- = 4(H_{aa} - S_{ab}H_{ab})/(1 - S_{ab}^2) \tag{39}$$

From them it may be deduced that, relative to the energies of 3α and 4α when $S_{ab} = 0$ at the same internuclear separation, $(\psi_{ab})^2(\psi^*_{ab})^1$ is antibonding[11-13, iii] if $S_{ab} > 1/3$ and $(\psi_{ab})^2(\psi^*_{ab})^2$ is antibonding if $S_{ab} > 0$. The latter result also pertains when electrostatic interactions between the electrons are explicitly included in the energy calculation – at least for He_2 and Ne_2·

The net antibonding character of $(\psi_{ab})^2(\psi^*_{ab})^2 \equiv (a)^2(b)^2/(1 - S^2_{ab})$ implies that destabilizing interactions exist when two lone-pair orbitals overlap. Thus, when two helium atoms in their ground-states approach each other, a repulsive potential is established at moderate internuclear separations[15]. The *trans* geometry of N_2H_4 and the non-planarity of H_2O_2 in their ground-states may also be associated with non-bonded repulsions between the lone-pair electrons; for a pair of non-bonding orbitals on different atomic centres, these geometries reduce the magnitude of the overlap integral S_{ab}, thereby decreasing the magnitude of the net antibonding destabilization.

Consideration of the electronic structure and geometry of the first excited (triplet-spin) state of ethylene provides an illustration of non-bonded repulsions between singly-occupied overlapping orbitals. Ethylene has two π-electrons that occupy a bonding molecular orbital in the lowest-energy configuration. If one of these electrons is excited into the antibonding π* orbital, then $(\pi_{CC})^1(\pi^*_{CC})^1$ configurations are obtained with parallel and antiparallel spins for the two electrons.

[iii] Because the Pauling "3-electron bond" structure $\dot{\mathbf{A}} \cdot \dot{\mathbf{B}}$ is equivalent to $\ddot{\mathbf{A}}\ \dot{\mathbf{B}}\cdot \leftrightarrow \cdot\dot{\mathbf{A}}\ \ddot{\mathbf{B}}$, $\dot{\mathbf{A}} \cdot \dot{\mathbf{B}}$ is stabilized relative to either of the component structures when the same internuclear separation and atomic orbital overlap are appropriate for each of the three structures. Using the molecular orbitals of Eqn. (37) to construct the $(\psi_{ab})^2(\psi_{ab})^1$ configuration for $\dot{\mathbf{A}} \cdot \dot{\mathbf{B}}$, it may be deduced[16] that the resonance stabilization energy $(\boldsymbol{E}(\dot{\mathbf{A}} \cdot \dot{\mathbf{B}}) - \boldsymbol{E}(\ddot{\mathbf{A}}\ \dot{\mathbf{B}}))$ is given by $(H_{ab} - S_{ab}H_{aa})/(1 + S_{ab})$. This energy is formally identical with the constructive interference energy for H_2^+ (Section 3-2).

Hund's rule of maximum spin multiplicity requires that the parallel $S = 1$ spin state has lower energy. The resulting spatial wave-function is given by Eqn. (40),

$$\{\pi_{CC}(1)\pi^*_{cc}(2) - \pi^*_{cc}(1)\pi_{CC}(2)\} / 2^{\frac{1}{2}} \tag{40}$$

$$\equiv -\{a(1)b(2) - b(1)a(2)\} / \{2(1 - S^2_{ab})\}^{\frac{1}{2}} \tag{41}$$

which is equivalent to Eqn. (41) (with a and b = carbon 2pπ atomic orbitals). This $(\pi_{CC})^1(\pi^*_{cc})^1$ configuration is net antibonding. Overlap repulsive interactions between the singly-occupied a and b orbitals of Eqn. (41) are reduced if these orbitals are rotated relative to each other around the C-C bond-axis. A non-planar $S = 1$ spin excited state is thus obtained.

Examples of Pauling "3-electron bond" destabilizations are described in Refs. 11-13, 17 and 18. One of them is concerned with the structures of $CH_{3-x}X_x$ radicals, with $X = NH_2$, OH or F. The ground-state of the CH_3 radical is nearly planar. On replacement of the H-atoms with the **X**-substituents, increasing pyramidalization is either predicted or observed to occur. The development of a Pauling "3-electron bond" $\dot{C} \stackrel{\bullet}{-} \dot{X}$ involves two competitive overlap effects, namely a tendency for stabilization of planar $CH_2 - X$ when the overlap is small, and a tendency for stabilization of non-planar $CH_2 - X$ when the overlap is large. The magnitude of the overlap integral becomes important in order to ascertain which of these predominates.

3-11 Bond-Orders

When overlap integrals are omitted from normalization constants for and orthogonality relationships between molecular orbitals, then the bonding and antibonding molecular orbitals of Eqn. (42)

$$\psi_{ab} = (a + kb) / (1 + k^2)^{\frac{1}{2}}, \; \psi^*_{ab} = (ka - b) / (1 + k^2)^{\frac{1}{2}} \tag{42}$$

$$P_{aa} = \sum_i n_i c^2_{ia}, \quad P_{bb} = \sum_i n_i c^2_{ib}, \quad P_{ab} = \sum_i n_i c_{ia} c_{ib} \tag{43}$$

are normalized and orthogonal. (The atomic orbitals a and b are assumed to be normalized.) For each of the $(\psi_{ab})^1$, $(\psi_{ab})^2$, $(\psi_{ab})^2(\psi^*_{ab})^1$ and $(\psi_{ab})^2(\psi^*_{ab})^2$ configurations, the atomic orbital charges P_{aa} and P_{bb}, and the A-B bond-order P_{ab} are then easily calculated from Eqs. (42) and (43), in which c_{ia} and c_{ib} are the atomic orbital coefficients and n_i is the occupation number for the i^{th} molecular orbital[19]. The resulting charges and bond-orders are reported in Table 3-3.

Table 3-3: Atomic orbital charges and bond orders for $\mathbf{A}\cdot\mathbf{B}$, $\mathbf{A}\text{—}\mathbf{B}$, $\dot{\mathbf{A}}\cdot\dot{\mathbf{B}}$ and $\ddot{\mathbf{A}}\ \ddot{\mathbf{B}}$.

	P_{aa}	$P_{\rm bb}$	$P_{\rm ab}$
$(\psi_{\rm ab})^1$	$1/(1+k^2)$	$k^2/(1+k^2)$	$k/(1+k^2)$
$(\psi_{\rm ab})^2$	$2/(1+k^2)$	$2k^2/(1+k^2)$	$2k/(1+k^2)$
$(\psi_{\rm ab})^2(\psi^*_{\rm ab})^1$	$1+1/(1+k^2)$	$1+k^2/(1+k^2)$	$k/(1+k^2)$
$(\psi_{\rm ab})^2(\psi^*_{\rm ab})^2$	2	2	0

For the Pauling "3-electron bond" $\left(\dot{\mathbf{A}}\cdot\dot{\mathbf{B}} \equiv \ddot{\mathbf{A}}\ \dot{\mathbf{B}} \longleftrightarrow \dot{\mathbf{A}}\ \ddot{\mathbf{B}}\right)$, we may write $(\psi_{\rm ab})^2(\psi^*_{\rm ab})^1 \equiv ({\rm a})^1(\psi_{\rm ab})^1({\rm b})^1 \equiv \{({\rm a})^2({\rm b})^1 + k({\rm a})^1({\rm b})^2\}/(1+k^2)^{\frac{1}{2}}$, from which it may be deduced that the weights for the component structures $\ddot{\mathbf{A}}\ \dot{\mathbf{B}}$ and $\dot{\mathbf{A}}\ \ddot{\mathbf{B}}$ are $1/(1+k^2)$ and $k^2/(1+k^2)$. These weights correspond[20] to the odd-electron charges for the b and a atomic orbitals of $\dot{\mathbf{A}}\cdot\dot{\mathbf{B}}$, which arise from single occupancy of the antibonding $\psi^*_{\rm ab}$ orbital in $(\psi_{\rm ab})^2(\psi^*_{\rm ab})^1$. This result will be required in Section 14-3.

More elaborate definitions of atomic orbital charges, bond-orders and valence-bond structural weights are needed when atomic orbital overlap integrals are included in normalization constants and orthogonality relationships. These are not required for the considerations of this book.

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Addendum Chapter 3

1) As is discussed in Ref. 21 for example, valence-bond structures of the types $\mathbf{A}\bullet\overset{\bullet}{}\bullet\mathbf{B}$ and $\mathbf{A}\overset{\bullet}{\text{—}}\mathbf{B}$ for two bonding electrons + one antibonding electron, are frequently used to represent a Pauling "3-electron bond". In each of these structures, the top dot is the antibonding electron. The basic theory is that for a diatomic system, with overlapping a and b atomic orbitals, two bonding electrons + one antibonding electron is proportional to two electrons with parallel spins occupying the a and b atomic orbital, + one AB bonding electron with opposed spin, regardless with how the wavefunction for the two bonding electrons is constructed, i.e the valence bond identity $\dot{\mathbf{A}}\cdot\dot{\mathbf{B}} \equiv \ddot{\mathbf{A}}\quad\dot{\mathbf{B}} \longleftrightarrow \dot{\mathbf{A}}\quad\ddot{\mathbf{B}}$ pertains.

   Although the Green-Linnett valence bond symbolisms are rarely used, each of the VB structures, $\overset{\bullet}{\mathbf{A}}\ \bullet\ \overset{\bullet}{\mathbf{B}}$, $\overset{\times}{\mathbf{A}}\ \circ\ \overset{\times}{\mathbf{B}}$ and $\overset{\circ}{\mathbf{A}}\ \times\ \overset{\circ}{\mathbf{B}}$ shows more clearly than do $\mathbf{A}\bullet\bullet\bullet\mathbf{B}$, $\mathbf{A}\bullet\overset{\bullet}{}\bullet\mathbf{B}$ and $\mathbf{A}\overset{\bullet}{\text{—}}\mathbf{B}$ that the Pauling 3-electron bond involves two "non-bonding" electrons with parallel spins (which are net antibonding when the atomic orbital overlap integral S_{ab} is included), and one bonding electron whose spin is opposed to that of the non-bonding electrons. The antibonding electron is available for external bonding to either another atom or another three-electron bond structure.

2) When the Heitler-London wavefunction a(1)b(2) + b(1)a(2) is used as the wavefunction for the **A-B** electron-pair bond, and an electron is added to the antibonding molecular orbital $\varphi^*_{ab} = a - kb$, the Pauling "3-electron bond" identity,

$\{a(1)b(2) + b(1)a(2)\}(\varphi^*_{ab})^1 = (\psi_{ab})^1(a)^1(b)^1 = (a + kb)^1(a)^1(b)^1 = (a)^2(b)^1 + k(a)^1(b)^2$

is obtained, which is analogous to that of Eqn (18). The Slater-determinantal derivation of this result goes as follows.

$$|a^\alpha b^\beta \varphi^*_{ab}{}^\alpha| + |b^\alpha a^\beta \varphi^*_{ab}{}^\alpha| = -k|a^\alpha b^\beta b^\alpha| + |b^\alpha a^\beta a^\alpha| = |(a + kb)^\beta a^\alpha b^\alpha| = |\psi_{ab}{}^\beta a^\alpha b^\alpha|$$

A similar type of identity is obtained when the a and b atomic orbitals are replaced by the Coulson-Fischer[22] type molecular orbitals a + k_1b and b + k_2a, in which k_1 and k_2 are polarity parameters.

3) The Pauling "3-electron bond" valence bond structure $(\bullet\mathrm{H} \bullet \mathrm{H}\bullet)^{(-)}$ is also appropriate for the ground-state of H_2^-. In Refs. 24 and 25, the non-Pauling "3-electron bond" formulation of the wavefunction for the electronic structure of H_2^- of Ref. 23 was shown to be fallacious.

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Chapter 4 Valence-Bond Structures for some Diatomic and related Molecules

4-1 Molecular Orbital Configurations for Homonuclear Diatomic Molecules

In this chapter, we shall generate valence-bond structures for some diatomic molecules and ions that involve atoms of first-row and second-row elements. To do this, initially we shall use their molecular orbital configurations together with the prototype valence-bond structures of Table 3-2. Green and Linnett[1] adopted this approach to the construction of valence-bond structures, and they have described many of the valence-bond structures that we shall consider here. We shall restrict our attention to the molecular orbitals that are constructed from the valence-shell 2s and 2p or 3s and 3p atomic orbitals, and for simplicity in the molecular orbital notation, neglect any hybridization that may occur between s and pσ (≡ p_z) atomic orbitals.

In Figs. 4-1 and 4-2, we display schematic contours for the molecular orbitals that can be constructed from 2p atomic orbitals, and the n = 2 molecular orbital energy levels for homonuclear diatomic molecules. To construct the ground-state molecular orbital configuration, we feed the electrons into the lowest-energy molecular orbitals and restrict the maximum orbital occupancy to two electrons. If only two electrons are to be allocated to a pair of degenerate molecular orbitals (for example, the antibonding π_x^* and π_y^* molecular orbitals of O_2), then the lowest-energy arrangement for these electrons occurs when each orbital is singly occupied with parallel spins for the two electrons. In Table 4-1, we have listed the valence-shell molecular orbital configurations for the ground states of a number of homonuclear diatomic systems that are formed from atoms of first-row elements, the molecular orbital bond-order (Section 3-9), and the resulting valence-bond structure. Here, as discussed in Section 3-3, we shall use **A─A** as the valence-

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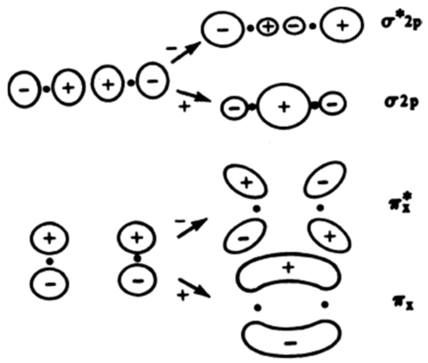

Figure 4-1: Schematic contours for σ2p, σ*2p, π_x and π_x^* molecular orbitals.

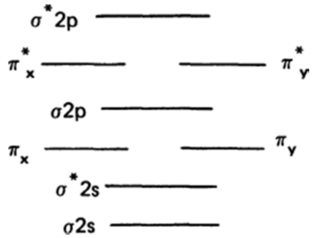

Figure 4-2: Energy levels for n = 2 homonuclear molecular orbitals.

bond structure for a doubly-occupied bonding molecular orbital (cf. Eqn. 3-5), which is equivalent to the covalent-ionic resonance formulation **A•—•A** ↔ $^{(-)}$**A: A**$^{(+)}$ ↔ $^{(+)}$**A :A**$^{(-)}$.

Table 4-1: Molecular orbital configurations and valence-bond structures for diatomic molecule ground-states, and an O_2 excited state (O_2^*). (For O_2^*, O_2^+ and O_2^-, degenerate configurations are not reported here, see also Figure 4-3).

	σ2s	σ*2s	π_x	π_y	σ2p	π_x^*	π_y^*	σ*2p	n	
Li_2	2								1	**Li—Li**
Be_2	2	2							0	**:Be Be:**
B_2	2	2	1	1					1	**:B** $^{x}_{x}$ **B:**
C_2	2	2	2	2					2	**:C = C:**
N_2	2	2	2	2	2				3	**:N ≡ N:**
O_2	2	2	2	2	2	1	1		2	x o x **:O — O:** x o x
O_2^*	2	2	2	2	2	2			2	**:Ö = Ö:**
O_2^{2-}, F_2	2	2	2	2	2	2	2		1	(−) (−) **:Ö—Ö:, :F—F:**
O_2^+	2	2	2	2	2	1			2.5	(+½) (+½) x o x **: O = O :**
O_2^-	2	2	2	2	2	2	1		1.5	(−½) (−½) **: Ö — Ö :** x o x

4-2 Li_2, Be_2, N_2, F_2 and O_2^{2-}

For Li_2 and Be_2, the molecular orbital configurations of Table 4-1 generate the valence-bond structures **Li — Li** and **:Be Be:**, with one bond and no bonds, respectively. In contrast to what is the case for Li_2, the diatomic molecule Be_2 does not exist as a stable species. For N_2 and F_2, we obtain the Lewis octet structures (namely **:N ≡ N:** and $:\ddot{\underset{..}{F}}—\ddot{\underset{..}{F}}:$) from the molecular orbital configurations, (with . These structures have triple and single bonds, respectively. The peroxide anion O_2^{2-} is isoelectronic with F_2, and its valence-bond structure $^{(-)}:\ddot{\underset{..}{O}}-\ddot{\underset{..}{O}}:^{(-)}$ also involves a single bond. The bond-lengths[i] for (F_2 and O_2^{2-} are 1.43 and 1.48 Å – both of which are appreciably longer than the 1.10 Å for the triple-bonded N_2. These lengths for the single-bonds of F_2 and O_2^{2-} are also much shorter than the 2.67 Å for the single-bond of Li_2. No doubt this reflects (at least partially) the different nature of the atomic orbitals that are used to form the bonds, namely (primarily) 2s for Li_2 and 2pσ for F_2 and O_2^{2-}.

4-3 O_2, O_2^+, O_2^- and O_2^{2-}

Molecular oxygen has 12 valence-shell electrons. The ground-state molecular orbital configuration involves single occupancy for the degenerate π_x^* and π_Y^* antibonding molecular orbitals, with parallel spins for the two electrons as is shown in Figure 4-3.

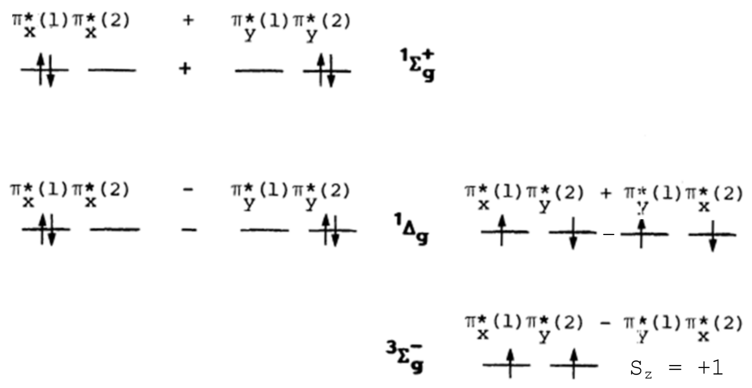

Figure 4-3: $(\pi^*)^2$ configurations.

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[i] Bond-lengths for diatomic species are taken from Ref. 2.

The resulting valence-bond structure of Table 4-1, (namely $\mathbf{:\dot{O}\div\dot{O}:}$, or $\mathbf{:\overset{x\,o\,x}{\underset{x\,o\,x}{O - O}}:}$ if the two antibonding π-electrons have $s_z = +\frac{1}{2}$ spin quantum numbers), has a double bond which consists of an electron pair σ-bond + two Pauling "3-electron π-bonds". This type of valence-bond structure shows more clearly than does the Pauling structure of Figure 2-1, (namely $\mathbf{:O \overset{\cdots}{\underset{\cdots}{-}} O:}$), that the double bond of O_2 involves only four bonding electrons.

The O-O bond-length of 1.207 Å for the O_2 ground-state is similar to the standard N-O and C-O double-bond lengths of 1.21 Å for each of **$CH_3N = O$** and **$H_2C = O$**, and intermediate between the single and triple bond-lengths of 1.43 Å and 1.10 Å for F_2 and N_2.

In Table 4-1, the valence-bond structures for O_2^+, O_2, O_2^- and O_2^{2-} have 2.5, 2, 1.5 and 1 covalent bonds respectively, which reflect the trend observed for the bond-lengths, namely 1.12, 1.21, 1.30 and 1.49 Å. The molecular orbital configuration and valence-bond structure are also reported in Table 4-1 for an O_2 excited state in which one of the antibonding π* molecular orbitals is doubly-occupied and the other is vacant. The Lewis-type valence-bond structure for this state, namely $\mathbf{:\ddot{O} = \ddot{O}:}$, involves a standard double bond, i.e., electron pair σ- and π-bonds. Its bond-length of 1.22 Å is slightly longer than that of the ground-state. The paramagnetism of the ground states for O_2, O_2^- and O_2^+, which is a consequence of the presence of unpaired spins (i.e. S = 1 or $\frac{1}{2}$), is implied by the nature of the electron spins in their valence-bond structures.

In Figure 4-3, the molecular orbital occupancies that arise from the presence of two antibonding π* electrons are displayed, together with a more complete formulation of the wave-functions for these two electrons.

4-4 CN^-, CO and NO^+

The heteronuclear species CN^-, CO and NO^+ are isoelectronic with N_2, and therefore their molecular orbital configurations and valence-bond structures should be similar to those for N_2, but with some polarity for their molecular orbitals. From the molecular orbital configurations, it is easy to generate the valence-bond structures $\mathbf{:\overset{(-)}{C} \equiv N:}$, $\mathbf{:\overset{(-)}{C} \equiv \overset{(+)}{O}:}$ and $\mathbf{:N \equiv \overset{(+)}{O}:}$ if it is assumed that bonding electrons are shared equally by each pair of atoms. The bond-lengths of 1.15, 1.10 and 1.06 Å for CN^-, N_2 and NO^+ are respectively 0.12, 0.14 and 0.15 Å shorter than estimates of 1.27, 1.24 and 1.21 Å for C=N, N=N and N=O double bonds, and it is probably reasonable to assume that the triple-bonded structures are the primary valence-bond structures for each of these three species. However for CO, the bond-length of 1.13 Å is only 0.08 Å shorter than the length of a C=O double bond, and this suggests that valence-bond structures such as $:\!C=\ddot{O}:$ and $:\!C=\underset{..}{O}:$ as well as $:\!\overset{(-)}{C}\equiv\overset{(+)}{O}:$ have appreciable weights. Presumably because they do not carry atomic formal charges, these CO double-bond structures are important, whereas such charges are present in $:\!\overset{(-)}{C}\equiv\overset{(+)}{O}:$. The electroneutrality principle requires that the formal charges of atoms in neutral molecules have small magnitudes, and the contributions to resonance from the double-bond structures will assist this requirement.

4-5 NO and SN

Each of O_2^+, NO and SN has 11 valence-shell electrons. The lowest-energy valence-shell molecular orbital configuration for NO is the same as that for O_2^+; that for SN may be written as $(\sigma s)^2(\sigma^* s)^2(\sigma p)^2(\pi_x)^2(\pi_y)^2(\pi_y^*)^1$ with the sulphur atom using its 3s and 3p orbitals to form the molecular orbitals.

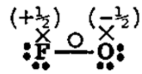
The resulting valence bond structures for NO and SN are $:\!\overset{(-\frac{1}{2})}{\dot{N}} \doteq \overset{(+\frac{1}{2})}{\dot{O}}:$ and $:\overset{(+\frac{1}{2})}{\dot{S}} \doteq \overset{(-\frac{1}{2})}{\dot{N}}:$, each of which has a Pauling "3-electron bond". The NO bond-length of 1.15 Å is intermediate between the lengths of 1.06 and 1.21 Å for the N-O triple bond of NO^+ and the double bond for $\mathbf{CH_3N=O}$, and the Pauling "3-electron bond" structure for NO is in accord with this observation; there are five bonding electrons in $:\!\overset{(-\frac{1}{2})}{\dot{N}} \doteq \overset{(+\frac{1}{2})}{\dot{O}}:$. The bond-length of 1.50 Å for SN is longer than the 1.44 Å for $:\!\overset{(+)}{S}\equiv N:$, thereby reflecting the presence of five instead of six bonding electrons in the valence-bond structure $:\overset{(+\frac{1}{2})}{\dot{S}} \doteq \overset{(-\frac{1}{2})}{\dot{N}}:$.

4-6 S_2, SO and NO^-

Each of S_2, SO and NO^- has 12 valence-shell electrons. As occurs with the O_2 ground-state, the degenerate antibonding π_x^* and π_y^* orbitals for these molecules are singly-occupied in the ground-state, with parallel spins for the two electrons. Therefore, the O_2, S_2, SO and NO^- valence-bond structures $\overset{\mathrm{x\ o\ x}}{\underset{\mathrm{x\ o\ x}}{:\!O—O:}}$, $\overset{\mathrm{x\ o\ x}}{\underset{\mathrm{x\ o\ x}}{:\!S—S:}}$, $\overset{\mathrm{x\ o\ x}}{\underset{\mathrm{x\ o\ x}}{:\!S—S:}}$ and $\overset{(-)\mathrm{x\ o\ x}}{\underset{\mathrm{x\ o\ x}}{:\!N—O:}}$ are similar, each having two Pauling "3-electron bonds" and a bond-order of 2. The bond-lengths for SO and S_2 are 1.48 and 1.89 Å.

For NO^-, the estimate of 1.268 Å for its bond-length is longer than the 1.21 Å for the N-O double-bond of $\mathbf{CH_3N=O}$; the reason for this appreciable bond-length difference is not apparent.

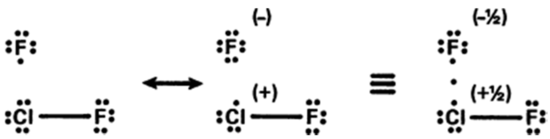
4-7 ClO and FO

The molecular orbital configuration for the 13 valence-shell electrons of the ClO ground-state is $(\sigma s)^2(\sigma^* s)^2(\sigma p)^2(\pi_x)^2(\pi_y)^2(\pi^*_x)^2(\pi^*_y)^1$, from which the valence-bond structure $\overset{(+\frac{1}{2})}{\underset{\cdot\cdot}{\overset{\mathrm{x}}{:\mathbf{Cl}}}} \overset{\mathrm{o}}{—} \overset{(-\frac{1}{2})}{\underset{\cdot\cdot}{\overset{\mathrm{x}}{\mathbf{O}:}}}$ may be generated with three bonding electrons. The ClO bond-length of 1.55 Å is appreciably shorter than the Cl-O single-bond length of 1.70 Å for Cl_2O, thereby reflecting the significant development of a Pauling "3-electron bond" for one set of π-electrons for ClO. Dimers of ClO are known (Section 11-7), one of which involves an O-O bond with a length[3] of 1.426 Å. For FO, the valence-bond structure  may be similarly generated from its molecular orbital configuration. However, in contrast to what occurs for Cl_2O_2, the dimer F_2O_2 has a strong O-O bond whose length of 1.217 Å is almost identical with that of the double bond for O_2 (Section 2-3(b)). Presumably, the very electronegative fluorine atom is not able to stabilize the Pauling "3-electron bond" of FO, and the valence-bond structure $:\ddot{\underset{\cdot\cdot}{F}}—\dot{\underset{\cdot\cdot}{O}}:$ with the odd-electron located in an oxygen atomic orbital provides a better representation of the electronic structure. This is equivalent to saying that the electronegativity of fluorine prevents it from acquiring a formal positive charge of appreciable magnitude in a neutral molecule.

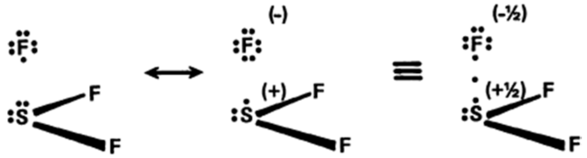
The results of calculations by Baird and Taylor[4] show that as the difference in electronegativity between **A** and **B** in the Pauling "3-electron bond" structure $\dot{\mathbf{A}} \cdot \dot{\mathbf{B}}$ increases, the stability of the bond decreases.

4-8 ClF_2 and SF_3

For the radicals ClF_2 and SF_3, valence-bond structures may be constructed by bonding a fluorine atom to the Lewis octet structures for ClF and SF_2. This leads to the development of a Cl-F and S-F Pauling "3-electron bond", viz



and



It is assumed here that a chlorine or sulphur 3pπ orbital is used for the σ-bonding in the Pauling "3-electron bond" to form 90° bond angles. Distortion of these angles away from 90° leads to sp^n hybridization for these orbitals. Molecular orbital[5] and experimental[6] estimates of the ClF_2 bond-angle are 149° has been calculated[4] using molecular orbital procedures – an experimental estimate for this angle is 136 ± 15°, respectively. However, from electron spin resonance measurements, Morton, Preston and Strach[7] have concluded that SF_3 is a planar σ-radical with two equivalent fluorine atoms. The resulting valence-bond structure is then the planar version of that displayed above. More recently, Kiang and Zare[8] have described Pauling "3-electron bond" theory for SF_3 and SF_5, and assumed that SF_3 is non-planar.

4-9 N-H Bond-Strengths of NH_3, N_2H_4, N_2H_2, and $HN_2 \rightarrow H + N_2$

For a number of polyatomic systems with diatomic Pauling "3-electron bonds", Baird has described some applications of Pauling "3-electron bond" theory[9,10]. We shall describe two of them here.

For the reactions $NH_3 \rightarrow NH_2^{\bullet} + H^{\bullet}$, $N_2H_4 \rightarrow N_2H_3^{\bullet} + H^{\bullet}$, and $N_2H_2 \rightarrow N_2H^{\bullet} + H^{\bullet}$, the (calculated) N-H bond dissociation energies[8] (D_e) are 435, 343 and 255 kJ mol^{-1}. The dissociation of NH_3 leaves the odd-electron of NH_2 located in a nitrogen atomic orbital. However, for each of $N_2H_3^{\bullet}$ and $N_2H^{\bullet}$, the odd-electron may be delocalized between two nitrogen atomic orbitals, thereby leading to the development of N-N Pauling "3-electron bonds" as follows:

$$\mathrm{H_2\ddot{N}-\dot{\underset{\cdot\cdot}{N}}H} \longleftrightarrow \mathrm{H_2\overset{(+)}{\dot{N}}-\overset{(-)}{\ddot{\underset{\cdot\cdot}{N}}}H} \equiv \mathrm{H_2\overset{(+\frac{1}{2})}{\dot{N}}\cdot\!\!-\overset{(-\frac{1}{2})}{\dot{\underset{\cdot\cdot}{N}}}H} \qquad \mathrm{H\ddot{N}=\dot{N}\!:} \longleftrightarrow \mathrm{H\overset{(+)}{\dot{N}}=\overset{(-)}{\ddot{N}}\!:} \equiv \mathrm{H\overset{(+\frac{1}{2})}{\dot{N}}\doteq\overset{(-\frac{1}{2})}{\dot{N}}\!:}$$

The $N_2H_3^{\bullet}$ and $N_2H^{\bullet}$ radicals are thereby stabilized relative to $\mathrm{H_2\ddot{N}-\dot{\underset{\cdot\cdot}{N}}H}$ and $\mathrm{H\ddot{N}=\dot{N}\!:}$ as dissociation products, with the odd electron located in only one nitrogen atomic orbital. Consequently, the N-H dissociation energies for N_2H_4 and N_2H_2 are smaller than for NH_3.

If the electronic structure for the ground-state of HN_2 is represented as $\overset{(+\frac{1}{2})}{\mathbf{H\dot{N}}} \doteq \overset{(-\frac{1}{2})}{\mathbf{\dot{N}:}}$, then the breaking of the N-H bond would generate an excited state of N_2, i.e. $\overset{(+\frac{1}{2})}{\mathbf{H\dot{N}}} \doteq \overset{(-\frac{1}{2})}{\mathbf{\dot{N}:}} \rightarrow \mathbf{H}^{\bullet} + \overset{(+\frac{1}{2})}{\mathbf{\cdot\dot{N}}} \doteq \overset{(-\frac{1}{2})}{\mathbf{\dot{N}:}}$.

To obtain the N_2 ground-state ($\mathbf{:N \equiv N:}$) as a dissociation product, it is necessary to consider another configuration for $N_2H^{\bullet}$, namely that obtained when the anti-bonding N-N π-electron of $\overset{(+\frac{1}{2})}{\mathbf{H\dot{N}}} \doteq \overset{(-\frac{1}{2})}{\mathbf{\dot{N}:}}$ is transferred into the antibonding N-H σ^*-orbital which is vacant in this structure. The molecular orbital configuration for the relevant electrons of $\overset{(+\frac{1}{2})}{\mathbf{H\dot{N}}} \doteq \overset{(-\frac{1}{2})}{\mathbf{\dot{N}:}}$ is $\Psi_1 = (\sigma_{NH})^2(\pi_{NN})^2(\pi^*_{NN})^1$. When the π^*_{NN} electron is transferred into the σ^*_{NH} molecular orbital, the configuration $\Psi_2 = (\sigma_{NH})^2(\sigma^*_{NH})^1(\pi_{NN})^2$ is obtained. The latter configuration generates the valence-bond structure $\overset{(-\frac{1}{2})}{\mathbf{\dot{H}}} \bullet \overset{(+\frac{1}{2})}{\mathbf{\dot{N}}} \equiv \mathbf{N:}$ with an N-H Pauling "3-electron bond". This structure can dissociate to generate $\mathbf{H}^{\bullet} + \mathbf{:N \equiv N:}$.

To describe the course of the reaction as the N-H bond is stretched, it is necessary to invoke configuration interaction (Section 3-3), i.e. to construct the linear combination $\Psi = C_1\Psi_1 + C_2\Psi_2$. When the r(N-H) bond length is close to the equilibrium bond-length, $|C_1| >> |C_2|$. As the N-H bond is stretched, the N-H overlap integral is reduced in magnitude, and therefore the vacant σ^*_{NH} orbital of Ψ_1 becomes less antibonding. This enables the energy separation between Ψ_1 and Ψ_2 to become smaller, thereby reducing the magnitude of C_1 / C_2. For large r(N-H) distance, $|C_2| >> |C_1|$, i.e. Ψ_2 is the predominant configuration, which leads to the formation of $\mathbf{H}^{\bullet} + \mathbf{:N \equiv N:}$ as dissociation products when $r(\mathrm{N-H}) = \infty$. The reaction is calculated to be exothermic, but because energy is required to stretch the N-H bond of configuration Ψ_1, a kinetic stability is associated with $N_2H^{\bullet}$.

Baird[9] has also provided similar types of descriptions of the dissociations $\mathbf{RCO} \rightarrow \mathbf{R}^{\bullet} + \overset{(-)}{\mathbf{:C}} \equiv \overset{(+)}{\mathbf{O:}}$ and $\mathbf{CH_2CO \rightarrow CH_2(\mathit{S} = 1) + \overset{(-)}{:C} \equiv \overset{(+)}{O:}}$.

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Addendum Chapter 4

1. Charge-shift Bonding

Covalent-ionic resonance (**A•—•A** ↔ $^{(-)}$**A: A**$^{(+)}$ ↔ $^{(+)}$**A :A**$^{(-)}$) pertains for the electron-pair single bonds of H_2 and F_2. For H_2, but not[11] for F_2, the covalent structure alone is stable relative to the separated atoms (cf. Table 3-1 for H_2). Charge-shift bonding[11] via covalent-ionic resonance is needed to bind F_2 relative to the dissociation products F + F.

2. Quadruple Bonding

Quadruple bonding have been calculated to occur in C_2[12,13] and analogous eight-valence electron species CN^+, BN and CB^- [13]. In Ref.[14], it is deduced that an ($S = 1$ spin) triple bonding might occur in B_2, in preference to the single bond that is associated with the molecular orbital configuration in Table 4 1. To help describe a quadruple bond for C_2, it is noted that for the eight valence-shell electrons, we may write:

$$\{(\sigma 2s)^2 - (\sigma{*}2s)^2\}\{(\sigma 2p)^2 - (\sigma{*}2p)^2\}\{(\pi_x)^2 - (\pi_x^*)^2\}\{(\pi_y)^2 - (\pi_y^*)^2\} \qquad (1)$$

$$\propto$$

$$\{2s_a.2s_b + 2s_b.2s_a\}\{\sigma_{za}.\sigma_{zb} + \sigma_{zb}.\sigma_{za}\}\{\pi_{xa}.\pi_{xb} + \pi_{xb}.\pi_{xa}\}\{\pi_{ya}.\pi_{yb} + \pi_{yb}.\pi_{ya}\} \qquad (2)$$

Each of these equations gives a (non-variational) linear combination of 16 Slater determinants. Only one of the 16 MO configurations involves four doubly-occupied bonding MOs. There is also one MO configuration in which the four antibonding MOs are doubly-occupied.

To allow for 2s-2pσ mixing, with the $2p_z$ AOs oriented so that the AO overlap integral $\langle\sigma_{za}|\sigma_{zb}\rangle$ is greater than zero, the 2s and σ_z AOs are replaced by the hybrid AOs of Eqn. (3),

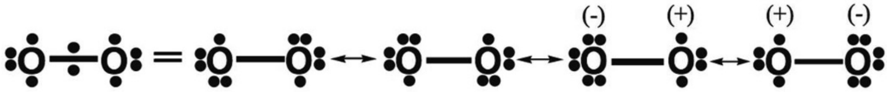
$$h_{3a} = 2s_a - \lambda\sigma_{za},\ h_{4b} = 2s_b + \lambda\sigma_{zb},\ h_{5a} = \sigma_{za} + \mu 2s_a,\ h_{6b} = -\sigma_{zb} + \mu 2s_b \tag{3}$$

for which the hybridization parameters λ and μ can be determined variationally.

To determine the strength of each valence shell electron-pair bond with a Heitler-London wavefunction, the energy of a(1)b(2) is compared with that of a(1)b(2) + b(1)a(2), to give a spin-coupling or constructive interference energy. For the eight valence shell electrons, a calculation with one a(1)b(2) configuration and three a(1)b(2) + b(1)a(2) configurations involves eight instead of 16 Slater determinants.

If each of the eight valence shell atomic orbitals in Equation (3) is replaced by a 2-centre Coulson-Fischer type orbital, for example the a and b atomic orbitals are replaced by a + *k*b and b + *k*a, ionic configurations of the type a(1)a(2) + b(1)b(2) can be introduced. The equivalent treatment in the molecular orbital formulation involves replacing each of the $\psi(1)\psi(2) - \psi^*(1)\psi^*(2)$ with $\psi(1)\psi(2) - \kappa\psi^*(1)\psi^*(2)$. For these two equivalent formulations, the parameters k and κ, with $2k/(1 + k^2) = (1 + \kappa)/(1 - \kappa)$, can be determined variationally.

3. One-electron and two-electron transfers



1 **2** **3** **4** **5**

Neglecting electron spins, the valence bond structure **1** for the O_2 ground-state, with two Pauling "3-electron bonds" is equivalent to resonance between the Lewis structures **2-5**[15]. One-electron transfers convert structures **2** and **4** into structures **3** and **5**, respectively, whereas **2** → **3** and **4** → **5** involve two-electron transfers[15]. The transition probabilities for the one-electron and two-electron transfers are dependent on $\langle a|b\rangle$ and $(\langle a|b\rangle)^2$ (or $\langle c|d\rangle$ and $(\langle c|d\rangle)^2$) respectively, in which a and b are $2p_x$ atomic orbitals c and d are $2p_y$ atomic orbitals. Examples of phenomena whose origins may be rationalized in terms of either one-electron or two-electron transfer processes include: (i) the mode of protonation[15] of symmetric anions such as HCO_2^- and NO_2^-, which occurs preferentially at one oxygen atom, to give asymmetric geometries for HCOOH and HONO; (ii) the asymmetry of xanthate and dithiocarbamate ligands in various complexes[16,17]; (iii) energy transfer between donor and acceptor chromophores[18]. The stability of the genetic code under normal conditions has been associated[14,] with the extent of electronic reorganization that is needed to interconvert important valence bond structures for different isomers of the DNA bases.

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Chapter 5 Pauling "3-Electron Bonds" and Hypoligated Transition Metal Complexes

Although it is not well-recognized, transition metal complexes exist for which Pauling "3-electron bond" theory is relevant. To illustrate this theory, consideration will be given to descriptions of the electronic structures for a number of octahedral complexes.

5-1 Hypoligated and Hyperligated Transition Metal Complexes

The low-energy valence-shell atomic orbitals for the transition metals are the five (inner) (n-1) d orbitals and the ns and three np atomic orbitals. (For atoms of first-row transition metals Sc,...,Cu, these are the $3d_{x^2-y^2}$, $3d_{z^2}$, $3d_{xy}$, $3d_{xz}$, $3d_{yz}$, 4s, $4p_x$, $4p_y$ and $4p_z$ orbitals; contours for 3d orbitals are displayed in Figure 1-1.) Pauling[1] has classified transition metal complexes of the general type ML_N (M = transition-metal ion, L = ligand, N = number of ligands) as either *hyperligated* or *hypoligated* according to whether there are sufficient valence-shell orbitals on the metal ion to form N electron-pair M-L σ-bonds. Thus the isoelectronic ions Co^{3+} and Fe^{2+} of $[Co(NH_3)_6]^{3+}$, $[CoF_6]^{3-}$ and $[Fe(H_2O)_6]^{2+}$ have $(3d)^6$ valence-shell configurations. However, magnetic susceptibility measurements for the three complexes indicate that the distributions of the six electrons amongst the 3d orbitals of the metal ions must differ. To account for the observed magnetic moment of zero[1] for $[Co(NH_3)_6]^{3+}$, it is necessary to assume that the three t_{2g} orbitals (d_{xy}, d_{xz} and d_{yz}) of Co^{3+} are doubly-occupied (Figure 5-1 (a)), thereby generating a low-spin (S = 0 spin) complex. The vacant e_g orbitals ($d_{x^2-y^2}$ and

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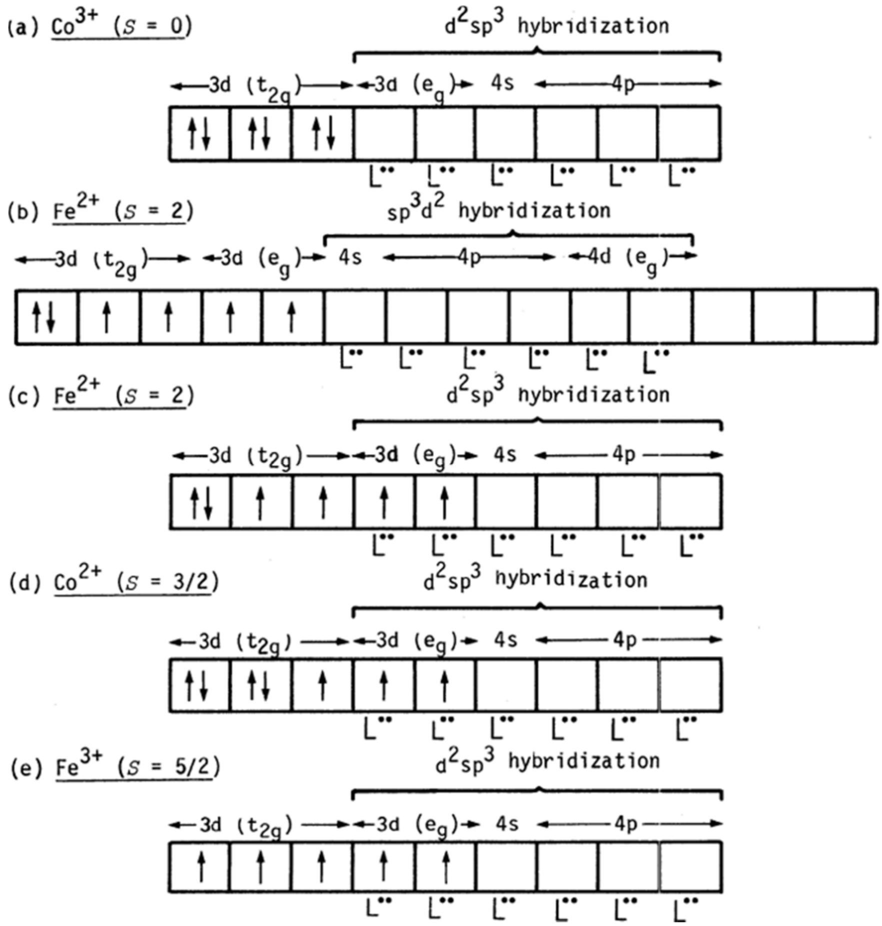
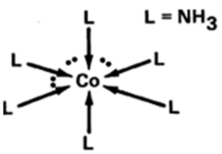
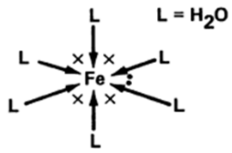


Figure 5-1: Orbital occupancies for some transition-metal ions (L = ligand).

d_{z^2}) and the 4s and 4p orbitals may be hybridized to form six octahedral (d^2sp^3) hybrid orbitals. These orbitals are available for coordination with the six NH_3 ligands, so that six Co-N electron-pair σ-bonds can be formed, as is shown in valence-bond structure (**1**).



(1)



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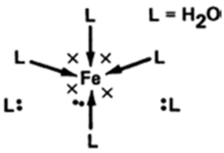


(3)

Because low-spin Co^{3+} has sufficient valence-shell orbitals to form six electron-pair Co-N bonds, $[Co(NH_3)_6]^{3+}$ may be classified as a *hyperligated* complex[1].

Isoelectronic $[Fe(H_2O)_6]^{2+}$ and $[CoF_6]^{3-}$ are paramagnetic complexes with magnetic moments of 5.3 Bohr magneton[1]; the "spin-only" formula for the magnetic moment $\sqrt{n(n+2)}$ generates a magnetic moment of 4.9 Bohr magneton when the number of unpaired-electron spins (n) is four. Therefore, each of these complexes is assumed to have this number of unpaired-electrons with parallel spins. The 3d-orbital occupations for the Fe^{2+} and Co^{3+} ions are then those that are displayed in Figure 5-1(b), and a high-spin (S = 2) complex is thereby generated. Because each of $[Fe(H_2O)_6]^{2+}$ and $[CoF_6]^{3-}$ has insufficient valence-shell orbitals to form six electron-pair bonds between the Fe^{2+} and Co^{3+} and the ligands, these complexes are classified as *hypoligated* complexes[1].

For hypoligated complexes, either of the following valence-bond procedures is sometimes used to describe the metal-ligand σ-bonding[2]:

(i) The outer $4d_{x^2-y^2}$ and $4d_{z^2}$ orbitals are hybridized with the 4s and 4p orbitals to form six octahedral (sp^3d^2) hybrid orbitals, as in Figure 5-1 (b). These hybrid orbitals may be used for coordination with the six ligands to form six electron-pair M-L σ-bonds as in valence-bond structures (**1**) and (**2**). This approach may be criticized, because the 4d orbitals lie too high in energy for them to be utilized in bonding to any significant extent.

(b) The vacant 4s and 4p orbitals, when suitably hybridized (i.e. as sp_x, p_y, and p_z, sp_y, p_z and p_x, and sp_z, p_x and p_y), may be used to form four electron-pair M-L bonds as in valence-bond structure (**3**). It is then necessary to invoke resonance between a set of 15 valence-bond structures of type (**3**), which differ in the locations of the four M-L σ-bonds.

In contrast to what pertains for the above valence-bond descriptions of $[Co(NH_3)_6]^{3+}$, the simplest molecular orbital descriptions for $[CoF_6]^{3-}$ and $[Fe(H_2O)_6]^{2+}$ use the same set of metal-ion orbitals for bonding, namely the *inner* $3d_{x^2-y^2}$ and $3d_{z^2}$ orbitals as well as the 4s and 4p orbitals. For $[Co(NH_3)_6]^{3+}$ the three non-bonding t_{2g} orbitals are doubly occupied, and all molecular orbitals that are M-L antibonding are vacant. In contrast, two antibonding M-L molecular orbitals and two t_{2g} orbitals are singly-occupied for the $[CoF_6]^{3-}$ complex[3]. The atomic orbitals for these molecular orbital schemes have also been used in the above valence-bond description for $[Co(NH_3)_6]^{3+}$; they may also be used to provide a valence-bond description for $[CoF_6]^{3-}$ or $[Fe(H_2O)_6]^{2+}$ if we avail ourselves of Pauling "3-electron bonds[4]".

5-2 Pauling “3-Electron Bonds” and the Electronic Structure of $[Fe(H_2O)_6]^{2+}$

For the purpose of bonding to the NH_3 ligands of $[Co(NH_3)_6]^{3+}$, the Co^{3+} is assumed to form six d^2sp^3 hybrid orbitals from the $3d_{x^2-y^2}$, $3d_{z^2}$, 4s and three 4p orbitals. For $[Fe(H_2O)_6]^{2+}$, we allow the Fe^{2+} to form a similar set of hybrid orbitals. However, in contrast to what is the case for the Co^{3+} in $[Co(NH_3)_6]^{3+}$, two of these Fe^{2+} orbitals are singly-occupied, and four are vacant, as is shown in Figure 5-1(c). The latter four orbitals are available to form four electron-pair σ-bonds between the Fe^{2+} and four H_2O ligands. The two singly-occupied d^2sp^3 orbitals are available to form two Pauling “3-electron bonds” when these orbitals overlap with oxygen lone-pair orbitals, as is shown in Figure 5-2(a).

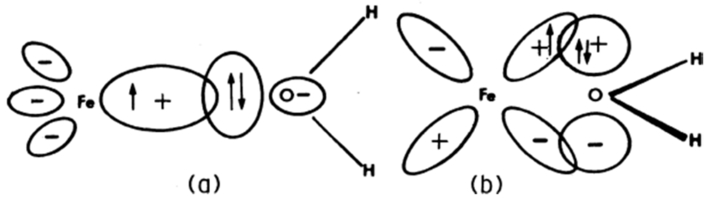


Figure 5-2: Overlap of metal-ion and ligand atomic orbitals for σ- and π-type Pauling “3-electron bonds” of $[Fe(H_2O)_6]^{2+}$ and $[Fe(H_2O)_6]^{3+}$.

Two Lewis-type valence-bond structures are possible for each of these two $FeOH_2$ linkages, namely $\mathbf{Fe\bullet\ :OH_2}$ and $\overset{(-)}{\mathbf{Fe:}}\ \overset{(+)}{\mathbf{\bullet OH_2}}$. Resonance between them generates a Pauling “3-electron bond”. Thus, we may write

$$\mathbf{Fe\cdot\ :OH_2 \leftrightarrow \overset{(-)}{Fe}:\ \cdot\overset{(+)}{O}H_2 \equiv Fe\cdots OH_2},\ \text{or}\ \overset{(-1/2)}{\bullet Fe}\ \overset{(+1/2)}{\bullet OH_2\bullet}.$$

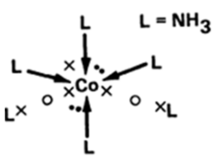
The resulting valence-bond structures for the $[Fe(H_2O)_6]^{2+}$ complex are of types (**4**) and (**5**), in which the singly-occupied orbitals have s_z spin quantum numbers of +1/2. Altogether, there are 15 valence-bond structures that differ in the locations of the $\mathbf{Fe\cdots OH_2}$ and $\mathbf{Fe \leftarrow OH_2}$ linkages, and all will contribute to the valence-bond resonance description of the complex. Similar types of valence-bond structures are also appropriate for $[CoF_6]^{3-}$.

(4) (5)

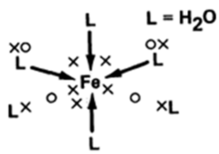
5-3 Metal-Ion Spin-State and Metal-Ligand Bond-Lengths

The nature of the spin-state of the metal ion may be reflected in the metal-ligand bond-lengths of the ML_N complex. This is well-exemplified for the hyperligated and hypoligated complexes $[Co(NH_3)_6]^{3+}$, and $[Co(NH_3)_6]^{2+}$, which have respectively low-spin $(3d)^6$ and high-spin $(3d)^7$ configurations for the Co^{3+} and Co^{2+} ions. The Co-N bond-lengths for these complexes are 1.94 Å and 2.11 Å, respectively[5, 6]. In Section 5-1, we have shown that the valence-bond description for the Co(III) complex permits the formation of six electron-pair Co-N σ-bonds, as in structure (**1**).

For the high-spin Co(II) complex, the orbital occupations for Co^{2+} displayed in Figure 5-1 (d) require that six NH_3 ligands form four Co-N single-bonds, and two Pauling "3-electron bonds" with maximum bond-orders of 0.5. The resulting valence-bond structures for $[Co(NH_3)_6]^{2+}$ are of type (**6**), and the average Co-N σ-bond order of 5/6 is in accord with the longer Co-N bonds for this complex relative to those of low-spin $[Co(NH_3)_6]^{3+}$.



(6)



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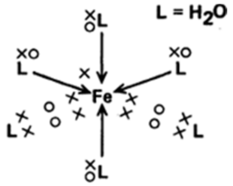


(8)

For high-spin $[Fe(H_2O)_6]^{2+}$, with valence-bond structures of types (**4**) and (**5**), the average Fe-O bond-order is also 5/6, and therefore it is not surprising that the Fe-O bond-lengths[7] of 2.12 Å are similar to the Co-N bond lengths of 2.11 Å for the high-spin $[Co(NH_3)_6]^{2+}$. In contrast, the Fe-O bond-lengths[8] of 1.99 Å for high-spin $[Fe(H_2O)_6]^{3+}$ are appreciably shorter. For this Fe(III) complex, the Fe^{3+} orbital occupations are displayed in Figure 5-1 (e) and the valence-bond structures of type (**7**) also generate Fe-O σ-bond orders of 5/6. We may account for the shorter Fe-O bonds in this complex by noting that the Fe^{3+} ion is more electronegative than the Fe^{2+} ion. The effect of this should be to induce a significant amount of delocalization of oxygen lone-pair electrons from hybrid orbitals that overlap with the singly-occupied t_{2g} orbitals of Fe^{3+}. The orbital overlap is displayed in Figure 5-2 (b). This delocalization will lead to the formation of Pauling "3-electron bond" Fe-O π-bonds, and thereby increase the Fe-O bond-orders above the value of 5/6 that pertains for the σ-bonding. In the $[Fe(H_2O)_6]^{3+}$ valence-bond structures, these π-bonds should be best developed between pairs of atoms that are linked by Pauling "3-electron bond" σ-bonds, as in valence-bond structure (**8**), in order that the oxygen atoms do not acquire formal positive charges greater than unity. Thus, to satisfy this requirement, we have indicated only two π-bonds in valence-bond structure (**8**), although on overlap considerations, three are possible. The average Fe-O bond-order for (**8**) is unity, but because part of the contribution arises from the π-bonding, it is not surprising that the Fe-O bond-lengths for $[Fe(H_2O)_6]^{3+}$ are longer than the estimate[9] of 1.92 Å for the length of an Fe-O σ-single bond. For the Co(II) and Co(III) complexes, the NH_3 ligands have no lone-pair electrons available for Co-N π-bonding.

5-4 Interconversion Between Hypoligated and Hyperligated Electronic States

The Pauling "3-electron bond" theory of hypoligation has wide applicability. All d^4-d^9 transition-metal complexes of the type ML_N will involve one or more Pauling "3-electron bonds" in their valence-bond structures, if the metal-ion has insufficient vacant inner d and valence-shell s and p orbitals available to form N electron-pair M-L σ-bonds with the N ligands.

In Table 5-1, the d^4-d^9 octahedral ML_6 complexes are classified according to the spin-states of the transition-metal ions, and the number of electron-pair bonds and Pauling "3-electron bonds". Fairly obviously, octahedral d^4-d^6 complexes that do not require Pauling "3-electron bonds" may be classified as hyperligated. Excited hypoligated states can be generated for such complexes by promoting one or more non-bonding t_{2g} electrons into antibonding σ^*_{ML} orbitals that are vacant in the hyperligated ground-states. In Section 3-6, we have deduced that two bonding electrons + one antibonding electron (i.e. $(\sigma_{\mathrm{ML}})^2(\sigma^*_{\mathrm{ML}})^1$ here) is the molecular orbital formulation of a Pauling "3-electron bond". Conversely, a $\sigma^*_{\mathrm{ML}} \rightarrow t_{2g}$ excitation will convert[4] high-spin and intermediate-spin d^5 and d^6 octahedral complexes (each of which has one Pauling "3- electron bond") into hyperligated excited states.

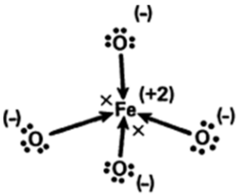
Table 5-1: Metal ion configurations and M-L σ-bond types for ML_6 complexes that can involve Pauling "3-electron bonds".

		Number of bonds	
Configuration	**Spin-state**	**electron-pair**	**"3-electron"**
d^4	high ($S = 2$)	5	1
d^5, d^6, d^7, d^8	high ($S = 5/2, 2, 3/2, 1$)	4	2
d^5, d^6	intermediate ($S = 3/2, 1$)	5	1
d^7	low ($S = 1/2$)	5	1
d^9	($S = 1/2$)	4	1

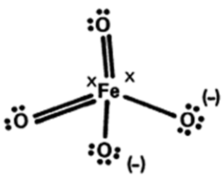
5-5 Metal-Ligand π-Bonding and Pauling "3-Electron Bonds"

A number of paramagnetic transition metal complexes must involve Pauling "3-electron bonds" for the π-electrons only. We shall consider one example here, namely the Fe(VI) tetrahedral anion FeO_4^{2-}. This anion may be considered to involve $Fe^{6+}(3d)^2$ bonded to four O^{2-} ligands. In a tetrahedral environment, the lowest- energy 3d orbitals are d_{xy} and d_{yz}, which are degenerate. Consequently, the $(3d)^2$ configuration of lowest energy is an $S = 1$ spin state, with parallel spins for the two electrons that occupy these orbitals. Magnetic susceptibility measurements[10] support this assignment of an $S = 1$ spin state for FeO_4^{2-}.

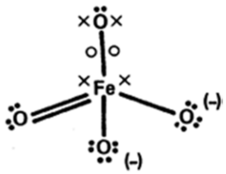
The remaining seven valence-shell orbitals of Fe^{2+} are vacant, and they are available for coordination with the O^{2-} ligands. Tetrahedral hybridization of the 4s and 4p orbitals can be used to form four Fe-O σ-bonds, as in valence-bond structure (**9**).



(9)



(10)



(11)

Two strong electron-pair π-bonds can also be formed by overlapping the doubly-occupied 2pπ (or $2p\bar{\pi}$) orbitals of the O^- with the vacant e_g orbitals[i], to give valence-bond structures of type (**10**). In structure (**10**), the unpaired electrons are localized in the d_{xy} and d_{yz} orbitals, and the formal charge on the Fe is zero. We can also obtain a zero formal charge on the Fe by forming one Fe-O electron-pair π-bond and two Pauling "3-electron bonds" of π- or $\bar{\pi}$-type, as in valence-bond structure (**11**). The unpaired electrons are then delocalized over all atomic centres. Valence-bond structures (**10**) and (**11**) involve Fe-O double-bonding, and therefore account for the observation that the Fe-O bond-lengths of 1.656 Å (as in K_2FeO_4)[12] are much shorter than the estimate[9] of 1.92 Å for the length of an Fe-O single bond.

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[i] The $d_{x^2-y^2}$ and d_{z^2} orbitals overlap better with the oxygen π- and $\bar{\pi}$-orbitals than do the d_{xz}, d_{yz} and d_{xz} orbitals of tetrahedral molecules. But because the latter overlaps are non-zero, we have indicated the presence of Fe-O bonding arising from them in valence-bond structure (**11**).

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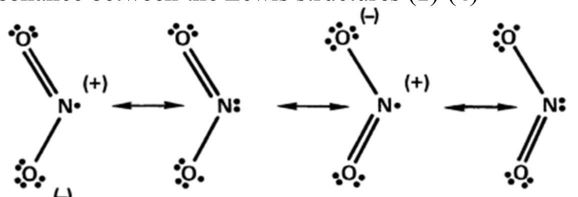
Chapter 6 Pauling "3-Electron Bonds", 5-Electron 3-Centre Bonding and Some Tetra-Atomic Radicals

Valence-bond structures with Pauling "3-electron bonds" between pairs of atoms may be constructed for a number of triatomic radicals. Here we shall examine these types of structures for some radicals with either 17 or 19 valence-shell electrons. For these systems, it is necessary to involve the participation in resonance of two Pauling "3-electron bond" structures. The delocalized molecular orbital equivalent of this resonance involves the construction of three 3-centre molecular orbitals to accommodate five electrons; this is described in Section 6-4.

6-1 NO_2

Nitrogen dioxide with 17 valence-shell electrons is perhaps the most familiar triatomic molecule for which Pauling "3-electron bond" theory is appropriate. Electron spin resonance measurements indicate that the odd electron is delocalized over the three atomic centres; estimates of the nitrogen and oxygen odd-electron charges are 0.52 and 0.24 (Table 6-1), respectively.

(For the purpose of qualitative discussion, we shall approximate these odd-electron charges to 0.5 and 0.25.) Each of the N-O bonds of NO_2 has a length[1] of 1.19 Å and the O-N-O bond angle[1] is 134°. These observations suggest that resonance between the Lewis structures (**1**)-(**4**)



(1) (2) (3) (4)

R.D. Harcourt, *Bonding in Electron-Rich Molecules*,
Lecture Notes in Chemistry 90, DOI 10.1007/978-3-319-16676-6_6

Table 6-1 Electron spin resonance estimates of A-atom odd-electron charges (ρ_A) for AY_2 radicals, (a) H.J. Bower, M.C.R. Symons and D.J.A. Tinling, *in* Radical Ions (E.T. Kaiser and L. Kevan, eds., Interscience, New York, 1968) Chapter 10; (b) M.C.R. Symons, Chem. Soc. Specialist Reports., Electron Spin Resonance **3,** 140 (1974); (c) W. Nelson and W. Gordy, J. Chem. Phys., **51,** 4710 (1969); (d) M.S. Wei, J.H. Current and J. Gendell, J. Chem. Phys. **57,** 2431 (1972). For reasons that are discussed in Ref. (d), the experimental estimates of the spin densities (which we have equated to the odd-electron charges) rarely add exactly to unity. However we shall make the simplifying assumption that they do, i.e. that $\rho_A + 2\rho_Y = 1$ with the ρ_A given in this table.

NO_2	(σ)	0.52[(a)]	NO_2^{2-}	(π)	0.80[(b)]
CO_2^-	(σ)	0.65[(b)]	ClO_2	(π)	0.59[(a)]
BF_2	(σ)	0.93[(c)]	NF_2	(π)	0.95[(a)], 0.77[(d)]
O_3^-	(σ)	0.58[(b)]	PF_2	(π)	0.91[(d)]
SO_2^-	(π)	0.74[(b)]	PCl_2	(π)	0.81[(d)]

is needed to account for the location of the odd-electron on all three atoms and for the equality of the N-O bond-lengths. If it is assumed that each of the structures (**1**)-(**4**) makes the same contribution to the resonance, then the nitrogen and oxygen odd-electron charges are 0.5 and 0.25, respectively. The relevant atomic orbitals that are occupied by the odd-electron are the oxygen 2p $\bar{\pi}$ orbitals and the nitrogen hybrid orbital displayed in Figure 6-1.

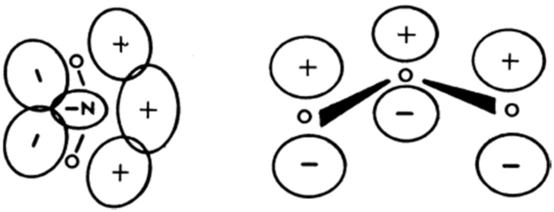
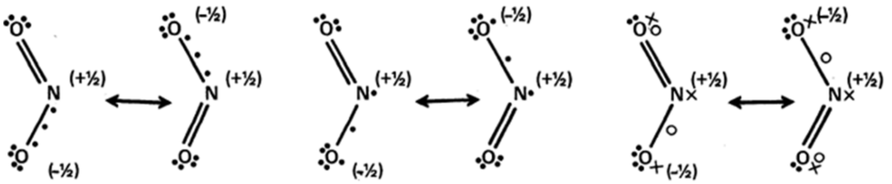


Figure 6-1: Atomic orbitals involved in the formation of Pauling "3-electron bonds" for NO_2 and O_3^-.

The electron spin resonance measurements indicate that the nitrogen orbital has 2s as well as 2p character, and therefore this orbital is a hybrid atomic orbital.

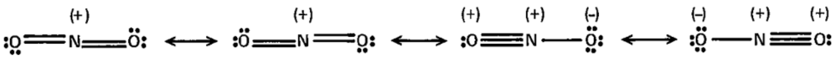
By utilizing Pauling "3-electron bonds", we can reduce the number of valence-bond structures that we need from four to two. Thus the resonance between Lewis structures (**1**) and (**2**) generates[2] the Pauling "3-electron bond" structure (**5**).

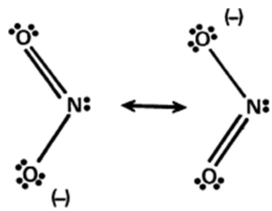


(5) (6) (7) (8) (9) (10)

Similarly, we may summarize resonance between Lewis structures (**3**) and (**4**) by using the Pauling "3-electron bond" structure (6). Therefore resonance between structures (**1**)-(**4**) is equivalent to invoking resonance between structures (**5**) and (**6**). When we introduce the Green and Linnett representation[3] for the Pauling "3-electron bond" (i.e. $\dot{\mathbf{A}} \cdot \dot{\mathbf{B}}$ instead of $\mathbf{A}\cdots\mathbf{B}$) we obtain structures (**7**) and (**8**) for NO_2. If we assume that the odd-electron has an s_z spin quantum number of +½, the Green-Linnett valence-bond structures become those of (**9**) and (**10**).

As does resonance between valence-bond structures (**1**)-(**4**), these Pauling "3-electron bond" structures account qualitatively for the distribution of the odd electron of NO_2, and for the equality of the N-O bond-lengths. They are also in accord with the observation that the N-O lengths of 1.19 Å are intermediate between those for NO_2^+ (1.15 Å)[4] and NO_2^- (1.24 Å)[5], as are the bond-angles (NO_2, 134°; NO_2^+, 180°; NO_2^-, 115°). The NO_2^+ and NO_2^- ions have, respectively, 16 and 18 valence-shell electrons, and standard Lewis structures for these ions are those of (**11**) and (**12**)

 (11)



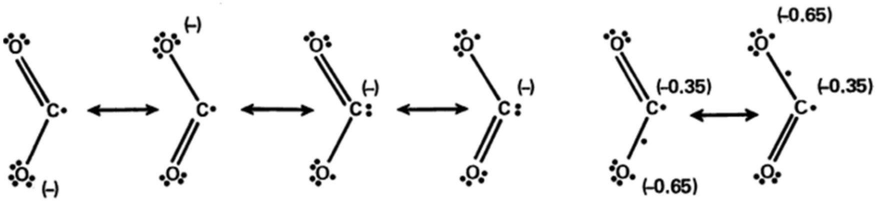
(12)

with eight and six N-O bonding electrons, respectively. The NO_2 valence-bond structures (**7**) and (**8**) (or (**9**) and (**10**)) each have seven N-O bonding electrons. Thus, as one proceeds from NO_2^+ to NO_2^-, the number of bonding electrons in these valence-bond structures decreases and the N-O bond-lengths increase. Similarly, the O-N-O bond-angle closes as the number of nitrogen non-bonding electrons in the valence-bond structures increases from 0 for NO_2^+ to 1.5 for NO_2, to 2 for NO_2^-.

Resonance between the Pauling "3-electron bond" structures (**7**) and (**8**) (or (**9**) and (**10**)) do not account for one NO_2 bond-property. The N-O bond-lengths of 1.19 Å are similar to Pauling's estimate of 1.20 Å for an N-O double bond (cf. 1.214 Å for $\mathbf{CH_3N=O}$)[6]. However, resonance between structures (**7**) and (**8**), each of which has seven bonding electrons, would imply that the N-O bonds for NO_2 should be longer than double bonds. To obtain an additional bonding electron in each structure, it is necessary to utilize the "increased-valence" procedures[i] that we shall describe in Chapters 11 and 12.

6-2 CO_2^- and BF_2

The anion CO_2^- is isoelectronic with NO_2. Electron spin resonance measurements (Table 6-1) indicate that the odd-electron of CO_2^- is more located on the carbon atom than is the odd-electron of NO_2 located on the nitrogen atom. Estimates of the carbon and oxygen odd-electron charges are 0.65 and 0.175, respectively. These charges imply that valence- bond structures (**13**) and (**14**)



(13) (14) (15) (16) (17) (18)

for CO_2^- (with the odd-electron located on the carbon atom) make a larger contribution to the ground-state resonance than do structures **(1)** and **(3)** for NO_2. This is in accord with what one may deduce from elementary electronegativity considerations; Lewis structures (**15**) and (**16**) with negative formal charges on the carbon atoms should be of higher energy than are (**13**) and (**14**). Therefore, the

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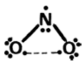
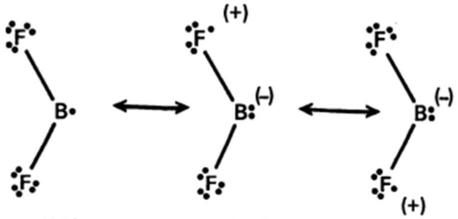
[i] In Section 6-1, we have followed convention by assuming that structures **(1)** and **(3)** are the primary valence-bond structures that locate the odd electron on the nitrogen atom of NO_2.

Another valence-bond structure, namely  with a "long" O-O bond, also locates the odd electron on the nitrogen atom. The absence of atomic formal charges for it suggests that it may also be an important valence-bond structure, and the results of quantum-mechanical valence-bond calculations[7] lend support to this hypothesis. In Section 11-8, "increased-valence" structures are described for NO_2; these structures summarize resonance between seven Lewis structures, five of which are structures (**1**)-(**4**) and this "long-bond" structure.

weights for (**13**) and (**14**) should be rather larger than are those for (**15**) and (**16**). Resonance between (**13**)-(**16**), with weights of 0.325, 0.325, 0.175 and 0.175 for these structures, will generate the carbon and oxygen odd-electron charges of 0.65 and 0.175. The resulting formal charges for the Pauling "3-electron bond" structures are those of structures (**17**) and (**18**).

The BF_2 radical is also isoelectronic with NO_2. Electron spin resonance studies of BF_2 locate the odd-electron primarily in a boron hybrid atomic orbital (Table 6-1). The Lewis structure (**19**),

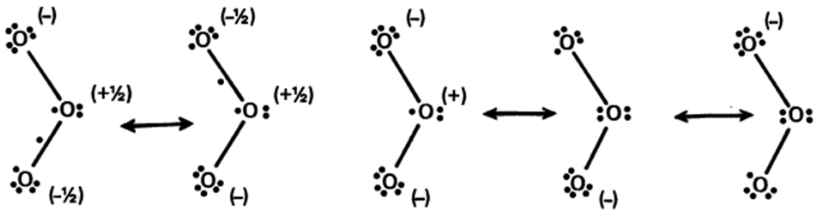


(19) (20) (21)

with zero formal charges on all atoms and the odd-electron located on the boron atom, is in accord with this observation. Because of the unfavourable formal charge arrangements for structures (**20**) and (**21**) - each involves F^+ and B^- - the contribution of these structures to the ground-state resonance must be small, i.e. (**19**) is the primary structure and little development of a Pauling "3-electron bond" must occur for the BF_2 radical.

6-3 Triatomic Radicals with 19 Valence-Shell Electrons: O_3^-, SO_2^-, NF_2 and ClO_2

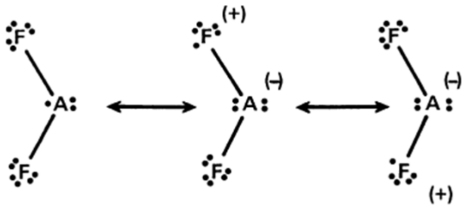
Valence-bond structures with Pauling "3-electron bonds" are also appropriate for a number of radicals with 19 valence-shell electrons[8]. As our first example, we shall examine the bonding for the anion O_3^-. The Pauling "3-electron bond" structures (**22**) and (**23**) for this radical summarize resonance between Lewis structures (**24**) and (**26**), and (**24**) and (**25**), respectively.



(22) (23) (24) (25) (26)

The latter three structures locate the odd-electron on one of each of the three atoms. Electron spin resonance measurements (Table 6-1) indicate that the odd electron is delocalized over all three atoms, and that it occupies the 2pπ-type atomic orbitals of Figure 6-1.

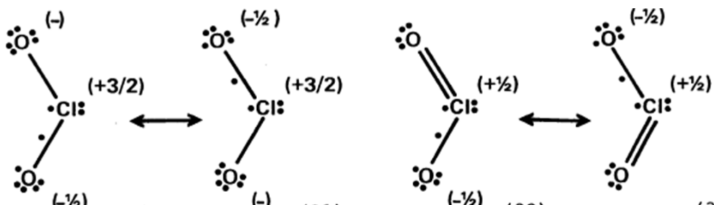
A similar valence-bond representation pertains for the anion SO_2^-, with a sulfur atom replacing the central oxygen atom. It is also appropriate for the anion NO_2^{2-} when $N^{(-\frac{1}{2})}$ replaces $O^{(+\frac{1}{2})}$ in structures (**22**) and (**23**), and N and $N^{(-)}$ replace the O^+ and (central) O atom of structures (**24**), (**25**) and (**26**). Formal charge considerations suggest that the odd-electron should be more located on the terminal oxygen atoms of O_3^- and SO_2^- than it is for NO_2^{2-} and the electron spin resonance estimates of the odd-electron charge on the central atom (Table 6-1) are in accord with this expectation. For NF_2 and PF_2, the three Lewis structures that are equivalent to (**24**), (**25**) and (**26**) are structures (**27**)-(**29**)



(27) (28) (29)

(with **A** = N or P), and the absence of an unfavourable formal charge distribution in structure (**27**) suggests that this structure is the most important structure. As is the case for BF_2, little development of the Pauling "3-electron bonds" is expected for NF_2 and PF_2, i.e. the odd-electron is located primarily in a nitrogen or phosphorus atomic orbital; electron spin resonance estimates for the boron, nitrogen, and phosphorus odd-electron charges for these radicals are (Table 6-1) 0.93, 0.95 or 0.77, and 0.91.

For ClO_2, the Pauling "3-electron bond" structures are (**30**) and (**31**), if only the chlorine 3s and 3p orbitals are utilized for bonding.



(30) (31) (32) (33)

These structures involve large formal charge separations. One way to reduce their magnitude involves allowing the chlorine 3d orbitals also to participate in bonding. We thereby obtain structures (**32**) and (**33**) as the Pauling "3-electron bond" structures. In the Chapter 6 Addendum (and also Figure 11-6) are used to reduce the formal charge separations of (**30**) and (**31**). The electron spin resonance measurements (Table 6-1) indicate that the odd-electron of ClO_2 is delocalized over the three atomic centres, with a chlorine odd-electron charge of 0.59, and therefore Pauling "3-electron bonds" are appropriate for any valence-bond structure for this radical.

6-4 3-Centre Molecular Orbitals and Pauling "3-Electron Bonds"

If we designate the three NO_2 atomic orbitals of Figure 6-1 as y, a and b, then we may construct the delocalized molecular orbitals of Eqn **(1)**

$$\psi_1 = (\mathrm{y}+\mathrm{b})/2^{\frac{1}{2}} + k_1\mathrm{a}\,,\ \psi_2 = (\mathrm{y}-\mathrm{b})/2^{\frac{1}{2}}\,,\ \psi_3 = k_3(\mathrm{y}+\mathrm{b})/2^{\frac{1}{2}} - \mathrm{a}\,, \qquad \textbf{(1)}$$

from them, for which k_1 and k_3 are constants, both > 0 and related through the requirement that ψ_1 and ψ_3 must be orthogonal. (These molecular orbitals are formally identical with those of Section 2-3.) With respect to each pair of nitrogen and oxygen atoms, molecular orbitals ψ_1, ψ_2 and ψ_3 are respectively bonding, non-bonding and antibonding. Five electrons are associated with the y, a and b atomic orbitals of Figure 6-1 in each of the Pauling "3-electron bond" structures **(7)** and **(8)**. Therefore, for the lowest-energy delocalized molecular orbital description of these electrons, orbitals ψ_1 and ψ_2 are doubly-occupied, and ψ_3 is singly-occupied. The molecular orbital configuration for the 5-electron 3-centre bonding unit is then $(\psi_1)^2(\psi_2)^2(\psi_3)^1$. We shall now deduce that use of this configuration is equivalent to invoking resonance between the Pauling "3-electron bond" structures that have been presented above. In general terms, we may write

when **Y** and **B** are equivalent atoms, and n is a node.

To provide a simple demonstration of this equivalence, it is only necessary to show that the molecular orbital configuration $(\psi_1)^2(\psi_2)^2(\psi_3)^1$ can be expressed as a linear combination of the configurations $(\mathrm{y})^2(\mathrm{a})^2(\mathrm{b})^1$, $(\mathrm{y})^2(\mathrm{a})^1(\mathrm{b})^2$ and $(\mathrm{y})^1(\mathrm{a})^2(\mathrm{b})^2$ for the Lewis structures **Y A B**, **Y A B** and **Y A B**. This is because resonance between the Pauling "3-electron bond" structures **Y A • B** and **Y • A B** is equivalent to resonance between $\ddot{\mathbf{Y}}\quad \dot{\mathbf{A}}\quad \ddot{\mathbf{B}}$, $\ddot{\mathbf{Y}}\quad \ddot{\mathbf{A}}\quad \dot{\mathbf{B}}$ and $\dot{\mathbf{Y}}\quad \ddot{\mathbf{A}}\quad \ddot{\mathbf{B}}$. We may write $(\psi_1)^2(\psi_2)^2(\psi_3)^1$ as $\psi_1^\alpha\psi_1^\beta\psi_2^\alpha\psi_2^\beta\psi_3^\alpha$, in which α and β are the spin wave-functions for electrons with s_z spin quantum numbers of +½ and -½, and the odd-electron is assumed to have s_z = +½. By substituting the linear combinations of atomic orbitals of Eqn. (6-1) into this configuration, and then expanding the configuration as a linear combination of atomic orbital configurations, we obtain Eqn. (6-2)

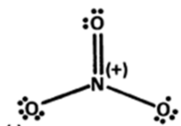
$$\psi_1^\alpha\psi_1^\beta\psi_2^\alpha\psi_2^\beta\psi_3^\alpha = \text{const x}[-2^{\frac{1}{2}}(y^\alpha y^\beta b^\alpha b^\beta a^\alpha) + k_1\{(y^\alpha y^\beta a^\alpha a^\beta b^\alpha) + (y^\alpha a^\alpha a^\beta b^\alpha b^\beta)\}] \quad (2)$$

To obtain this expression, we have omitted all atomic orbital configurations for which two or more electrons occupy the same atomic orbital with the same s_z spin quantum numbers. Such configurations are forbidden by the Pauli exclusion principle. A derivation of the above linear combination that takes proper account of electron indistinguishability is provided in Refs. 9a, b.

For the 19 valence-electron systems O_3^-, SO_2^-, ClO_2 and other isoelectronic species, the pπ-atomic orbitals that are associated with the odd electron are displayed in Figure 6-1. The molecular orbitals that may be constructed from these orbitals are also given by Eqn. (**1**) (with y, a and b ≡ pπ), and the π-electron configuration for the 5-electron 3-centre bonding is $(\psi_1)^2(\psi_2)^2(\psi_3)^1$.

6-5 Some Tetra-Atomic Radicals

The isoelectronic radicals NO_3 and CO_3^- with 23 valence-shell electrons, are predicted to be planar[10]. Their standard Lewis structures are of types (**34**) and (**35**)



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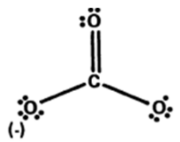

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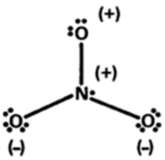

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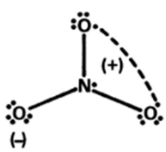

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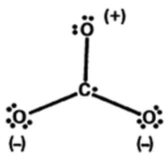

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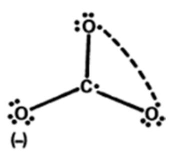
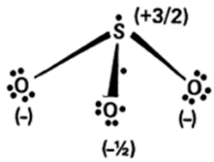


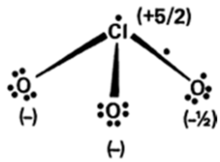
(39)

(together with two other equivalent structures). For each of these structures, the odd-electron occupies an oxygen atomic orbital. To locate the odd-electron in a carbon or nitrogen atomic orbital, it is necessary to reduce the number of C-O and N-O covalent bonds, as occurs in structures (**36**)-(**39**), for example. These latter structures do not have a more favourable distribution of atomic formal charges than do structures (**34**) and (**35**). This fact, taken together with the smaller number of C-O or N-O covalent bonds, suggests that structures (**36**)-(**39**) should be unimportant valence-bond structures for the ground-states of these radicals. This expectation is in accord with the electron spin resonance observations that the odd-electron for either NO_3 or CO_3^- occupies primarily atomic orbitals that are located on the oxygen atoms. Therefore, no appreciable development of a Pauling "3-electron bond" may occur for these systems.

In contrast, the radicals NO_3^{2-}, PO_3^{2-}, SO_3^- and ClO_3 with 25 valence shell electrons, have been found to have their odd electron delocalized over all atomic centres[10]. For these radicals, Pauling "3-electron bonds" may be developed without reducing the number of **A**-O (with **A** ≡ P, S or Cl) bonding electrons. Thus we may write

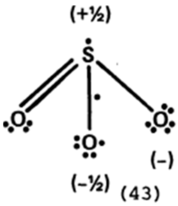

(40)

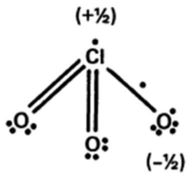

(41)

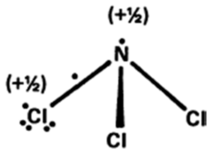

(42)

to locate the odd-electron in an **A** atom orbital as well as the oxygen atomic orbitals. (For each of the structures (**40**)-(**42**), there are two other equivalent structures that participate in resonance with these structures). The atomic formal charges in these structures reflect the reduced importance of $\dot{\mathbf{A}}\ddot{\mathbf{O}}$ to the Pauling "3-electron bond" resonance $\dot{\mathbf{A}}\ddot{\mathbf{O}} \leftrightarrow \ddot{\mathbf{A}}\dot{\mathbf{O}}$ as one proceeds from PO_3^{2-} to ClO_3. This is reflected in the values of the P, S and Cl odd-electron charges, namely (Ref. (a) of Table 6-1) 0.68, 0.58 and 0.36.

As is the case for ClO_2 (Section 6-3), the possibility exists that sulphur and chlorine 3d orbitals may participate appreciably in bonding for SO_3^- and ClO_3. If this occurs, the resulting valence-bond structures of types (**43**) and (**44**)


(43)


(44)


(45)

also have Pauling “3- electron bonds”. The presence of non-bonding electrons on the **A** atoms of each the structures (**40**)-(**44**) is in accord with the prediction that these 25 valence-electron radicals are non-planar[10].

Using ClO_2 as the example, the Addendum 2014 provides an alternative, non d-orbital approach that can be used to reduce the magnitudes of the atomic formal charges of valence-bond structures (**30**), (**31**), (**41**) and (**42**) for ClO_2, ClO_3 and SO_3^-.

Group (V) trihalides are isoelectronic with PO_3^{3-}, SO_3^{2-} and ClO_3^-. Photo-electron spectrum studies permit features of the electronic structures of different states for the singly-charged cations of the trihalides to be examined[11]. If a non-bonding electron is ionized, a Pauling “3-electron bond” can be developed, as is displayed in structure (**45**) for the cation NCl_3^+. These types of valence-bond structures are similar to structures (**40**)-(**42**) for PO_3^{2-}, SO_3^- and ClO_3.

The influence of overlap on the stabilization or destabilization of Pauling “3-electron bonds” has been discussed in Section 3-10, together with the consequent effect on competition between planarity and pyramidalization for radicals such as CH_3, CH_2F, CHF_2 and CF_3. Each of CF_3 and NCl_3^+ has 25 valence-shell electrons.

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Addendum Chapter 6

1. Alternative valence-bond structures for symmetrical 5-electron 3-centre bonding units.

Three types of symmetric 5-electron 3-centre valence-bond structures[12,13] are displayed in Figure 6-2, for which the k and k^* are proportional to $2^{1/2}k_1$ and $2^{1/2}/k_3$ of Eqn. (1) above. Applications to NO_2, ClO_2, the NSN^- dimer and an excited state of SO_2, are described in Refs. 12 and 13.

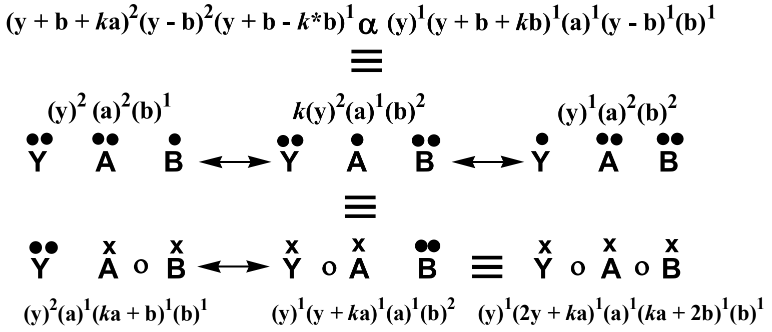
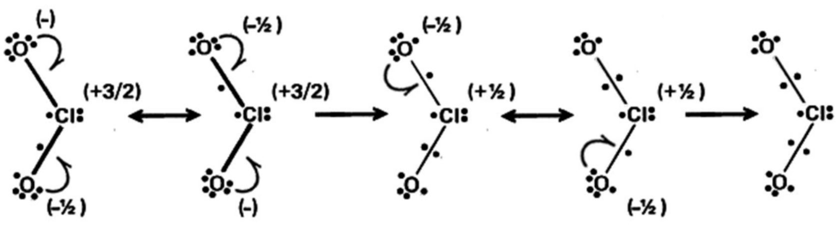


Figure 6-2: Lowest-energy symmetric 5-electron 3-centre molecular orbital configuration and the equivalent valence bond structures, with y, a and b as the overlapping atomic orbitals. The atomic orbital overlap integrals, $S_{ay} = S_{ab}$, are greater than zero.

2. Alternative non d-orbital valence-bond structures for ClO_2, SO_3^- and ClO_3

Alternatives to the d-orbital types of valence-bond structures (**32**), (**33**), (**43**) and (**44**) for ClO_2, SO_3^- and ClO_3 are obtained by using the electron delocalization procedure used in Chapter 12. It involves delocalizing a non-bonding $2p\bar{\pi}$ electron from each oxygen atom in structures (**30**), (**31**), (**41**) and (**42**) into a Cl-O or S-O bonding molecular orbital. For ClO_2, the delocalizations are shown in structures (**46**) and (**47**), to give the non-d orbital valence-bond structures[12(b)] (**48**) and (**49**), with fractional Cl-O and S-O σ-bonds.



(46) (47) (48) (49) (50)

When $\overset{\times}{\mathbf{O}} \circ \overset{\times}{\mathbf{Cl}} \circ \overset{\times}{\mathbf{O}}$ is used to represent the five π-electrons (cf. Figure 6-2), valence-bond structure (**50**) is obtained[12(b)] (without electron spins). It is equivalent to resonance between valence-bond structures (**48**) and (**49**). In Figure 11-6, another procedure is used to construct valence-bond structures that are analogous to structures (**48**) and (**49**).

12. R.D. Harcourt (a) J. Chem. Soc. Faraday Trans., **87**, 1089 (1991). (b) J. Phys. Chem. **97**, 1351 (1993). (c) Z. anorg. allgem. Chemie. **636**, 1962 (2010).
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Chapter 7 Some Dimers of Triatomic Radicals with 17 and 19 Valence-Shell Electrons

A number of triatomic radicals can form dimers whose geometries have been well-characterized. A study of the electronic structures of these dimers can illustrate aspects of qualitative valence-bond and molecular orbital theory for electron-rich polyatomic molecules, and interconnections between these theories can be demonstrated. Dinitrogen tetroxide is a molecule *par excellence* that may be used for these purposes, and here we shall give primary consideration to its electronic structure and bond properties.

7-1 The Long, Weak N-N Bond of N_2O_4: Lewis Valence-Bond Theory

NO_2 with 17 valence-shell electrons can form several dimers whose geometries are displayed in Figure 7-1.

The most stable dimer is planar with a long, weak N-N bond. The N-N bond-length for this dimer is 1.78 Å[2], which is 0.33 Å longer than the N-N single bond of N_2H_4[3]. The N-N bond-dissociation energy of 57 kJ mol^{-1} for N_2O_4 is much smaller than that of 250 kJ mol^{-1} for N_2H_4[4, 5]. Both molecular orbital and valence-

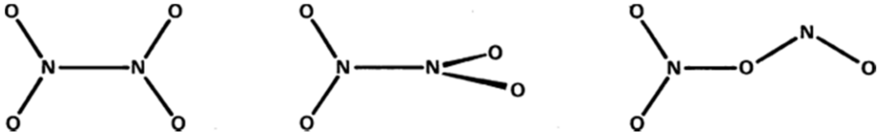
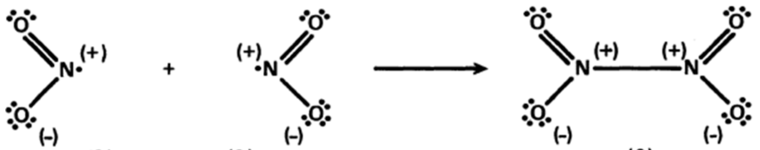


Figure 7-1: N_2O_4 isomers[1]

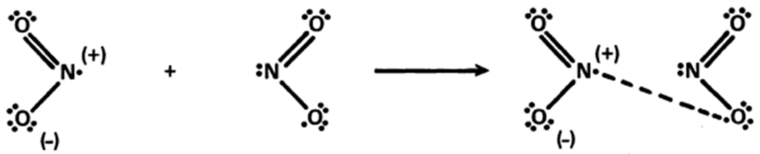
R.D. Harcourt, *Bonding in Electron-Rich Molecules*,
Lecture Notes in Chemistry 90, DOI 10.1007/978-3-319-16676-6_7

bond theory may be used to explain why the N-N bond is long and weak. The Lewis-type valence-bond explanation follows immediately from the valence-bond description of the electronic structure of NO_2 (Section 6-1).

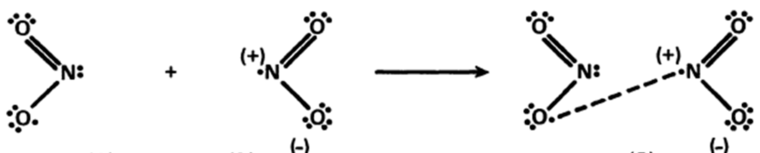
We shall assume here that the electronic structure of the ground-state for NO_2 may be described by invoking resonance between the valence-bond structures (**1**)-(**4**) of Section 6-1. (For convenience only, we shall initially restrict our attention to structures (**1**) and (**2**), but is to be understood that these valence-bond structures participate in resonance with the symmetrically-equivalent structures (**3**) and (**4**).) When NO_2 dimerizes, the odd-electrons of the two monomers must be spin-paired to form an electron-pair bond that links the two radicals. By using Lewis valence-bond structures of types (**1**) and (**2**) to represent each monomer, the Lewis structures (**3**)-(**6**) for the dimer can be generated



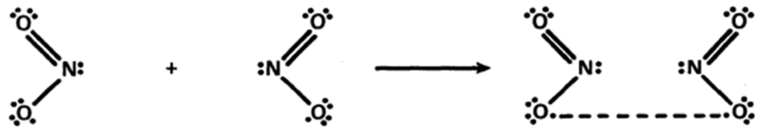
(1) (1) (3)



(1) (2) (4)

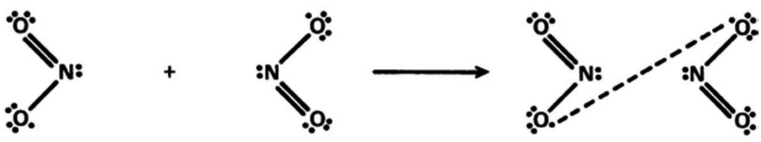


(2) (1) (5)



(2) (2) (6)

In structures (**4**)-(**6**), we have used pecked bond-lines (----) to indicate the formation of "long-bonds" between pairs of non-adjacent atoms. Because of the small overlap that exists between atomic orbitals located on non-adjacent atomic centres, these bonds have negligible strength (Section 2-5(b)), and have been designated as "formal bonds"[8]. It follows that if resonance between structures (**1**) and (**2**) (together with their mirror-images) is used to represent the electronic structure of NO_2, then resonance between the structures (**3**)-(**6**) (together with their mirror images, and their *trans* analogues (cf. for example structure (**7**),



(7)

which is a *trans* analogue of structure **6**)[i], may be used to describe the electronic structure of N_2O_4 when charge-transfer between the NO_2 moieties is not considered. Therefore, the N-N bond number for N_2O_4 (i.e. the number of pairs of electrons that form the N-N bond) must be smaller than the bond-number of unity that pertains for the N-N single-bond of N_2H_4 (as in $H_2\ddot{N}—\ddot{N}H_2$). A less-than-unity bond-number implies that the N-N bond is longer than a single bond. Estimates of the N-N bond-number are 0.34 from the bond-length and 0.24 from the photo-electron spectrum[7c].

In valence-bond structures (**6**) and (7), a lone-pair of electrons occupies each of the nitrogen hybrid atomic orbitals (h_2 and h_3 of Figure 7-2) that pertain to the N-N σ-bond of structure (**3**). For this pair of orbitals, the overlap integral is 0.3, and therefore non-bonded repulsions (Section 3-10) between the nitrogen atoms will be established as a consequence of the contributions of structures (**6**) and (**7**) to the ground-state resonance. This repulsion will also lead to some lengthening of the N-N bond.

It has been suggested that the N-N bond-number for N_2O_4 is equivalent to the nitrogen odd-electron charge for the NO_2 monomer[9]. In Section 6-1, a value of approximately 0.5 was assigned to this odd-electron charge. If no reorganization

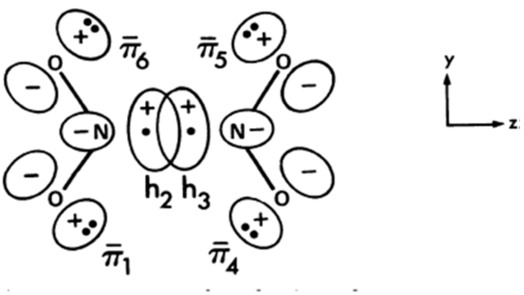


Figure 7-2: Mobile σ-electron atomic orbitals for planar N_2O_4 isomer[7].

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[i] By bonding together the NO_2 Lewis structures (**1**)-(**4**) of Section 6-1, eight *cis* and eight *trans* Lewis structures (such as *cis* (**3**)-(**6**) and *trans* (**7**)) can be constructed for O_2NNO_2. Twelve of these structures involve a long or formal N-O or O-O bond, and, as indicated in Section 2-2, they are examples of singlet-diradical/Dewar-type/long-bond/formal bond Lewis structures. Although the discussions focus attention primarily on the Lewis structures (**3**)-(**6**), of course the twelve other Lewis structures participate in resonance with them. When the formal bond is included, each of the 16 Lewis structures obeys the Lewis-Langmuir octet rule.

of the electronic structure of NO_2 is assumed to occur when NO_2 dimerizes, then it has been argued that spin-pairing of the nitrogen odd-electron charge of 0.5 for each monomer generates an N-N σ-bond-number of 0.5 for the dimer, i.e. one half of an N-N electron-pair is formed for the N_2O_4 dimer. This argument is not valid[7b, 10]. Inspection of the valence-bond structures (**3**)-(**5**) shows that a nitrogen atom can share its odd-electron charge to form a "long" N-O bond as well as the N-N bond. Consequently, if the nitrogen odd-electron charge for NO_2 is 0.5[i], resonance between the N_2O_4 Lewis structures (**3**)-(**6**) generates an N-N bond-number of 0.25.

Each of the 16 N_2O_4 Lewis structures (such as (**3**)-(**7**)) obeys the Lewis-Langmuir octet rule for atoms of first-row elements (Section 2-4a), and twelve of these structures have a "long-bond" linking a pair of non-adjacent atoms. Why should these latter structures be considered to be of importance for the ground-state resonance description of N_2O_4? In Section 2-4, we have referred to the *electroneutrality principle*, which states that if atoms of a neutral molecule have similar electronegativities, the atomic formal charges for the ground-state of the molecule will have small magnitudes. For N_2O_4, appreciable weights for at least some of the "long-bond" structures such as (**4**)-(**7**) (whose formal charges are smaller than are those for the standard Lewis structure (**3**)) help ensure that this requirement is satisfied.

Because each NO_2 moiety of structures (**3**)-(**7**) has 17 valence-shell electrons, these structures will be designated as "covalent" structures with the electron distributions of NO_2NO_2. In Section 7-3, "ionic" or charge-transfer structures of the type $NO_2^+NO_2^-$ (or $NO_2^-NO_2^+$) will also be included in the description of the electronic structure. As is the case for H_2 (Section 3-3), the ionic structures are less important than are the corresponding covalent structures for the ground-state resonance[7b, c, 10].

Molecular orbital calculations for NO_2 and N_2O_4, with configuration interaction (C.I.) (Sections 3-3 and 10-3) included for N_2O_4, have been parameterized so that the experimental values for the first two ionization potentials of NO_2, the first ionization potential of N_2O_4, and the nitrogen odd-electron charge of NO_2 (Section 6-1) are reproduced[7b, c, 13]. The NO_2 parameters have been transferred into the N_2O_4 calculations. From the resulting molecular orbital-CI wave-function for N_2O_4, weights of 0.24, 0.24, 0.24, 0.13 and 0.13 have been calculated for sets of covalent structures of types (**3**)-(**7**). The remaining weight of 0.02 is shared amongst various ionic structures. The covalent weights are similar to those obtained from spin-pairing the odd-electrons of two NO_2 monomers with nitrogen odd-electron charges of 0.5, namely 0.25, 0.25, 0.25, 0.125 and 0.125, and support the hypothesis that dimerization of NO_2 involves primarily the spin-pairing of the odd-electrons of two NO_2 radicals.

The odd-electron of NO_2 is delocalized amongst a nitrogen hybrid atomic orbital and the oxygen 2p $\bar{\pi}$-orbitals that overlap with this nitrogen orbital. The three orbitals are displayed in Figure 6-1. The atomic orbitals whose occupancies

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[i] To obtain a nitrogen odd- electron charge of 0.5, the NO_2 structures (**1**) and (**2**) must have equal weights. Therefore, the weights for the N_2O_4 structures (**3**)-(**6**) are each equal to 0.25.

differ in valence-bond structures (**3**)-(**7**) for N_2O_4 are therefore those that are displayed in Figure 7-2, namely two nitrogen hybrid and four oxygen $2p\bar{\pi}$-orbitals, which have been designated as "mobile σ-electron" orbitals[6, 7, 10-13]. The "mobile σ-electron" wavefunctions for the electron-pair bonds of structures (**3**)-(**7**) are assumed to be constructed using the Heitler-London procedure (Section 3-3). For example, the wave-function for the N-N bond of the standard Lewis structure (**3**) is $h_2(1)h_3(2) + h_3(1)h_2(2)$ in which h_2 and h_3 are the hybrid orbitals displayed in Figure 7-2. But it is also possible to construct a molecular orbital wave-function for this bond, namely $\sigma(1)\sigma(2)$ for which $\sigma = h_2 + h_3$ is the N-N bonding molecular orbital. We shall now use this latter formulation of the N-N bond wave-function to provide a molecular orbital explanation[11, 12] for the existence of a long, weak N-N bond for N_2O_4.

7-2 The Long Weak N-N Bond of N_2O_4: Molecular Orbital Theory[11,12]

For the molecular orbital description of the N-N bond of structure (**3**), two electrons with opposite spins occupy the N-N σ-bonding molecular orbital $\sigma = h_2 + h_3$. In this structure, the oxygen $2p\bar{\pi}$ orbitals, which overlap with the nitrogen h_2 and h_3 orbitals, are doubly-occupied. However, the appreciable electronegativity of N^+ relative to O^- in structures of type (**3**) induces substantial delocalization of the oxygen $2p\bar{\pi}$ electrons into the antibonding N-N σ^*-orbital, $\sigma^* = h_2 - h_3$, which is vacant in these structures. The N-N σ-bond order[i] is then reduced below the value of unity that pertains to structure (**3**), thereby generating a long, weak N-N bond. An estimate of 0.525 for this bond-order has been obtained from molecular orbital studies of the photoelectron spectrum[7c].

To obtain the "long-bond" Lewis structures (**4**)-(**6**) from the standard Lewis structure (**3**), either one or two electrons have been delocalized from the oxygen $\bar{\pi}_1$ and $\bar{\pi}_4$ orbitals of Figure 7-2 into the singly occupied nitrogen hybrid orbitals h_2 and h_3. We shall now use these orbitals to construct the 4-centre delocalized molecular orbitals for the mobile σ-electrons. (A fuller treatment that includes the $\bar{\pi}_5$ and $\bar{\pi}_6$ orbitals is described in Refs. 7b, c, 11 and 12.)

Initially we shall form the bonding and antibonding linear combinations of each pair of nitrogen and oxygen atomic orbitals. The resulting symmetry orbitals are given in Eqs. (1) and (2),

$$s_1 = (h_2 + h_3)/2^{\frac{1}{2}}, \quad s_2 = (h_2 - h_3)/2^{\frac{1}{2}}, \tag{1}$$

[i] These delocalizations are calculated to occur at the N-N single-bond length of 1.45 Å as well as at the experimental length of 1.78 Å.

$$s_3 = (\bar{\pi}_1 + \bar{\pi}_4)/2^{\frac{1}{2}}, \; s_4 = (\bar{\pi}_1 - \bar{\pi}_4)/2^{\frac{1}{2}}, \tag{2}$$

$$\psi_1 = (s_3 + \lambda s_1)/(1+\lambda^2)^{\frac{1}{2}} \equiv (\bar{\pi}_1 + \lambda h_2 + \lambda h_3 + \bar{\pi}_4)/\{2(1+\lambda^2)\}^{\frac{1}{2}} \tag{3}$$

$$\psi_2 = (s_4 + \mu s_2)/(1+\mu^2)^{\frac{1}{2}} \equiv (\bar{\pi}_1 + \mu h_2 - \mu h_3 - \bar{\pi}_4)/\{2(1+\mu^2)\}^{\frac{1}{2}} \tag{4}$$

$$\psi_3 = (\lambda s_3 - s_1)/(1+\lambda^2)/^{\frac{1}{2}} \equiv (\lambda\bar{\pi}_1 - h_2 - h_3 + \lambda\bar{\pi}_4)/\{2(1+\lambda^2)\}^{\frac{1}{2}} \tag{5}$$

$$\psi_4 = (\mu s_4 - s_2)/(1+\mu^2)^{\frac{1}{2}} \equiv (\mu\bar{\pi}_1 - h_2 + h_3 - \mu\bar{\pi}_4)/\{2(1+\mu^2)\}^{\frac{1}{2}} \tag{6}$$

in which for simplicity only we have omitted the atomic orbital overlap integrals from the normalization constants. The symmetry orbitals s_1 and s_2 are the N-N σ-bonding and σ^*-antibonding molecular orbitals. The s_1 and s_3 orbitals are symmetric with respect to reflection through the xy plane of symmetry (Figure 7-2), whereas s_2 and s_4 are antisymmetric with respect to this reflection. Because orbitals with the same symmetry can overlap, we may linearly combine s_1 with s_3 , and s_2 with s_4, to obtain the delocalized 4-centre molecular orbitals of Eqs. (3)-(6). The parameters λ and μ are constants, both > 0. In particular, as will become more evident below, the parameter μ provides a measure of the extent of delocalization of the oxygen $2p\bar{\pi}$ electrons into the antibonding σ^* orbital (s_2).

Inspection of the signs of the atomic orbital coefficients shows that molecular orbital ψ_4 is both N-N and N-O antibonding, and therefore it is the highest-energy molecular orbital for the mobile σ-electrons. For the six electrons that occupy the $\bar{\pi}_1$, h_2, h_3 and $\bar{\pi}_4$ orbitals of Figure 7-2, the molecular orbital configuration of lowest energy is given by Eqn. (7), with orbital ψ_4 vacant.

$$\Psi_1(MO) = (\psi_1)^2(\psi_2)^2(\psi_3)^2 \tag{7}$$

It is instructive to transform the molecular orbitals of Eqn. (7) by applying the identity that we have deduced in Section 3-5 (or Section 3-7), namely

$$(a + kb)^1(k^*a - b)^1 = -(1 + kk^*)(a)^1(b)^1 \tag{8}$$

provided that the two electrons which occupy the bonding and antibonding orbitals $a + kb$ and $k^*a - b$ have parallel spins. Because the overlap integrals have been omitted from the normalization and orthogonality relationships, the molecular orbitals of Eqs. (3)-(6) are normalized and orthogonal. For these orbitals, the appropriate form of Eqn. (8) is Eqn. (9),

$$\{(a+kb)/(1+k^2)^{\frac{1}{2}}\}^1\{(ka-b)/(1+k^2)^{\frac{1}{2}}\}^1 = -(a)^1(b)^1 \tag{9}$$

in which a and b now correspond to a pair of symmetry orbitals from Eqs. (1) and (2), and k is either λ or μ.

When this identity is applied to the ψ_1 and ψ_3 orbitals of Eqn. (7), we obtain Eqn. (10),

$$\Psi_1(\text{MO}) = (\psi_1)^2(\psi_2)^2(\psi_3)^2 \equiv (s_1)^2(\psi_2)^2(s_3)^2 \tag{10}$$

which shows that the N-N σ-bonding orbital s_1 is doubly occupied regardless of the value of μ in molecular orbital ψ_2.

If the parameter μ is set equal to zero in the ψ_2 of Eqn. (4), then $\psi_2 = s_4$, and $\Psi_1(\text{MO})$ reduces to $(s_1)^2(s_4)^2(s_3)^2 \equiv (s_1)^2(\bar{\pi}_1)^2(\bar{\pi}_4)^2$. This latter configuration corresponds to double-occupancy of the $\bar{\pi}_1$ and $\bar{\pi}_4$ orbitals of Figure 7-2, i.e. no delocalization of electrons has occurred from these orbitals. When $\mu \neq 0$, the s_4 and s_2 symmetry orbitals mix according to Eqn. (4), i.e. $\bar{\pi}$-electrons delocalize into the antibonding N-N σ^* orbital which is vacant in the standard Lewis structure (**3**). The parameter μ therefore provides a measure of the extent of this delocalization, which may be calculated from the N-N σ-bond order for $\Psi_1(\text{MO})$ of Eqn. (7). Using the bond-order formula of Eqn. (3-43), together with the molecular orbital coefficients of Eqs. (3)-(5), this bond-order may be expressed as $1/(1+\mu^2)$. (This formula is also appropriate[12] when the $\bar{\pi}_5$ and $\bar{\pi}_6$ atomic orbitals of Figure 7-2 are included to construct 6-centre molecular orbitals.) With $1/(1+\mu^2) = 0.525$, $\mu = 0.951$ is obtained.

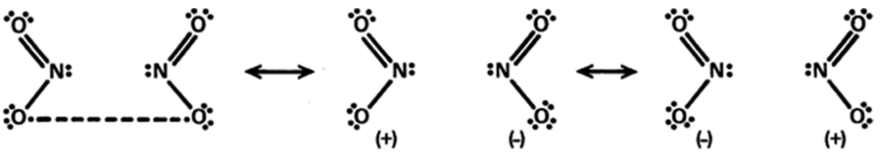
Further transformations of the orbitals for molecular orbital configuration $\Psi_1(\text{MO})$ are possible, but a discussion of them will be postponed until Chapter 10. These transformations enable a connection to be made between the molecular orbital and valence-bond descriptions of the electronic structure of N_2O_4 that we have described here.

The results of some molecular orbital calculations[14-18] that treat explicitly either all of the electrons or all of the valence-shell electrons, support the molecular orbital theory[11, 12] that has been described in this Section. It may also be noted that the "through-bond" coupling[19] of lone-pair orbitals over three σ-bonds is equivalent to lone-pair delocalization into the antibonding σ^* orbital between the central σ-bond.

7-3 The Planarity of N_2O_4, Covalent-Ionic Resonance and *cis* O-O Pauling "3-Electron Bonds"

The planarity of N_2O_4 is concomitant with a barrier to rotation[1, 20] around the N-N bond of 8-12 kJ mol^{-1}. The origin of this barrier was initially associated with weak π-bonding across the N-N bond[21]. However, the results of molecular orbital calculations[14, 15, 22] now indicate that the overlap between σ-orbitals on pairs of *cis* oxygen atoms provides the primary contribution to this barrier. For these calculations, the oxygen orbitals were oriented parallel to the N-N bond axis. For the valence-bond structures (**3**)-(7), the corresponding oxygen orbitals are the $2p\bar{\pi}$-orbitals of Figure 7-2. The overlap integral between a pair of *cis* $2p\bar{\pi}$-orbitals (for example $\bar{\pi}_1$ and $\bar{\pi}_4$, or $\bar{\pi}_5$ and $\bar{\pi}_6$) is 0.01[7a]. Using valence-bond theory, we shall now give consideration to how this overlap can generate a contribution to the rotation barrier via covalent-ionic resonance. Fuller numerical details are provided in Refs. 7a and 7c.

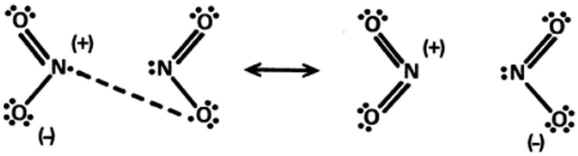
For valence-bond structure (**6**), there is a "long" *cis* O-O bond formed by the overlap of singly-occupied $2p\bar{\pi}$-orbitals. If this structure has appreciable weight in the ground-state resonance description of the electronic structure, it might be thought that this bond could provide the valence-bond explanation of the *cis* O-O overlap contribution to the barrier. However, it has been calculated[7a] that this bond has negligible strength (< 0.2 kJ mol^{-1}), and that it is not appreciably strengthened when structure (**6**) participate in resonance with the ionic ($NO_2^+NO_2^-$ and $NO_2^-NO_2^+$) structures (**8**) and (**9**)



(6) (8) (9)

(cf. the covalent-ionic resonance **H—H** ↔ **H$^+$:H$^-$** ↔ **H$^-$:H$^+$** for H_2 of Section 3-3).

A much larger *cis* O-O binding energy of 20 kJ mol^{-1} is calculated when each of the covalent structures (**4**) and (**5**) participate in resonance with the ionic structures (**10**) and (**11**).



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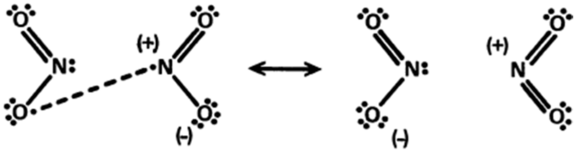


(5) (11)

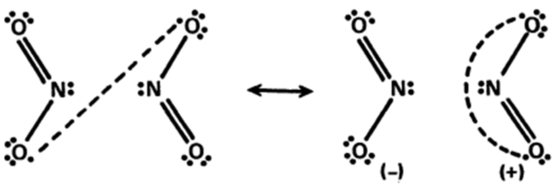
This resonance that has been calculated[7] to be primarily responsible for the *cis* O-O overlap contribution to the rotation barrier for N_2O_4.

It is of interest to examine the nature of the electronic reorganization that occurs when covalent structure (**4**) participates in resonance with the ionic structure (**10**). In structures (**12**) and (**13**),

(12) (13)

we have indicated the relevant electrons, namely those that occupy the oxygen $\bar{\pi}_1$ and $\bar{\pi}_4$ orbitals, and the nitrogen hybrid orbital h_2. Inspection of these latter structures reveals that the (**4**) ↔ (**10**) resonance leads to the development of a Pauling "3-electron bond" $(\mathrm{O}\cdots\mathrm{O} \equiv \dot{\mathrm{O}} \cdot \dot{\mathrm{O}} \equiv (\mathrm{O}{:}\ {\cdot}\mathrm{O}) \longleftrightarrow (\mathrm{O}{\cdot}\ {:}\mathrm{O}))$ between the *cis* oxygen atoms. We may therefore associate the *cis* O-O overlap contribution to the rotation barrier with the formation of this type of bond.

Other types of covalent-ionic resonance can also lead to the development of a Pauling "3-electron bond" between a pair of *cis* oxygen atoms. One such example involves the structures (**7**) and (**14**).



(7) (14)

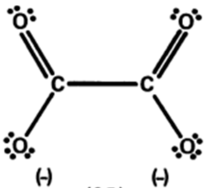
However, it has been calculated that resonance between these structures generates a much smaller stabilization of the planar conformer than do the

(**4**) ↔ (**10**) and (**5**) ↔ (**11**) resonances. Simple electrostatic considerations show why this is the case; due to the distribution of formal charges in structures (**4**) and (**10**) (or (**5**) and (**11**)), the energy difference between a pair of these structures is much smaller than it is between structures (**7**) and (**14**). Therefore a more effective linear combination of the wave-functions for structures (**4**) and (**10**) may be formed. Similar electrostatic considerations indicate why the (**4**) ↔ (**10**) resonance generates a larger stabilization than does the (**6**) ↔ (**8**) ↔ (**9**) resonance.

Further theory for covalent-ionic resonance and Pauling "3-electron bonds" for 6-electron 4-centre bonding is described in Chapter 24.

7-4 $C_2O_4^{2-}$ and $S_2O_4^{2-}$ Anions

The oxalate anion dimer of CO_2^- (i.e. $C_2O_4^{2-}$) is isoelectronic with N_2O_4. Its C-C bond-length of 1.57 Å (average)[23] is only a little longer than the C-C single-bond length of 1.54 Å for C_2H_6. In contrast, the N-N bond of N_2O_4 is 0.33 Å longer than the N-N single bond for N_2H_4. A comparison of the standard Lewis structures (**3**) and (**15**)



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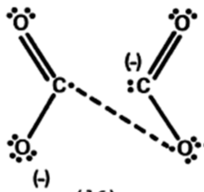

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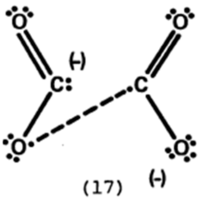

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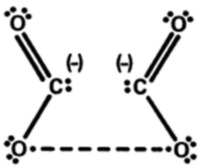


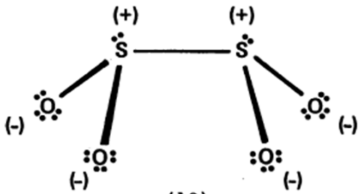
(18)

indicates immediately why the difference occurs. Relative to the lone-pair $2p\bar{\pi}$ -orbitals on the oxygen atoms of these structures, the carbon atoms of structure (**15**) must be less electronegative than are the N^+ of structure (**3**). Consequently the delocalization of the oxygen $\bar{\pi}$-electrons into the antibonding C-C σ^* orbital of structure (**15**) must occur to a smaller extent than does that which occurs into the antibonding N-N σ^* orbital of structure (**3**). Therefore the C-C σ-bond order for $C_2O_4^{2-}$ must be larger than the N-N σ-bond order for N_2O_4, and a shorter C-C bond results.

The reduction in the extent of delocalization of oxygen $\bar{\pi}$-electrons generates a smaller *cis* O-O overlap stabilization for $C_2O_4^{2-}$ than for N_2O_4. Non-planar as well as planar $C_2O_4^{2-}$ conformers have been reported[23].

A Lewis-type valence-bond explanation for the difference in N-N and C-C bond-lengths can also be provided. When CO_2^- monomers with the valence-bond structures (**13**) and (**15**) of Section 6-2 dimerize, the Lewis structures of types (**15**)-(**18**) are obtained. These structures are equivalent to structures (**3**)-(**6**) for N_2O_4. For $C_2O_4^{2-}$, the formal charge arrangements for structures (**16**)-(**18**) are no better than are those for the standard Lewis structure (**15**). Therefore, the "long-bond" structures (**16**)-(**18**), each with no C-C bond, would be expected to make a smaller contribution to the ground-state resonance than do the corresponding structures (**4**)-(**6**) for N_2O_4. Consequently, the standard Lewis structure (**15**) with a C-C electron-pair σ-bond has a larger weight than has structure (**3**) (with an N-N σ-bond for N_2O_4), thereby generating a larger C-C bond-number for $C_2O_4^{2-}$.

The dithionite anion $S_2O_4^{2-}$ is non-planar[24, 25]. Its S-S bond-length of 2.39 Å[24, 25] is 0.33 Å longer than the S-S single-bond of H_2S_2[26]. The standard (octet) Lewis structure (**19**)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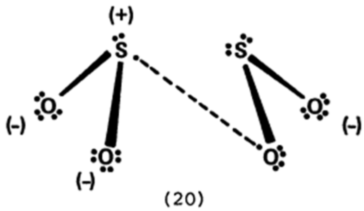
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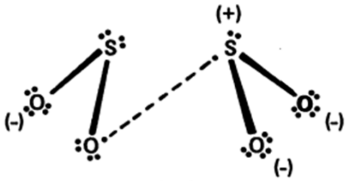
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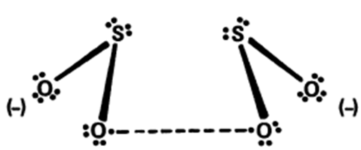
(22)

has a lone-pair of electrons on each of the sulphur atoms, and these should be responsible for the non-planarity (cf. non-planar :NH_3 and :SO_3^{2-} each of which has a lone-pair of electrons on the nitrogen or sulphur atom). Because of the non-planarity, the lone-pair 2pπ and 2p$\bar{\pi}$ orbitals on each oxygen atom can both overlap with the atomic orbitals that form the S-S σ-bond of structure (**19**). The S^+ of this structure should be strongly electronegative relative to the O^-, thereby inducing appreciable delocalization of the oxygen π and $\bar{\pi}$ electrons into the antibonding S-S σ^* orbital. An S-S σ-bond-order which is rather less than unity will then result, and so the S-S bond will be lengthened substantially relative to the single-bond length[12a].

A Lewis-type valence-bond explanation[27] for the existence of a long S-S bond in $S_2O_4^{2-}$ is the following. On dimerization of the SO_2^- valence-bond structures (**24**) and (**26**) of Section 6-3 (with a sulphur atom replacing the central oxygen atoms of these structures), we obtain the Lewis structures (**19**)-(**22**). The nature of the formal charge distributions - particularly that of structure (**22**) - implies that the "long- bond" structures (**20**)-(**22**) with no S-S bonds should have appreciable weights. One consequence is that the S-S bond-number for $S_2O_4^{2-}$ must be rather less than unity, and the S-S bond is therefore substantially longer than a single bond.

In structure (**22**), the sulphur orbitals that form the S-S σ-bond of structure (**19**) are both doubly-occupied. As is the case for N_2O_4 (Section 7-1), the resulting non-bonded repulsions must contribute to some of the lengthening of the S-S bond.

7-5 B_2Y_4 (Y = F, Cl or Br), N_2F_4 and P_2F_4

The **A-A** bond-lengths for some A_2Y_4 systems, with **A** ≡ B, N or P, and **Y** ≡ halogen, are reported in Table 7-1. These lengths are a little longer than the single bonds of B_2H_4, N_2H_4 and P_2H_4, and may be attributed to a small amount of delocalization of halogen pπ electrons into the antibonding **A-A** σ^* orbitals that are vacant in the Lewis structures (**23**)-(**25**).

Table 7-1: A-A bond-lengths for A_2H_4 and A_2Y_4 (Y = halogen) molecules.

B_2H_4	1.644[a],1.619[b]	N_2H_4	1.453[d]
B_2F_4	1.720[c]	N_2F_4	1.489[e], 1.495[f]
B_2Cl_4	1.702[c]	P_2H_4	2.216[g]
B_2Br_4	1.689[c]	P_2F_4	2.281[h]

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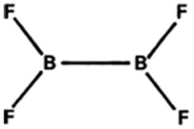

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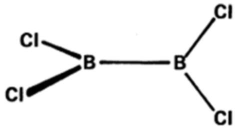

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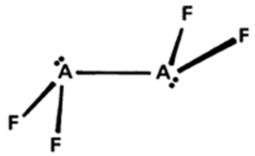

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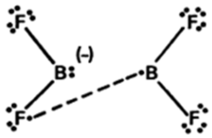

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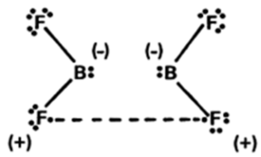

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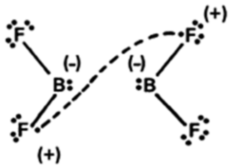


(28)

Alternatively, the odd electron for each of the AY_2 monomers (Table 6-1) is not localized entirely in a boron, nitrogen or phosphorus atomic orbital, and on dimerization an incomplete electron-pair bond is formed between pairs of these atoms. Consequently, valence-bond structures of the types (**26**)-(**28**) for B_2F_4, for example, must also contribute slightly to the ground-state resonance description of the electronic structure. If dimerization is assumed to involve solely the spin-pairing of the odd-electrons of the monomers, then a boron odd-electron charge of 0.93 for BF_2 generates a weight (Section 7-1) of 0.86 for structure (**23**), i.e. the B-B bond-number is 0.86.

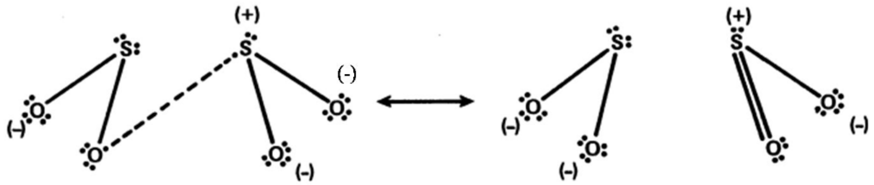
For NF_2 and PF_2, the odd-electrons occupy π-electron molecular orbitals (cf. Section 6-4), but spin-pair to form σ-bonds in the dimers. Therefore it may be less appropriate to obtain realistic estimates of the A-A bond-numbers for N_2F_4 and P_2F_4 from the odd-electron charges of the monomers. However, they should provide a qualitative guide to the relative importance of the different types of structures.

In the gas phase, B_2F_4 is planar, and B_2Cl_4 and B_2Br_4 have perpendicular conformations; experimental estimates (Ref. (c) of Table 7-1) of the rotation barriers relative to the most stable conformers are 1.8, 7.7 and 12.1 kJ mol^{-1}.

From *ab-initio* molecular orbital studies, Clark and Schleyer[16] have concluded that π-electron effects stabilize the planar conformation for B_2F_4, whereas hyperconjugation across the B-B bond of B_2Cl_4 helps stabilize the perpendicular conformation.

7-6 The Geometries of P_2F_4 and $S_2O_4^{2-}$

The $S_2O_4^{2-}$ anion has an eclipsed geometry, whereas isoelectronic P_2F_4 is *trans*, as in structures (**19**) and (**25**), respectively. Similarly, P_2H_4 has a *trans* geometry. For P_2F_4, "long-bond" structures similar to structures (**20**)-(**22**) with formal +ve charges on either one or two of the fluorine atoms, must have much smaller weights than do those for $S_2O_4^{2-}$; the monomer odd-electron charges (Table 6-1) give weights for these structures of 0.19, 0.19 and 0.03 for $S_2O_4^{2-}$ and 0.08, 0.00 and 0.00 for P_2F_4. The staggered *trans* geometries for P_2F_4 and P_2H_4 are due primarily to the non-bonded repulsions between the phosphorus lone-pair electrons (Section 3-10) and repulsions between net charges on the fluorine and hydrogen atoms. Similar effects for $S_2O_4^{2-}$ might be overcome by covalent-ionic resonance of the type (**21**) ↔ (**29**), (cf. (**4**) ↔ (**10**) for N_2O_4), which could introduce a significant *cis* O-O overlap stabilization energy. Due to the much smaller weight for covalent eclipsed (or staggered) structures of type (**30**)



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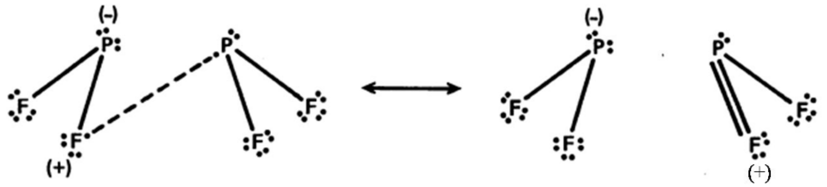


(30) (31)

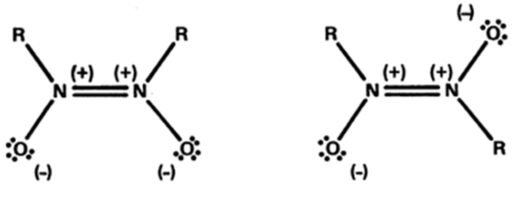
for P_2F_4, a *cis* F-F overlap stabilization energy through the resonance (**30**) ↔ (**31**) will be of negligible importance for this molecule, and cannot operate for P_2H_4. Similar theory accounts for the existence of *trans* and *gauche* rather than eclipsed conformers for N_2F_4.

It has been suggested[25] that structures of type (**22**) should help stabilize the eclipsed conformation for $S_2O_4^{2-}$. However, as is the case for structure (**6**) for N_2O_4, the *cis* O-O bond of structure (**22**) must have negligible strength; its bond-length is 2.86 Å.

7-7 C-Nitroso Dimers and S_4N_4

In their standard Lewis structures (**1**) and (**19**), both N_2O_4 and $S_2O_4^{2-}$ carry positive formal charges on the adjacent nitrogen and sulphur atoms. The presence of such charges helps to induce considerable delocalization of oxygen lone-pair electrons into an antibonding σ^*-orbital between the nitrogen or sulphur atoms, with a consequent lengthening of the N-N and S-S bonds relative to single-bond lengths. A similar arrangement of positive formal charges occurs in the standard Lewis structures for a number of other molecular systems[6, 12a, 28-30] and we shall discuss two examples here, namely the C-nitroso dimers $(RNO)_2$ (R = alkyl or aryl) and S_4N_4.

The standard Lewis structures for these molecules, structures (**32**) and (**33**),



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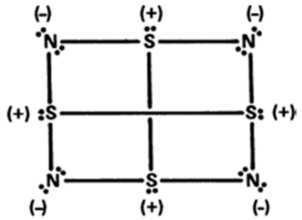
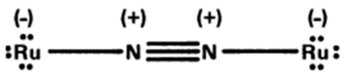


(33)

carry positive formal charges on the adjacent nitrogen and sulphur atoms, respectively. If we assume that the greater electronegativity of the N^+ and S^+ relative to the O^- and N^- leads to appreciable delocalization of the O^- and N^- lone-pair electrons into the antibonding N-N π^* and S-S σ^* orbitals that are vacant in structures (**32**) and (**33**), we can explain the observed lengthenings of the N-N and S-S bonds relative to double and single bond lengths. For a number of C-nitroso dimers, the N-N bond-lengths range in value between 1.30 Å and 1.32 Å[31]; the length of an N-N double bond (as in $CH_3N=NCH_3$) is 1.24 Å. For S_4N_4, the S-S bond-lengths of 2.58 Å[32] may be compared with the S-S single-bond length of 2.06 Å.

Other systems with adjacent positive charges in their standard Lewis structures include $Ru(II)-N_2-Ru(II)$ and S_2O_2. Two of their standard Lewis structures are (**34**) and (**35**),



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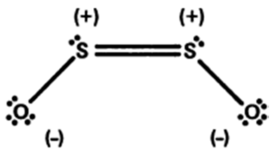

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and the bonding for these systems is discussed in Sections 18-2 and 11-7.

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Addendum Chapter 7

Additional references on conformational studies for N_2O_4, $S_2O_4^{2-}$ and *cis* and *trans* nitroso (and CHO) dimers include:

33. R.D. Harcourt, (a) Chem. Phys. Letts. **218**, 175 (1994). (b) and F.L. Skrezenek, J. Phys. Chem. **94**, 7007 (1990).(c) and B.J. Smith and C.J. Marsden, Aust. J. Chem. **37**, 1553 (1984) (d) and F.L. Skrezenek and B.G. Gowenlock, J. Mol. Struct. (Theochem) **284**, 87 (1993).
34. (a) Y. Mo, W. Wu and Q. Zhang, J. Mol. Struct. (Theochem) 315, 173 (1994). (b) Y. Mo and Q. Zhang, Int. J. Quantum Chem., **56**, 19 (1995)

Chapter 8 Some Cu(II) Binuclear Transition-Metal Complexes

With little modification, we may use the N_2O_4 valence-bond and molecular orbital theory of Sections 7-1 and 7-2 to examine the magnetic behaviour for some binuclear Cu(II) complexes with $(3d)^9$ configurations for the Cu^{2+} ions. As examples, we shall consider the Cu(II)-carboxylate, Cu(II)-chloro and Cu(II)-hydroxo dimers $(Cu_2(RCO_2)_4, L_n$ with n = 0 or 2, and $Cu_2X_2^{2+}$ with X = Cl or OH. Their geometries are displayed in Figure 8-1. Initially we shall not include the copper 4s and 4p orbitals in the bonding schemes.

8-1 Cu(II) Carboxylate Dimers, $Cu_2(RCO)_4L_n$

8-1(a) Valence-Bond Structures For those Cu(II) carboxylate dimers that have the geometries displayed in Figure 8-1, singly-occupied $3d_{x^2-y^2}$ orbitals of the Cu^{2+} ions can overlap with a lone-pair atomic orbital on each of the oxygen atoms of the carboxylate ligands, as shown in Figure 8-2 for two ligands. The $3d_{x^2-y^2}$ orbitals also overlap with each other to form a very weak δ-bond[4]. In Fig. 8-2, each O-Cu(II)-O moiety involves five electrons and three overlapping atomic orbitals, as is also the case for NO_2 and both O-N-O linkages of N_2O_4 (see Figs. 6-1 and 7-2). The Cu^{2+} ions of Cu(II) carboxylate dimers are equivalent[5] to the nitrogen atoms of NO_2 and N_2O_4. Therefore, for each O-Cu(II)-O moiety, with one unpaired or magnetic electron, we can write down Lewis structures of the types (**1**), (**2**) and (**3**); resonance between them may be summarized by using the Pauling "3-electron bond" structures (**4**) and (**5**).

R.D. Harcourt, *Bonding in Electron-Rich Molecules*,
Lecture Notes in Chemistry 90, DOI 10.1007/978-3-319-16676-6_8

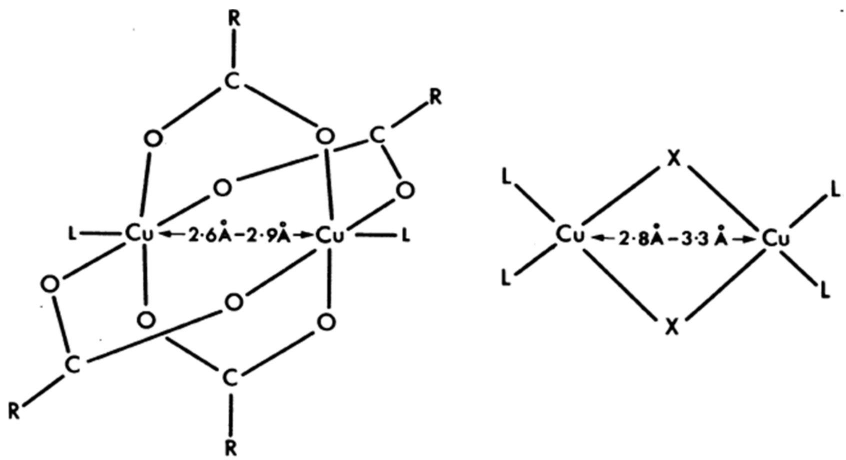
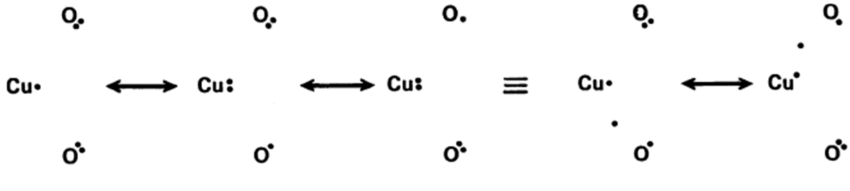


Figure 8-1: Geometrical structures for some Cu(II) carboxylate, hydroxo and chloro dimers.



(1) (2) (3) (4) (5)

The atomic orbitals for each O-Cu(II)-O moiety of Figure 8-2 overlap weakly with those of the other moiety which involves the same RCO_2^- ligands. Therefore, the delocalized magnetic electrons of the two moieties may be spin-paired to generate the S = 0 valence-bond structures[i] of the types (**6**)-(**9**) (together with equivalent mirror-image structures). These structures have the same distribution for the delocalized bond (•----•) as have the N_2O_4 structures (**3**)-(**7**) of Section 7-1. With respect to each O-N-O or O-Cu(II)-O moiety, both sets of structures are of the "covalent" type.

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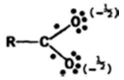
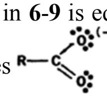
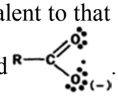
[i] With respect to formal charge distribution, the Linnett structure (Section 2-2)  that we have used for the carboxylate linkages in **6-9** is equivalent to that obtained from resonance between the standard Lewis structures  and .

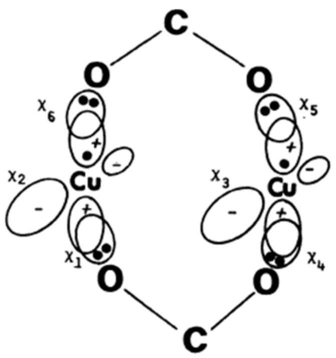
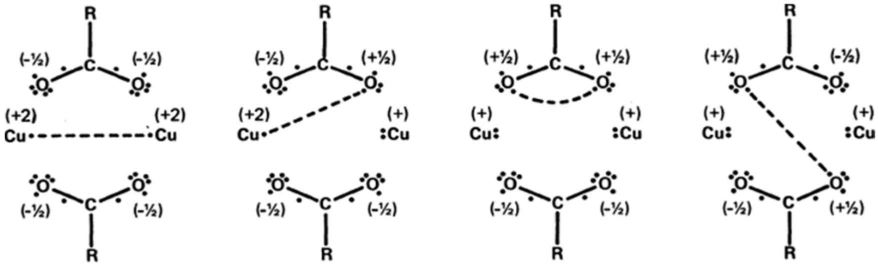


Figure 8-2: Overlap of copper $3d_{x^2-y^2}$ orbitals with oxygen lone-pair orbitals of two carboxylate ligands[5]. The overlap between the copper orbitals generates Cu-Cu δ bonding.

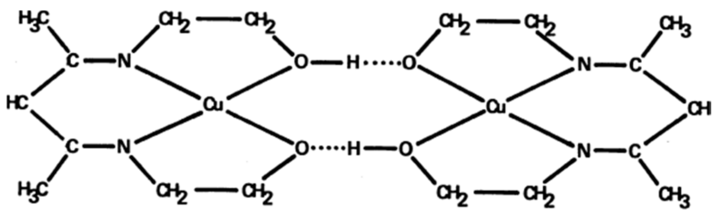


(6) (7) (8) (9)

The Cu-Cu δ-bond of valence-bond structure (**6**) corresponds to the N-N σ-bond of valence-bond structure (**3**) in Section 7-1. However, whereas the overlap integral involving the nitrogen hybrid orbitals of Figure 7-2 has an appreciable magnitude (∽0.3), the overlap integral for the copper $3d_{x^2-y^2}$ orbitals of Figure 8-2 is very small[4, 6] (0.003-0.01). If it is assumed that the magnetic electrons of the Cu(II) carboxylate dimers are localized entirely in these copper orbitals, only a very weak Cu-Cu interaction can occur[4-8]. The results of some molecular orbital calculations[7] indicate that the magnetic electrons can be significantly located in the oxygen as well as the copper atomic orbitals (as occurs in valence-bond structures (**7**)-(**9**)), and that the overlap between each pair of cis-oxygen atomic orbitals (overlap integral for sp^2 hybridization = 0.012) provides a stronger spin-coupling of the two magnetic electrons than does the $3d_{x^2-y^2} - 3d_{x^2-y^2}$ overlap. However, as we shall discuss in Section 8-1(c), the concomitant bonding interaction between two O-Cu(II)-O moieties arises primarily from covalent-ionic resonance of the Pauling "3-electron bond" type (cf. Section 7-3) rather than from the spin-pairing of the unpaired-electrons in the covalent structures.

8-1 (b) The Antiferromagnetism of Cu(II) Carboxylate Dimers Because the overlap between the atomic orbitals of two O-Cu(II)-O moieties is small, the spin-pairing of the two delocalized magnetic electrons to generate an $S = 0$ spin-state with antiparallel (↑↓) spins for the two electrons is weak. Little energy is required to uncouple their spins to generate an $S = 1$ spin excited state with parallel (↑↑) spins for these electrons. Measurements of the temperature-dependent magnetic susceptibilities for a large number of Cu(II) carboxylate dimers[2, 9] indicate that for each of these complexes an $S = 1$ spin excited state lies only ∽ 100-500 cm^{-1} (1-6 kJ mol^{-1}) above the $S = 0$ spin ground-state[ii]. In Table 8-1, we have reported energy separations (via $-2J \equiv E(S = 1) - E(S = 0)$) for a selection of these compounds. By contrast, the much larger overlap which exists between the nitrogen atomic orbitals that form the N-N σ-bond of N_2O_4 helps to generate a relatively stronger spin-coupling for the unpaired-electrons of the two NO_2 moieties. The dissociation energy of 57 kJ mol^{-1} for N_2O_4 (Section 7-1) reflects the stronger coupling relative to what occurs for the Cu(II) carboxylate dimers.

In Table 8-1, the lack of correlation that exists between the Cu-Cu bond-lengths and the energy separation between the $S = 0$ and $S = 1$ spin states suggests that the Cu-Cu δ bonding is not the primary antiferromagnetic interaction that occurs between the odd-electrons of the O-Cu(II)-O moieties. If it were, then a lengthening of the Cu-Cu bond would decrease the energy separation, because the overlap between the $3d_{x^2-y^2}$ orbitals would be smaller. It may also be noted that in Cu(II) complexes of amino alcohols (**10**), the Cu(II) ions are[10] separated by 4.94Å, and therefore for these complexes, no antiferromagnetic coupling could arise through spin pairing of the magnetic electrons if these electrons are located solely in the $d_{x^2-y^2}$ orbitals. However, $-2J$ has a value[10] of +95 cm^{-1}. This can only arise through *cis* O-O overlap, and the concomitant $S = 0$ spin stabilization becomes operative when oxygen lone-pair electrons delocalize into the $d_{x^2-y^2}$ orbitals in a manner identical with that described for the Cu(II) carboxylate dimers. In general, if the primary interaction between the odd-electrons occurs via some of the orbitals of the bridging ligand rather than through overlap of the metal-ion orbitals, the mechanism for the interaction is designated as a "superexchange" mechanism[11].



(10)

[ii] Because the $S = 1$ spin states are thermally accessible, these dimers exhibit antiferromagnetic behaviour. For some of the Cu(II)-hydroxo and chloro dimers of Section 8-2, the ground-states have $S = 1$ spin-states, and excited $S = 0$ spin-states are thermally accessible. When this occurs, the complex is ferromagnetic.

Table 8-1: Cu-Cu bond-lengths and –2*J* for dimeric copper (II) carboxylates, $Cu_2(RCO_2)_4$, L_n, with *n* = 0 or 2.

R	L	Cu–Cu (A)	–2*J*(cm^{-1})
H	1/2 dioxan	2.58	+555
H	NCS^-	2.716	+485
H	Urea	2.657	----
CH_3	H_2O	2.614	+284
CH_3	H_2O	2.616	+284
CH_3	Pyridine	2.630	+325
CH_3	Pyridine	2.645	----
CH_3	Quinoline	2.642	+320
CH_3	NCS^-	2.643	+305
CH_3	urea	2.637	---
C_2H_5	---	2.578	+300
C_3H_7	---	2.565	+322
CH_2Cl	α picoline	2.747	+ 321
CF_3	quinoline	2.886	+310
Succinate	H_2O	2.610	+330
o–BrC_6H_4	H_2O	2.624	+250
Acetyl Salicylate	----	2.617	+340

8-1 (c) Covalent-Ionic Resonance and the Antiferromagnetism of Cu(II) Carboxylate Dimers Because of the small overlap that exists between atomic orbitals located on non-adjacent atomic centres, the "long" Cu   O and O   O covalent bonds of valence-bond structures (**7**)-(**9**) have negligible strengths. Therefore these structures are essentially degenerate with the corresponding *S* = 1 spin structures that have parallel spins for the two magnetic electrons. Similarly the small overlap between the $d_{x^2-y^2}$ orbitals for the Cu•----•Cu bond of structure (**6**) renders this structure almost degenerate with the corresponding *S* = 1 spin structure. We can demonstrate these types of near-degeneracies by calculating -2*J* for two hydrogen atoms separated so that the overlap between the 1s orbitals is 0.01. A value of –2*J* = 7 cm^{-1} is thereby obtained[12] by using tabulated values for the integrals[13]. A much larger stabilization of 240 cm^{-1} is obtained when the *S* = 0 spin covalent structure **H—H** participates in resonance with the ionic structures $\mathbf{H^+}$ $\mathbf{:H^-}$ and $\mathbf{H:^-}$ $\mathbf{H^+}$. For H_2, the covalent-ionic resonance involves the two electrons that form the electron-pair bond. In Section 7-3, we have described how covalent-ionic resonance of the Pauling "3-electron bond" type (**O• :O ↔ O: •O**) in particular, leads to a substantial cis O-O overlap stabilization of the planar conformation for

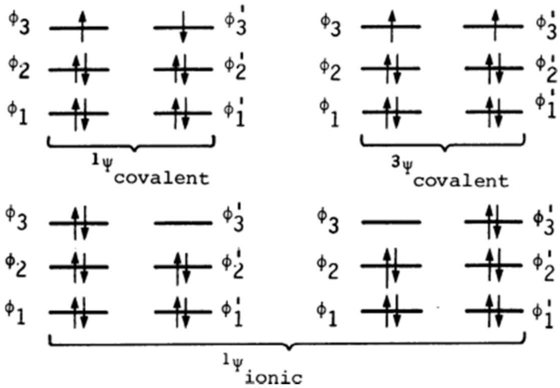


Figure 8-3: Covalent and ionic configurations for two O-Cu-O moieties.

N_2O_4. Similar types of covalent-ionic resonance are also responsible[7,14] for the cis O-O overlap stabilization of the $S = 0$ spin state for the Cu(II) carboxylate dimers. This is most easily demonstrated by using molecular orbital descriptions for a pair of O-Cu(II)-O moieties, in the following manner.

For each O-Cu-O moiety, the molecular orbitals are given by Eqn. 6-1, in which y and b are oxygen atomic orbitals (e.g. χ_1 and χ_6, or χ_4 and χ_5 of Figure 8-2), and a is the copper orbital χ_2 or χ_3. We shall designate these 3-centre molecular orbitals here as $\varphi_i\,(i = 1-3)$ and $\varphi_i'\,(i = 1-3)$, and construct the $S = 0$ and $S = 1$ spin configurations of Figure 8-3 for the ten electrons. In them, the two magnetic electrons are located in the Cu-O antibonding molecular orbitals φ_3 and φ_3'. If it is assumed that the $S = 0$ and $S = 1$ spin configurations ${}^1\Psi_{\text{covalent}}$ and ${}^3\Psi_{\text{covalent}}$ are degenerate, then the degeneracy can be removed through covalent-ionic resonance for the $S = 0$ spin state, i.e. by construction of the wave-function

$$ {}^1\Psi = {}^1\Psi_{\text{covalent}} + \lambda\,{}^1\Psi_{\text{ionic}} \tag{1} $$

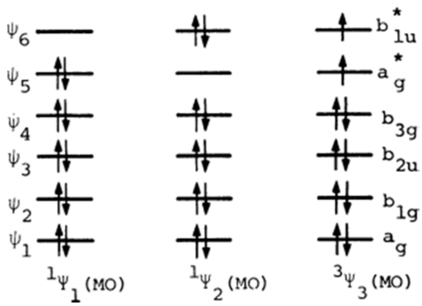
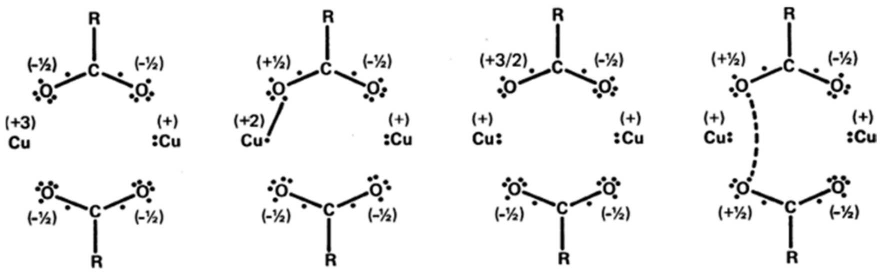


Figure 8-4: 6-centre molecular orbital configurations for two O-Cu-O moieties.

At this level of approximation, the S = 1 spin state involves no ionic components. Small S = 1 spin ionic contributions do enter through consideration of excited configurations, but any additional stabilization of ${}^{3}\Psi_{\text{covalent}}$ through interaction with them will be of less importance than is that which arises for the S = 0 spin state through interaction of ${}^{1}\Psi_{\text{covalent}}$ with ${}^{1}\Psi_{\text{ionic}}$. The calculations of Ref. 7 provide a further illustration of this point.

We have already indicated that the valence-bond structures which contribute to ${}^{1}\Psi_{\text{covalent}}$ are of types (**6**)-(**9**), together with their equivalent forms. Similar structures with parallel spins for the two magnetic electrons contribute to ${}^{3}\Psi_{\text{covalent}}$. For ${}^{1}\Psi_{\text{ionic}}$, the component valence-bond structures are of types (**11**)-(**14**). The *cis* O-O overlap that has been calculated[7] to be of primary importance for stabilization of the S = 0 spin state will manifest itself in covalent-ionic resonance of the types (**7**) ↔ (**12**), (**8**) ↔ (**13**) and (**9**) ↔ (**14**). The arrangements of formal charges for these structures indicate that the energy differences $E_{12} - E_7$ and $E_{14} - E_9$ will have smaller magnitudes than has $E_{13} - E_8$. Therefore the resonances of types (**7**) ↔ (**12**) and (**9**) ↔ (**14**) should be primarily responsible for the antiferromagnetism. These two resonances are of the Pauling "3-electron bond" type, i.e. they involve $\mathrm{O}{:}\quad {\bullet}\mathrm{O} \leftrightarrow \mathrm{O}{\bullet}\quad {:}\mathrm{O} \equiv \mathrm{O}{\bullet}\ {\bullet}\ {\bullet}\mathrm{O}$.



(**11**) (**12**) (**13**) (**14**)

In the addendum for this chapter, the contribution to antiferromagnetism that arises from the overlap between the nearest-neighbour copper and oxygen atomic orbitals is discussed.

8-1(d) Covalent-ionic Resonance and Approximate 6-Centre Molecular Orbitals The covalent-ionic resonance described in the previous section may be related to an approximate 6-centre molecular orbital treatment for a pair of O-Cu(II)-O moieties. (The extension to form 10-centre molecular orbitals requires an elaboration of the 6-centre treatment). Because the overlap between the molecular orbitals φ_i and φ_i' of the two moieties is small, it is a good approximation to construct the canonical molecular orbitals (ψ_i) with D_{2h} symmetry by adding and subtracting pairs of equivalent φ_i and φ_i' Thus, ignoring overlap integrals in the normalizing constants, and assuming that the φ_i and φ'_i are normalized, we obtain

$$\psi_1 = (\phi_1 + \phi'_1)/2^{\frac{1}{2}}, \ \psi_2 = (\phi_1 - \phi'_1)/2^{\frac{1}{2}}$$

$$\psi_3 = (\phi_2 + \phi'_2)/2^{\frac{1}{2}}, \ \psi_4 = (\phi_2 - \phi'_2)/2^{\frac{1}{2}} \tag{2}$$

$$\psi_5 = (\phi_3 + \phi'_3)/2^{\frac{1}{2}}, \ \psi_6 = (\phi_3 - \phi'_3)/2^{\frac{1}{2}}$$

The $S = 0$ and $S = 1$ spin canonical molecular orbital configurations ${}^1\Psi_1(\text{MO})$, ${}^1\Psi_2(\text{MO})$ and ${}^3\Psi_3(\text{MO})$ of Figure 8-4 transform with A_g, A_g and B_{1u} symmetries, respectively. By using the identity of Eqn. 3-15 for pairs of electrons with parallel spins – for example

$$\psi_1^\alpha \psi_2^\alpha \equiv -\phi_1^\alpha \phi_1'^\alpha, \ \ \psi_3^\alpha \psi_4^\alpha \equiv -\phi_2^\alpha \phi_2'^\alpha \text{ and } \psi_5^\alpha \psi_6^\alpha \equiv -\phi_3^\alpha \phi_3'^\alpha$$

it is easy to deduce that

$${}^1\Psi_1(\text{MO}) = {}^1\Psi_{\text{covalent}} + {}^1\Psi_{\text{ionic}} \tag{3}$$

$${}^1\Psi_2(\text{MO}) = -{}^1\Psi_{\text{covalent}} + {}^1\Psi_{\text{ionic}} \tag{4}$$

$${}^3\Psi_3(\text{MO}) = {}^3\Psi_{\text{covalent}} \tag{5}$$

Configuration interaction (Section 3-3) is possible between the $S = 0$ spin configurations, to give

$$\Psi(\text{CI}) = C_1\,{}^1\Psi_1(\text{MO}) + C_2\,{}^1\Psi_2(\text{MO}) \tag{6}$$

$$\equiv (C_1 - C_2)\,{}^1\Psi_{\text{covalent}} + (C_1 + C_2)\,{}^1\Psi_{\text{ionic}} \tag{7}$$

In Section 10-3, the configuration interaction theory is described for (symmetrical) 6-electron 4-centre bonding units using non-approximate canonical molecular orbitals.

8-2 Cu(II)-X-Cu(II) Linkages

The 4-electron 3-centre bonding for linear triatomic **M**-**X**-**M** linkages has received much attention since it was first described by Kramers[11]. For this type of linkage, each **M** is a paramagnetic cation with a singly-occupied orbital that overlaps with a doubly-occupied orbital of a closed-shell anion **X** (cf. Figure 2-4 for $Ni^{2+}O^{2-}Ni^{2+}$). The paramagnetic cations are too widely separated for their orbitals to overlap significantly, and the phenomenon of superexchange (Section 8-1), i.e. the delocalization of electrons from the doubly occupied ligand orbital into the singly occupied cation orbitals, has been invoked to account for the observed antiferromagnetism of solids such as NiO and $KNiF_3$ with linear **M**-**X**-**M** linkages.

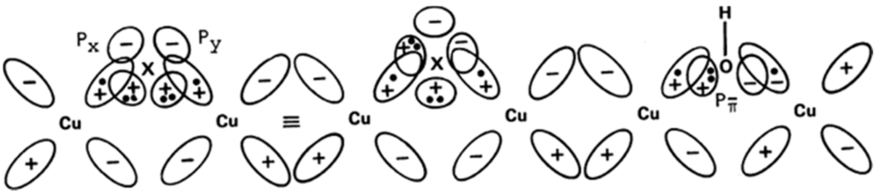


Figure 8-5: Atomic orbitals for Cu(II)-Cl-Cu(II) and Cu(II)-OH-Cu(II) linkages. The d-orbital for each Cu(II) ion may involve some hybridization with other d-orbitals; see for example Ref. 27.

In numerous binuclear transition metal complexes with **M**-**X**-**M** linkages, the **M**-**X**-**M** bond-angles deviate appreciably from 180°. For non-linear **M**-**X**-**M** linkages, a 6-electron 3-centre bonding unit can be established, as shown in Figure 8-5 for a Cu(II)-Cl-Cu(II) linkage of $Cu_2Cl_6^{2-}$. The singly-occupied orbital of the metal ion can overlap simultaneously with two orthogonal p orbitals on each ligand. Both ferro and antiferromagnetic complexes have been characterized. In Tables 8-2 and 8-3, we have reported experimental estimates of the values for the singlet-triplet energy separation ($-2J$) for some Cu(II)-OH-Cu(II) and Cu(II)-Cl-Cu(II) complexes. For the hydroxo-complexes, a near linear relationship has been found to exist[3] between the M-OH-M bond-angle and $-2J$. (Some exceptions to this linear relationship have also been reported[20].) We shall now give consideration to different types of theories that have been invoked to rationalize the variation in magnetic behaviour with bond-angle for **M**-**X**-**M** linkages.

(a) van Kalkeren, Schmidt and Block[16] have shown that if the **M**-**X**-**M** linkage is treated as a 4-electron 3-centre bonding unit for all bond-angles, the wave function for the valence-bond structure $\mathbf{M}\cdot\ :\ddot{\underset{\cdot\cdot}{\mathbf{X}}}\cdot\ \cdot\mathbf{M}$ exhibits ferromagnetic coupling for the metal-ion electrons when the bridging bond-angle is around 90°, and antiferromagnetic coupling for rather smaller and larger bond-angles. In these calculations, full account is taken of the overlap that exists between the ligand and metal-ion orbitals, and no superexchange seems to be involved in the treatment.

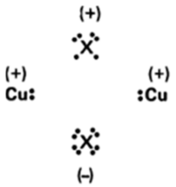
Table 8-2: -2J and Cu-OH-Cu bond-angle for Cu(II) hydroxo-bridged dimers (bpy = 2,2′-bipyridine, eaep = 2-(2-ethylaminoethyl)pyridine, dmaep = 2-(2-dimethylaminoethyl) pyridine, tmen = N, N, N′, N′-tetramethylethylenediamine, teen = N, N, N′, N′-tetraethylethylenediamine).

	$-2J(\mathrm{cm}^{-1})$	$\Theta(^{\circ})$
$[\mathrm{Cu(bpy)OH}]_2(\mathrm{NO_3})_2$	-172	95.6 (1)
$[\mathrm{Cu(bpy)OH}]_2(\mathrm{ClO_4})_2$	-93	96.9 (2)
$[\mathrm{Cu(bpy)OH}]_2\mathrm{SO_4}\cdot 5\mathrm{H_2O}$	-49	97.0 (2)
$[\mathrm{Cu(eaep)OH}]_2(\mathrm{ClO_4})_2$	+130	98.8-99.5 (3)
$\beta-[\mathrm{Cu(dmaep)OH}]_2(\mathrm{ClO_4})_2$	+200	100.4 (1)
$[\mathrm{Cu(tmen)OH}]_2(\mathrm{ClO_4})_2$	+360	102.3 (4)
$[\mathrm{Cu(teen)OH}]_2(\mathrm{ClO_4})_2$	+410	103.0 (3)
$[\mathrm{Cu(tmen)OH}]_2\mathrm{Br_2}$	+509	104.1 (2)

The S = 0 spin valence-bond structure  is an example of a "long-bond" structure. A similar type of magnetic behaviour has been calculated by these workers using the molecular orbital procedures described in Refs. 8, 14 and 19 for the 4-electron 3-centre bonding unit.

(b) If the M-X-M linkages are treated as 6-electron 3-centre bonding units, an understanding of the magnetic behaviour must involve the following types of superexchange considerations[14], for which the Goodenough-Kanamori theories[21-28] provide particular examples.

For the Cu(II) carboxylates, the $^1\Psi_{\text{covalent}}$ and $^3\Psi_{\text{covalent}}$ configurations of Figure 8-3 are essentially degenerate (Section 8-1 (b)) if the very weak overlap that exists between the orbitals of two O-Cu-O moieties is neglected. However, for the Cu(II)-X dimers, $^3\Psi_{\text{covalent}}$ must have significantly lower energy than $^1\Psi_{\text{covalent}}$. This is primarily because although the two p-orbitals of each bridging ligand are orthogonal, the one-centre exchange integral $\iint \mathrm{p_x}(1)\mathrm{p_y}(2)\mathrm{r}_{12}^{-1}\mathrm{p_y}(1)\mathrm{p_x}(2)\mathrm{d}v_1\mathrm{d}v_2$ has appreciable magnitude. Consequently, if the p-orbitals become singly-occupied, as in valence-bond structure (**15**), Hund's rule of maximum spin multiplicity (Section 1-2) requires that the electron spins be parallel in the lowest-energy state. Valence-bond structures of type (**15**), together with structures of types (**16**)-(**18**), are those that contribute to the $^1\Psi_{\text{covalent}}$ and $^3\Psi_{\text{covalent}}$ of Figure 8-3. The contribution of structure (**15**) with parallel spins to $^3\Psi_{\text{covalent}}$ ensures that this latter function has a lower energy than has $^1\Psi_{\text{covalent}}$ alone (with antiparallel spins for the two magnetic electrons of valence-bond structures of types (**15**)-(**18**)). Therefore consideration of $^3\Psi_{\text{covalent}}$ and $^1\Psi_{\text{covalent}}$ leads to the prediction that Cu(II)-X dimers



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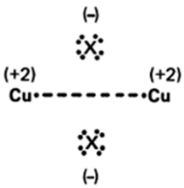

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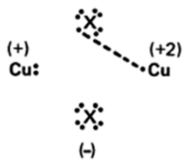

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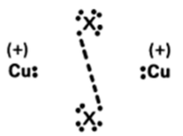

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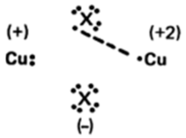

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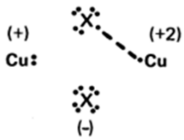

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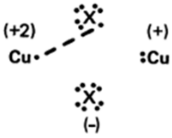

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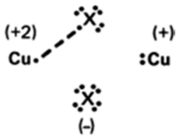

(21)

Table 8-3: $-2J$ and bridging Cu–Cl–Cu bond angle for Cu(II) chloro dimers. From R.D. Willett, Chem. Comm. 607 (1973) and R.F. Drake, V.H. Crawford, N.W. Laney and W.E. Hatfield, Inorg. Chem. **13,** 1246 (1974). [a] DMG = dimethylgloximine [b] Guan = guaninium [c] 2 – Me(py) = 2 – methylpyridine .

	$-2J(\mathrm{cm}^{-1})$	**Θ(°)**
$[(DMG)CuCl_2]_2^a$	-6.3	88
$[Ph_4AsCuCl_3]_2$	-33	93.6
$[LiCuCl_3,\ 2H_2O]_2$	>0	95.1
$Cu_2Cl_8^{4-}$	+14.6	95.2
$[Me_2NH_2CuCl_3]_2$	+5	95.6
$[KCuCl_3]_2$	+55	95.9
$[(Guan)CuCl_3]_2^b 2H_2O$	+82.6	98
$[(2-Me(py))_2CuCl_2]_2^c$	+7.4	101.4

have ferromagnetic ground-states, if each of the structures (**15**)-(**18**) participates in resonance for both the $S = 0$ and $S = 1$ spin states. However, ${}^1\Psi_{\text{covalent}}$ can interact with ${}^1\Psi_{\text{ionic}}$, and some stabilization of ${}^1\Psi_{\text{covalent}}$ may then occur[i].

Thus, according to this 6-electron 3-centre analysis for Cu(II)-**X**-Cu(II) complexes, there is a competition between an tendency for ferromagnetism due to a preference for parallel spins in valence-bond structures of type **15**, and a tendency for antiferromagnetism when the $S = 0$ spin "covalent" structures of types **17** and **20** participate in resonance with $S = 0$ spin "ionic" structures of types **19** and **21**. Whichever has the greater tendency for a particular complex will determine the magnetic properties of the ground-state.

For angular Cu-**X**-Cu linkages, the simplest type of Goodenough-Kanamori theory involves resonance between "covalent" structures of types (**16**) and (**17**). Calculations of this type (together with the mirror-image for structure (**17**), namely (**20**)) have been reported by Barraclough and Brookes[30].

The 6-electron 3-centre bonding scheme for Cu(II)-**X**-Cu(II) linkages with **X** = halide or O^{2-}, is also appropriate for **X** = OH^- if it is assumed that two equivalent p-orbitals of OH^- accommodate the lone-pairs of electrons. The O-H σ-bond of HO^- must then utilize the oxygen 2s orbital for bonding. The oxygen (O^-) valence-state now involves the promoted sp^6, V_1 configuration. If it is considered that the non-promoted s^2p^2, V_1 configuration is the primary valence-state configuration (as it would be in free OH^-), then the primary oxygen orbital involved in the 3-centre bonding is the $2p\bar{\pi}-\text{orbital}$ of Figure 8-5. The 4-electron 3-centre bonding theory then becomes relevant for the Cu(II)-OH-Cu(II) linkages.

For both types of Cu(II) complexes of this chapter, we have not given consideration to the utilization of the copper 4s and 4p orbitals for bonding to the oxygen atoms of the carboxylate, hydroxo and chloride ligands. If these orbitals are included, Pauling "3-electron bond" theory is still appropriate for the valence-bond descriptions of the bonding. Geometrical requirements would require the utilization of (approximately) dsp^2 hybrid orbitals of Cu^{2+}. Prior to bonding to the ligands, three of these orbitals are vacant, and one is singly-occupied. Because each Cu^{2+} ion of either complex is involved in bonding to four oxygen or halide ligand atoms (see Fig. 8-1), it can participate in the formation of three electron-pair bonds and one Pauling "3-electron bond", as shown in valence-bond structure (**22**), for example. The Cu(II) carboxylate and Cu(II) hydroxo or chloro dimers are, therefore, examples of *hypoligated* complexes (Section 5-1). In the discussion of this chapter, we have omitted the 4s and 4p orbitals, because the odd-electron charge in a copper orbital is considered to be primarily 3d in character.

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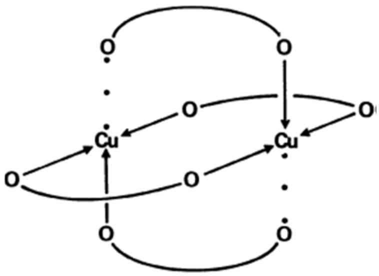
[i] This must include at least the overlap between the oxygen and copper atomic orbitals that are singly-occupied in structures of types (**17**) and (**20**). This overlap is non-zero when the Cu-**X**-Cu bond-angle is not equal to 90°. For Cu(II)-Cl-Cu(II) linkages, this overlap is the only type between the Cu(II)-Cl moieties that can be non-negligible in magnitude; the Cu-Cu distances, which are greater than 3.2 Å are too large for the copper orbitals of Figure 8-5 to overlap significantly.



(22)

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Addendum Chapter 8

The covalent-ionic resonance valence bond theory for the origin of the antiferromagnetism of the Cu^{II} carboxylate dimers described in Sections 8-1(c) is appropriate when nearest-neighbour Cu-O overlap integrals are omitted. When these integrals are included[31,32], the theory has been modified[32(c,d)] as follows. We restrict our attention to the origin of the antiferromagnetism for one $Cu^{II}(RCOO^-)Cu^{II}$ component of the dimer.

The primary type of $[(CuO)(CuO) \leftrightarrow (CuO)^-(CuO)^+ \leftrightarrow (CuO)^+(CuO)^-]$ covalent-ionic resonance involves the $S = 0$ and $S = 1$ spin VB structures of Fig. 8-22[31,32]. These structures arise from the delocalization of one oxygen lone-pair electron of Figure 8-2 into a singly-occupied copper AO. Because the overlap between the singly-occupied non-adjacent AOs is small, the covalent structures are essentially degenerate, i.e. ${}^3E_{\mathrm{cov}} \approx {}^1E_{\mathrm{cov}} = E_{\mathrm{cov}}$.

Each of the $S = 0$ spin ionic structures involves a nearest-neighbour Cu–O electron-pair bond. It has been deduced[32(c,d)] that the resulting expression for the magnetic exchange parameter is given approximately by Eqn. (8),

$$J = (\beta_{\mathrm{ad}} + \beta_{\mathrm{bc}})^2 J_{\mathrm{CuO}}/({}^1E_{\mathrm{ion}} - E_{\mathrm{cov}})^2 \tag{8}$$

in which β_{ad} and β_{bc} are O–O and Cu–Cu overlap-dependent resonance integrals, and $J_{\mathrm{CuO}} = \frac{1}{2}\{{}^1E(\mathrm{Cu–O}) - {}^3E(\mathrm{Cu–O})\}$ is the (negative) exchange integral for the nearest-neighbour Cu–O electron-pair bond that is present in each of the $S = 0$ spin ionic structures.

The $S = 0$ spin covalent valence-bond structures **1** and **3** of Fig. 8-6 correspond to the valence-bond structures (**9**) and (**10**) in Section 13-3, in which **A** and **D** are oxygen atoms and **B** and **C** are copper atoms. The ionic structures **2** and **4** of Fig. 8-6 correspond to the structures

$$\overset{\oplus}{\mathrm{A{-}B}} \quad \ddot{\mathrm{C}}\ \overset{\ominus}{}\ \ddot{\mathrm{D}} \qquad \text{and} \qquad \ddot{\mathrm{A}}\ \overset{\ominus}{}\ \ddot{\mathrm{B}} \quad \overset{\oplus}{\mathrm{C{-}D}}$$

here. Of course the covalent structures of types (**8**) and (**11**) in Section 13-3, together with their ionic partners, participate in resonance with structures (**9**), (**10**) and their ionic partners. Altogether there are ten $S = 0$ spin structures. A similar type of covalent-ionic resonance scheme is also appropriate for the six $S = 1$ spin structures, and their contributions to the magnetic exchange parameter will modify Eqn. (1) here. With $\psi_{ab} = a + kb$ and $\psi_{dc} = d + kc$, the simplest expression[32(c,d)] for J is then given by Eqn. (9),

$$J = -2[(\beta_{bc})^2/\{(bb|bb) - (bb|cc)\} - k^2 J_{CuO}(\beta_{bc} + \beta_{ad})^2/\{(aa|bb) - (aa|cc)\}^2 + k^4(\beta_{ad})^2/\{(aa|aa) - (aa|dd)\}]/(k^2 + 1)^2 \qquad (9)$$

in which the (ii|jj) are 2-electron repulsion integrals when the electrons occupy the i and j AOs.

In Eqn. (9), k is the "superexchange" parameter, which measures the extent of delocalisation of electrons from the oxygen AOs (a and d) into the copper AOs (b and c). The ($\mu\mu|\nu\nu$) are (two-electron) Coulomb repulsion integrals which involve a pair of AOs.

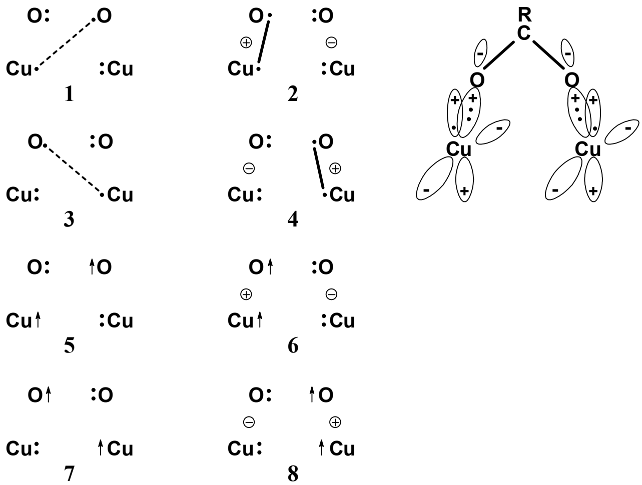

Figure 8-6: Atomic orbitals[32(c,d)] for a 6-centre bonding unit of $Cu^{II}(CH_3COO^-)Cu^{II}$, and the associated primary Lewis-type VB structures for a VB rationalization of the origin of the anti-ferromagnetism of Cu^{II} carboxylate dimers. (Reproduced with permission from Wiley.)

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Chapter 9 Excited States

It is frequently considered that valence-bond theory is not easily adapted to provide qualitative descriptions of molecular excited states. No doubt this is often true. However, for some simple systems, there exists an elementary valence-bond counterpart for each molecular orbital description of the excited state. To demonstrate this point, we shall give consideration here to a few types of electronic excitations.

9-1 $H_2 : \sigma \rightarrow \sigma^*$; $C_2H_4 : \pi \rightarrow \pi^*$

For the H_2 ground-state, the covalent bond for the valence-bond structure **H—H** involves a pair of shared electrons with opposite spins. In Section 3-3, we have discussed the simplest wave-functions that can be associated with the electron-pair bond, namely the molecular orbital and Heitler-London wave-functions of Eqs. (1) and (2) here, in which $1s_A$ and $1s_B$ are a pair of overlapping 1s atomic orbitals. The appropriate spin wave-function for either of these spatial wave-functions is the $S = 0$ spin wave-function of Eqn. (3).

$$\Psi_1(\mathrm{MO}) = \sigma(1)\sigma(2) \text{ with } \sigma = 1s_A + 1s_B \tag{1}$$

$$\Psi_+(\mathrm{HL}) = 1s_A(1)1s_B(s) + 1s_B(1)1s_A(2) \tag{2}$$

$$\psi_{\mathrm{spin}}(S = 0) = \{\alpha(1)\beta(2) - \beta(1)\alpha(2)\}/2^{\frac{1}{2}} \tag{3}$$

Let us now excite an electron from an orbital of each of the two spatial wave-functions, and examine the resulting wave-functions and valence-bond structures. When an electron is excited from the bonding σ-molecular orbital of $\Psi_1(\mathrm{MO})$ into the vacant antibonding orbital $\sigma^* = 1s_A - 1s_B$, we obtain the excited-state

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Lecture Notes in Chemistry 90, DOI 10.1007/978-3-319-16676-6_9

wave-functions of Eqs. (4) and (5), which have respectively parallel and anti-parallel spins for the two electrons. (In Eqs. (4) and (5) the S and S_z spin quantum numbers have the following values: $\Psi_2(\text{MO}): S = 1$, $S_z = 1$, 0 and –1; $\Psi_3(\text{MO}): S = S_z = 0$.)

$$\Psi_2(\text{MO}) = \{\sigma(1)\sigma^*(2) - \sigma^*(1)\sigma(2)\} \times \begin{cases} \alpha(1)\alpha(2) \\ \{\alpha(1)\beta(2) + \beta(1)\alpha(2)\}/2^{\frac{1}{2}} \\ \beta(1)\beta(2) \end{cases} \tag{4}$$

$$\Psi_3(\text{MO}) = \{\sigma(1)\sigma^*(2) + \sigma^*(1)\sigma(2)\} \times \{\alpha(1)\beta(2) - \beta(1)\alpha(2)\}/2^{\frac{1}{2}} \tag{5}$$

If we substitute $1s_A + 1s_B$ and $1s_A - 1s_B$ for σ and σ* into the spatial components of these wave functions, we obtain Eqs. (6) and (7) (with the same spin wave-functions as for Eqs. (4) and (5)).

$$\Psi_2(\text{MO}) \equiv \Psi_-(\text{HL}) = -2\{1s_A(1)1s_B(2) - 1s_B(1)1s_A(2)\} \tag{6}$$

$$\Psi_3(\text{MO}) \equiv \Psi_-(\text{ionic}) = -2\{1s_A(1)1s_A(2) - 1s_B(1)1s_B(2)\} \tag{7}$$

From each of these latter wave-functions, we may generate a valence-bond structure for an excited state. If we designate the two electrons with parallel spins for $\Psi_2(\text{MO})$ as crosses (×), we obtain the valence-bond structure $\overset{\times}{\mathbf{H}}\ \overset{\times}{\mathbf{H}}$ from $\Psi_2(\text{MO})$, because each atomic orbital is singly-occupied. For $\Psi_3(\text{MO})$, the two electrons have opposed spins, and the configurations $1s_A(1)1s_A(2)$ and $1s_B(1)1s_B(2)$ of Eq. (7) locate the two electrons in the same atomic orbital. The resulting valence-bond structures are the ionic structures $\mathbf{H{:}}^{(-)}\ \mathbf{H}^{(+)}$ and $\mathbf{H}^{(+)}\ \mathbf{{:}H}^{(-)}$ and these participate in resonance. The $\Psi_3(\text{MO})$ of Eq. (7) involves a minus (–) linear combination. It is also possible to write down the (+) linear combination, namely the $\Psi_+(\text{ionic})$ of Eqn. (8). Therefore, there are two types of resonance between ionic structures, which correspond to the existence of the two ionic wave-functions of Eqs. (7) and (8). To distinguish them, we shall put a + and – sign above the resonance symbol. Thus

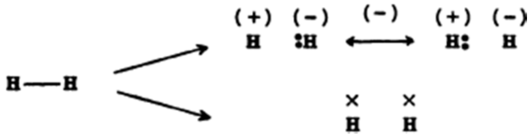
$$\Psi_3(\text{MO}) \equiv \Psi\_(\text{ionic}) \rightarrow \overset{(-)}{\mathbf{H{:}}}\ \ \overset{(+)}{\mathbf{H}} \overset{(-)}{\leftrightarrow} \overset{(+)}{\mathbf{H}}\ \ \overset{(-)}{\mathbf{{:}H}}$$

and

$$\Psi_+(\text{ionic}) = 1\mathbf{s}_\mathbf{A}(1)1\mathbf{s}_\mathbf{A}(2) + 1\mathbf{s}_\mathbf{B}(1)1\mathbf{s}_\mathbf{B}(2) \rightarrow \overset{(-)}{\mathbf{H{:}}}\ \ \overset{(+)}{\mathbf{H}} \overset{(+)}{\leftrightarrow} \overset{(+)}{\mathbf{H}}\ \ \overset{(-)}{\mathbf{{:}H}} \tag{8}$$

Inspection of Eqn. (6) for $\Psi_2(\mathrm{MO})$ shows that it corresponds to the Heitler-London function obtained when the + of Eqn. (2) is replaced by a – ; this is a result that we have obtained previously in section 3-5. We may also obtain $\Psi_3(\mathrm{MO})$ $(\equiv \Psi_-$ (ionic)) from $\Psi_+(\mathrm{HL})$ by exciting an electron from one atomic orbital into the other and changing the sign of the linear combination. (The sign change is necessary in order to satisfy the spectroscopic rule that an "even" → "odd" excitation is allowed, whereas both "even" → "even" and "odd" → "odd" excitations are forbidden. The "even" and "odd" characters of $\Psi_+(\mathrm{HL})$ and $\Psi_-(\mathrm{ionic})$ refer to the behaviour of the wave-functions with respect to inversion through the centre of symmetry of the molecule. Thus $\Psi_+(\mathrm{HL})$ and $\Psi_+(\mathrm{ionic})$ are symmetric (even) and $\Psi_-(\mathrm{HL})$ and $\Psi_-(\mathrm{ionic})$ are antisymmetric (odd).)

To summarize this section, we may write[i]



to obtain valence-bond structures for the singly-excited states of H_2. According to Hund's rule of maximum spin multiplicity, the parallel-spin state ($\overset{\mathrm{x}}{\mathbf{H}}\ \overset{\mathrm{x}}{\mathbf{H}}$) has a lower energy than has $\overset{(-)}{\mathbf{H}}\mathbf{:}\ \overset{(+)}{\mathbf{H}}\overset{(-)\ (+)}{\leftrightarrow}\mathbf{H}\ \mathbf{:}\overset{(-)}{\mathbf{H}}$ with antiparallel spins.

The π-electrons of ethylene may be similarly treated. When one π-electron of the ground state $\mathbf{H_2C=CH_2}$ is excited, we obtain the valence-bond structures

$$\mathbf{H_2\overset{x}{C}—\overset{x}{C}H_2} \text{ and } \mathbf{H_2\overset{(-)}{\overset{xo}{C}}—\overset{(+)}{C}H_2 \leftrightarrow H_2\overset{(+)}{\overset{(-)}{C}}—\overset{(-)}{\overset{xo}{C}}H_2}$$

for the $S = 1$ and $S = 0$ (the V state) spin excited states of lowest energy.

For isoelectronic formaldehyde $\mathbf{H_2C=\underset{\cdot\cdot}{O}:}$ the corresponding valence-bond structures are

$$\mathbf{H_2\overset{x}{C}—\overset{x}{\underset{\cdot\cdot}{O}}:} \text{ and } \mathbf{H_2\overset{(-)}{\overset{xo}{C}}—\overset{(+)}{\underset{\cdot\cdot}{O}}: \leftrightarrow H_2\overset{(+)}{\overset{(-)}{C}}—\overset{(-)}{\overset{xo}{\underset{\cdot\cdot}{O}}}:}$$

---

[i] More fully, the parallel-spin states have the valence-bond structures $\overset{\mathrm{x}}{\mathbf{H}}\ \overset{\mathrm{x}}{\mathbf{H}}$, $\overset{\mathrm{x}}{\mathbf{H}}\ \overset{\mathrm{o}}{\mathbf{H}}\overset{(-)}{\leftrightarrow}\overset{\mathrm{o}}{\mathbf{H}}\ \overset{\mathrm{x}}{\mathbf{H}}$, and $\overset{\mathrm{o}}{\mathbf{H}}\ \overset{\mathrm{o}}{\mathbf{H}}$ for each of the spin-states of Eqn. (4) with $S_z = +1$, 0 and –1. However, we shall usually use only a single valence-bond structure to represent an $S = 1$ spin-state.

However, because oxygen is more electronegative than carbon, the weight for $\overset{(+)}{\mathbf{H_2C}}\mathbf{—}\overset{(-)}{\ddot{\underset{..}{\mathbf{O}}}}\mathbf{:}$ would be expected to be larger than that for $\mathbf{H_2}\overset{(-)}{\ddot{\mathbf{C}}}\mathbf{—}\overset{(+)}{\underset{..}{\mathbf{O}}}\mathbf{:}$.

9-2 n → π* Transitions

For H_2CO, low-lying excited states are obtained when (essentially) a non-bonding (or lone-pair) oxygen electron of the ground state is promoted into a π-electron orbital. This excitation is normally discussed in terms of a molecular orbital description for the π-electrons, and we shall initially use this type of treatment here.

The oxygen non-bonding electrons for the ground state occupy the 2s and 2p $\bar{\pi}_O$ orbitals of Fig. 9-1. The C-O π-bond involves a doubly-occupied π-electron molecular orbital, namely

$$\pi_{CO} = \pi_C + k\pi_O \tag{9}$$

in which π_C and π_O are carbon and oxygen 2pπ-orbitals and $k > 1$.

The $2p\bar{\pi}-$electrons are less firmly bound than the 2s electrons. Therefore, less energy is required to excite a $2p\bar{\pi}-$electron. The $2p\bar{\pi}-$orbital is often designated as n, and we shall use this notation here. The antibonding C-O π*-orbital of Eqn. (10),

$$\pi^*_{CO} = k^*\pi_C - \pi_O \tag{10}$$

$$(\pi_{CO})^2(\pi^*_{CO})^1(\mathrm{n})^1, \quad S = 1; \quad \pi^*_{CO}(1)\mathrm{n}(2) - \mathrm{n}(1)\pi^*_{CO}(2) \tag{11}$$

$$(\pi_{CO})^2(\pi^*_{CO})^1(\mathrm{n})^1, \quad S = 0; \quad \pi^*_{CO}(1)\mathrm{n}(2) + \mathrm{n}(1)\pi^*_{CO}(2) \tag{12}$$

with $k^* > 1$, is the vacant orbital of lowest-energy into which the n electron can be excited. Two excited configurations may be constructed according to whether the two singly-occupied orbitals (n and π^*_{CO}) have parallel or antiparallel spins for the two electrons. Each excitation is designated as n → π*, and the resulting configurations are given by Eqs. (11) and (12), together with the spatial wave-functions for the two singly-occupied orbitals.

Each of these excited configurations has a Pauling "3-electron bond" component, namely $(\pi_{CO})^2(\pi^*_{CO})^1$, which is equivalent to the configuration $(\pi_C)^1(\pi_{CO})^1(\pi_O)^1$ with two non-bonding electrons and one bonding electron (cf.

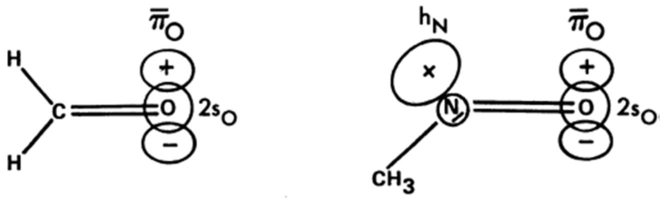


Figure 9-1: Lone-pair atomic orbitals for H_2CO and CH_3NO .

Section 3-6). The non-bonding electrons, which occupy the π_C and π_O atomic orbitals, have parallel spins. If the π^*_{CO} electron is assumed to have an $S_z = +\frac{1}{2}$ spin quantum number, then the valence-bond structure for this π-electron configuration is $\overset{\mathrm{x}}{\mathbf{C}}\ \mathbf{o}\ \overset{\mathrm{x}}{\mathbf{O}}$. In the configurations of Eqs. (11) and (12), the n electron has its spin either parallel with or opposed to that of the π^*_{CO} electron. Therefore the resulting valence-bond structures for the two excited states that are obtained from the n → π* excitations are

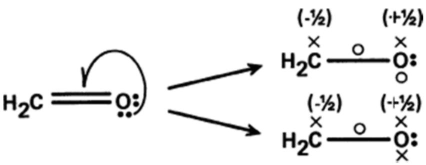
$$\mathbf{H_2}\,\overset{(-\frac{1}{2})}{\overset{\mathrm{x}}{\mathbf{C}}}\ \overset{\mathrm{o}}{—}\ \underset{\mathrm{x}}{\overset{(+\frac{1}{2})}{\overset{\mathrm{x}}{\mathbf{O}}}}\!\mathbf{:}\quad \text{and}\quad \mathbf{H_2}\,\overset{(-\frac{1}{2})}{\overset{\mathrm{x}}{\mathbf{C}}}\ \overset{\mathrm{o}}{—}\ \underset{\mathrm{o}}{\overset{(+\frac{1}{2})}{\overset{\mathrm{x}}{\mathbf{O}}}}\!\mathbf{:}$$

In Section 3-6 we have deduced that for any Pauling "3-electron bond", the valence-bond structure $\dot{\mathbf{A}}\cdot\dot{\mathbf{B}}$ is equivalent to the resonance of $\ddot{\mathbf{A}}\ \dot{\mathbf{B}} \longleftrightarrow \dot{\mathbf{A}}\ \ddot{\mathbf{B}}$. Therefore, we may write

$$\mathbf{H_2}\,\overset{(-\frac{1}{2})}{\overset{\mathrm{x}}{\mathbf{C}}}\ \overset{\mathrm{o}}{—}\ \underset{\mathrm{x}}{\overset{(+\frac{1}{2})}{\overset{\mathrm{x}}{\mathbf{O}}}}\!\mathbf{:} \equiv \mathbf{H_2}\overset{\mathrm{x}}{\mathbf{C}}—\underset{\mathrm{x}}{\overset{\mathrm{ox}\ (+)}{\mathbf{O}}}\!\mathbf{:} \leftrightarrow \mathbf{H_2}\overset{(-)}{\overset{\mathrm{xo}}{\mathbf{C}}}—\underset{\mathrm{x}}{\overset{(+)}{\overset{\mathrm{x}}{\mathbf{O}}}}\!\mathbf{:}\ \text{ and}$$

$$\mathbf{H_2}\,\overset{(-\frac{1}{2})}{\overset{\mathrm{x}}{\mathbf{C}}}\ \overset{\mathrm{o}}{—}\ \underset{\mathrm{o}}{\overset{(+\frac{1}{2})}{\overset{\mathrm{x}}{\mathbf{O}}}}\!\mathbf{:} \equiv \mathbf{H_2}\overset{\mathrm{x}}{\mathbf{C}}—\underset{\mathrm{o}}{\overset{\mathrm{ox}\ (+)}{\mathbf{O}}}\!\mathbf{:} \leftrightarrow \mathbf{H_2}\overset{(-)}{\overset{\mathrm{xo}}{\mathbf{C}}}—\underset{\mathrm{o}}{\overset{(+)}{\overset{\mathrm{x}}{\mathbf{O}}}}\!\mathbf{:}$$

Because the n orbital is orthogonal to each of the π_C and π_O atomic orbitals, no bonding can arise because of the existence of opposed spins for the n and unpaired π electrons in each of the $S = 0$ spin structures. In summary, the valence-bond descriptions of the n → π* excitations may be written as



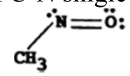
with the parallel-spin state having the lower energy.

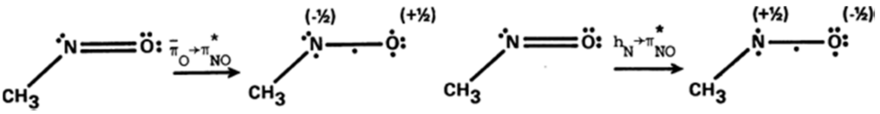
If a Heitler-London description of the C–O π-bond is used, the $S = 0$ spin ground-state configuration involves the atomic orbital occupancies of $(\pi_C)^1(\pi_O)^1(n)^2$, with antiparallel spins for the π_C and π_O electrons. When an n electron is excited, either one of the π_C or π_O orbitals becomes doubly-occupied to generate $(\pi_C)^2(\pi_O)^1(n)^1$ and $(\pi_C)^1(\pi_O)^2(n)^1$ configurations. Ignoring electron spins, the resulting valence-bond structures are

$$\mathbf{H_2\overset{(-)}{\ddot{C}}—\overset{(+)}{\dot{\underset{\cdot}{O}}}:} \text{ and } \mathbf{H_2\dot{C}—\ddot{\underset{\cdot}{O}}:}$$

and resonance between these structures generates the Pauling "3-electron bond" structures that we have previously described.

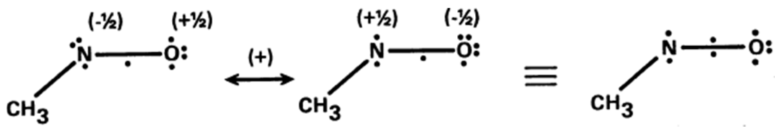
9-3 CH3NO and O3: "n → π*"

The measured C-N and N-O bond-lengths for CH_3NO are 1.48 Å and 1.21 Å (Section 2-3). Pauling's estimates of 1.47 and 1.20 Å for the lengths of C-N single and N=O double bonds suggest that the standard Lewis structure  reasonably represents the ground-state electronic structure for CH_3NO. The descriptions of the electronic states that are obtained by π → π* excitations are similar to those described for both C_2H_2 and H_2CO in Section 9-1. However because a lone-pair electron can be excited from either an oxygen 2pπ orbital or a nitrogen hybrid orbital, the descriptions for the n → π* excitations require some elaboration. Thus, we may write



in which the electron spin designations have been omitted. In each of the excited-state structures, there is a Pauling "3-electron bond" for the π electrons.

Because the h_N and $\bar{\pi}_O$ atomic orbitals overlap (Figure 9-1), these two structures will participate in resonance, and a second Pauling "3-electron bond" will be generated, i.e. we may write



Alternatively, because the n-orbital configuration $(h_N)^1(n_{NO})^1(\bar{\pi}_O)^1$ for the Pauling "3-electron bond" is equivalent to $(n_{NO})^2(n^*_{NO})^1$ in which

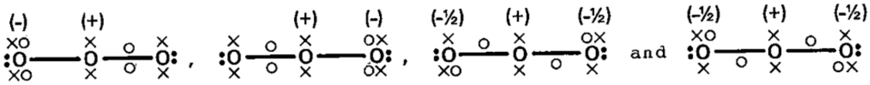
$$n_{NO} = h_N + k\bar{\pi}_O \text{ and } n^*_{NO} = k^* h_N - \bar{\pi}_O$$

we may describe the electronic excitation as an $n^*_{NO} \rightarrow \pi^*_{NO}$ excitation, i.e. as

$$(n_{NO})^2(n^*_{NO})^2(\pi_{NO})^2 \rightarrow (n_{NO})^2(n^*_{NO})^1(\pi_{NO})^2(\pi^*_{NO})^1 .$$

The S = 1 spin excited state is predicted to have an N-O bond-length which is similar to that of the ground-state, and a linear arrangement for the C, N and O atoms. The linearity will improve the overlap that exists between the h_N and $\bar{\pi}_N$ orbitals (h_N "grows" into $\bar{\pi}_N$) and thereby increases the strength of the Pauling "3-electron bond" for the three n electrons (provided that the overlap integral does not exceed 1/3 cf. Section 3-10).

O_3 is isoelectronic with CH_3NO, and a linear S = 1 spin excited state may similarly be obtained by $n^*_{OO} \rightarrow \pi^*_{OO}$ excitation. The resulting valence-bond structures are



In each of these structures, there are five π- and five $\bar{\pi}-$ (or five π_x and five π_y) electrons, which form two orthogonal 5-electron 3-centre bonding units. The S = 1 spin delocalized molecular orbital configuration for the ten electrons is formally identical with that for ${}^3\Psi_{covalent}$ of Figure 8-3, and is equivalent (Section 6-4) to resonance between the four valence-bond structures with an equal contribution from each structure.

9-4 O2: $\pi_x^* \rightarrow \pi_y^*$ and $\pi_x \rightarrow \pi_x^*$

For the $({}^3\Sigma_g^-)$ ground-state of O_2, the π-electron configuration is $(\pi_x)^2(\pi^*_x)^1(\pi_y)^2(\pi^*_y)^1$ in which $\pi_x \equiv \pi_{OO} = \pi_A + \pi_B$, $\pi_y \equiv \bar{\pi}_{OO} = \bar{\pi}_A + \bar{\pi}_B$ etc., and the antibonding π^*_x and π^*_y electrons have parallel spins (Section 4-3). If a $\pi^*_x \rightarrow \pi^*_y$ excitation occurs, with spin inversion, the $(\pi_x)^2(\pi_y)^2(\pi^*_y)^2$ configuration is obtained with valence-bond structure $:\underset{\cdot\cdot}{O} = \underset{\cdot\cdot}{O}:$. Similarly a $\pi_y^* \rightarrow \pi_x^*$ excitation with spin inversion generates the $(\pi_x)^2(\pi_x^*)^2(\pi_y)^2$ configuration with valence-bond structure $:\ddot{O} = \ddot{O}:$. Two linear combinations of these degenerate excited configurations may be constructed, and therefore two types of valence-bond resonance are possible, namely

$$:\underset{\cdot\cdot}{O} = \underset{\cdot\cdot}{O}: \overset{(+)}{\leftrightarrow} :\ddot{O} = \ddot{O}: \quad \text{and} \quad :\underset{\cdot\cdot}{O} = \underset{\cdot\cdot}{O}: \overset{(-)}{\leftrightarrow} :\ddot{O} = \ddot{O}:$$

In Section 4-3, it was indicated that the two electronic states that correspond to these resonances are designated as $^1\Sigma_g^+$ and $^1\Delta_g$ respectively. A second $^1\Delta_g$ state, which can be shown to be degenerate with that described above, is obtained from the $(\pi_x)^2(\pi_x^*)^1(\pi_y)^2(\pi_y^*)^1$ configuration, with opposed spins for the antibonding π_x^* and π_y^* electrons. The valence-bond representation for this latter state is

$$\begin{array}{ccccccc} \mathrm{x} & \mathrm{o} & \mathrm{x} & (+) & \mathrm{o} & \mathrm{x} & \mathrm{o} \\ :O & — & O: & \leftrightarrow & :O & — & O: \\ \mathrm{o} & \mathrm{x} & \mathrm{o} & & \mathrm{x} & \mathrm{o} & \mathrm{x} \end{array}$$

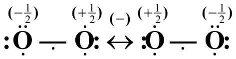
if the order of the antibonding spatial orbitals is $(\pi_x^*)^1(\pi_y^*)^1$ in each of the two configurations. (We may note here that the

$$\begin{array}{ccccccc} \mathrm{x} & \mathrm{o} & \mathrm{x} & (-) & \mathrm{o} & \mathrm{x} & \mathrm{o} \\ :O & — & O: & \leftrightarrow & :O & — & O: \\ \mathrm{o} & \mathrm{x} & \mathrm{o} & & \mathrm{x} & \mathrm{o} & \mathrm{x} \end{array}$$

resonance represents the $S_z = 0$ spin component of the $^3\Sigma_g^-$, ground state.)

If a bonding π_x electron is promoted into the singly-occupied antibonding π_x^* orbital of the ground-state, the configuration $(\pi_x)^1(\pi_x^*)^2(\pi_y)^2(\pi_y^*)^1$ is obtained (with either parallel or antiparallel spins for the two unpaired-electrons). The $(\pi_y)^2(\pi_y^*)^1$ and $(\pi_x)^1(\pi_x^*)^2$ configurations are respectively equivalent to $(\bar{\pi}_A)^1(\pi_y)^1(\bar{\pi}_B)^1$ and $(\pi_A)^1(\pi_x^*)^1(\pi_B)^1$. The first of these configurations generates the Pauling "3-electron bond" structure $\dot{O} \cdot \dot{O} \equiv \ddot{O}\ \dot{O} \overset{(+)}{\leftrightarrow} \dot{O}\ \ddot{O}$. However, the $(\pi_A)^1(\pi_x^*)^1(\pi_B)^1$ configuration is antibonding, and no single valence-bond structure may be used to indicate the presence of an electron in an antibonding orbital. The only obvious representation involves the use of two structures, i.e. to write $\ddot{O}\ \dot{O} \overset{(-)}{\leftrightarrow} \dot{O}\ \ddot{O}$ with $\overset{(-)}{\leftrightarrow}$ originating from the antibonding character of $\pi_x^* = \pi_A - \pi_B$. When the electron spins are not indicated, the

$(\pi_x)^1(\pi_x^*)^2(\pi_y)^2(\pi_y^*)^1$ configuration may be represented by the following resonance:



Corresponding valence-bond structures may also be constructed for the $(\pi_x)^2(\pi_x^*)^1(\pi_y)^1(\pi_y^*)^2$ configuration, and all four structures participate in resonance to generate excited ${}^1\Sigma_u^-$ and ${}^1\Delta_u$ states. We shall not elaborate on the nature of these states here; the chief purpose for introducing them is to show that $(\pi)^1(\pi^*)^2$ diatomic configurations (and their $(\sigma)^1(\sigma^*)^2$ equivalents) require two valence-bond structures to represent them, i.e. no single valence-bond structure is available to represent configurations that are overall antibonding.

Reference

See for example (a) N.J· Turro, Modern Molecular Photochemistry (Benjamin-Cummings) 1978; (b) W.G. Dauben, L. Salem and N.J. Turro, Accounts Chem. Res. **8,** 41 (1975).

Addendum Chapter 9

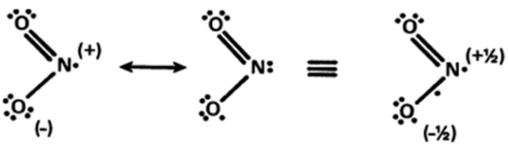
A.C. Hurley, R.D. Harcourt and P.R. Taylor, Israel J. Chem **19**, 215 (1980) use group theoretical projection operators to generate symmetry-adapted wavefunctions for O_2.

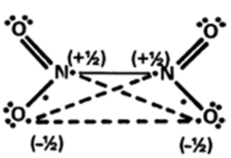
W. Wu, H. Zhang, B. Braida, S. Shaik, P.C. Hiberty, Theoret. Chem. Acc. **133**, 1441 (2014) provide accurate valence-bond studies of the first $S = 0$ spin excited state (the V state) for C_2H_4.

Chapter 10 Pauling "3-Electron Bonds" and "Increased-Valence" Theory for N_2O_4

10-1 Pauling "3-Electron Bonds" and "Increased-Valence" Structures for N_2O_4

In Section 7-1, we used the NO_2 Lewis structures of types (**1**) and (**2**) to construct Lewis structures for N_2O_4. To do this, we have spin-paired the odd-electron of one NO_2 moiety with the odd-electron of the other moiety, to obtain the Lewis octet structures (**3**)-(7) of Section 7-1 for N_2O_4. In Section 6-1, we have also indicated that resonance between the NO_2 Lewis structures (**1**) and (**2**) may be summarized by using the Pauling "3-electron bond" structure (**3**), which has (fractional) odd-electron charge located in both the nitrogen and oxygen atomic orbitals. Because structure (**3**) (in resonance with its mirror image) helps to provide a more economical valence-bond representation of the electronic structure for NO_2, it should be possible to use (**3**) to provide a more economical representtation of the electronic structure for N_2O_4. We can achieve this by bonding together two NO_2 molecules, each of which is represented by valence-bond structures of type (**3**). The resulting N_2O_4 valence-bond structure is (**4**),





(1) (2) (3) (4)

which has both a (fractional) N-N bond, and (fractional) "long" N-O and O-O bonds. It then follows that because the Pauling "3-electron bond" structure (**3**) summarizes resonance between the Lewis structures (**1**) and (**2**) for NO_2, valence-

R.D. Harcourt, *Bonding in Electron-Rich Molecules*,
Lecture Notes in Chemistry 90, DOI 10.1007/978-3-319-16676-6_10

bond structure (**4**) for N_2O_4 must be equivalent to resonance between the Lewis (octet) structures (**3**)-(**6**) of Section 7-1. Consequently, valence-bond structure (**4**) provides a considerable economy in the valence-bond representation of the electronic structure of N_2O_4.

A comparison of the valence-bond structure (**4**) above with each of the Lewis structures (**3**)–(**6**) of Section 7-1 reveals that there are two additional bonding electrons in (**4**). Therefore to indicate that additional bonding electrons are present, this valence-bond structure has been designated as an "*increased-valence*" structure. From the discussion presented in the previous paragraph, it follows that because structure (**4**) summarizes resonance between the Lewis structures (**3**)–(**6**) of Section 7-1, this "increased-valence" structure must be more stable than any of the component Lewis structures. N_2O_4 is an example from a large class of molecules, namely the "electron-rich" tri- and polyatomic molecules, for which "increased-valence" structures can be constructed. In Chapters 11, 12 and 14 we shall describe in more detail how this may be done. Here, we have introduced the subject to demonstrate a further connection between the Pauling "3-electron bond" theory for NO_2 and the Lewis valence-bond theory for N_2O_4. These theories may also be related to the molecular orbital theory of Section 7-2, and we shall review these latter connections in the next section.

10-2 "Increased-Valence" Structures and Molecular Orbital Theory for N_2O_4

Here, it is initially helpful to re-examine the molecular orbital configuration $(\sigma 1s)^2$ for H_2 (Section 3-3), with $\sigma 1s = 1s_A + 1s_B$. This configuration may be expressed as $\Psi_{covalent} + \Psi_{ionic}$, in which the $\Psi_{covalent}$ and Ψ_{ionic} are given by Eqs. (1) and (2).

$$\Psi_{covalent} = 1s_A(1)1s_B(2) + 1s_B(1)1s_A(2) = \Psi(\mathbf{H—H}) \tag{1}$$

$$\Psi_{ionic} = 1s_A(1)1s_A(2) + 1s_B(1)1s_B(2) = \Psi(\overset{-}{\mathbf{H:}}\ \mathbf{H}^+) + \Psi(\mathbf{H}^+\ \mathbf{:H}^-) \tag{2}$$

The $\Psi_{covalent}$ is the Heitler-London wave-function for the electron-pair bond of H_2 (Section 3-3). For the ten "mobile σ-electrons" of Figure 7-2 for N_2O_4 (with the remaining electrons localized as they are in the valence-bond structures of types (**3**)-(**7**) of Section 7-1), the lowest-energy molecular orbital configuration may be expressed as $\Psi_{covalent} + \Psi_{ionic}$, in which $\Psi_{covalent} = \Psi(O_2N—NO_2)$ and $\Psi_{ionic} = \Psi(NO_2^+NO_2^-) + \Psi(NO_2^-NO_2^+)$. The $\Psi_{covalent}$ is the wave-function for "increased-valence" structures of type (**4**), with a Heitler-London type wave-function used to describe the covalent bonding that occurs between the NO_2 moieties.

We can obtain a simplified derivation of this result for N_2O_4 from further transformations of the orbitals for the six-electron configuration of Eqn. (7-10), namely the $\Psi_1(\mathrm{MO})$ of Eqn. (8) here[i]. For this configuration, the s_1, s_3 and ψ_2 orbitals are defined in Eqs. (7-1), (7-2) and (7-4). The symmetry orbitals s_1 and s_3 of Eqn. (8) may now be linearly combined to form the new molecular orbitals ψ_1' and ψ_3' of Eqs. (3) and (4), for which the parameter μ is the same as that which occurs in the ψ_2 of Eqn. (7-4). The latter molecular orbital may also be expressed as Eqn. (5). In Eqs. (3)-(5), the ϕ_L, ϕ_R, ϕ^*_L and ϕ^*_R are the L-moiety and R-moiety N-O bonding and antibonding molecular orbitals defined in Eqs. (6) and (7). The molecular orbital configuration $\Psi_1(\mathrm{MO})$ of Eqn. (8) may therefore be transformed to give Eqs. (9) and (10). On expansion of Eqn. (10) in terms of the NO_2-moiety molecular orbital configurations, we obtain Eqn. (11) with the Ψ_{covalent} and Ψ_{ionic} defined in Eqs. (12) and (13).

$$\psi_1' = (s_3 + \mu s_1)/(1+\mu^2)^{\frac{1}{2}} = (\phi_L + \phi_R)/2^{\frac{1}{2}} \tag{3}$$

$$\psi_3' = (\mu s_3 - s_1)/(1+\mu^2)^{\frac{1}{2}} = (\phi_L^* + \phi_R^*)/2^{\frac{1}{2}} \tag{4}$$

$$\psi_2 = (s_4 + \mu s_2)/(1+\mu^2)^{\frac{1}{2}} = \left(\phi_L - \phi_R\right)/2^{\frac{1}{2}} \tag{5}$$

$$\phi_L = (\bar{\pi}_1 + \mu h_2)/(1+\mu^2)^{\frac{1}{2}}\ ;\ \phi_R = (\mu h_3 + \bar{\pi}_4)/(1+\mu^2)^{\frac{1}{2}} \tag{6}$$

$$\phi_L^* = (\mu\bar{\pi}_1 - h_2)/(1+\mu^2)^{\frac{1}{2}};\ \phi_R^* = (-h_3 + \mu\bar{\pi}_4)/(1+\mu^2)^{\frac{1}{2}} \tag{7}$$

$$\Psi_1(\mathrm{MO}) = \left|\psi_1^\alpha\psi_1^\beta\psi_2^\alpha\psi_2^\beta\psi_3^\alpha\psi_3^\beta\right| \equiv \left|(\psi_1)^2(\psi_2)^2(\psi_3)^2\right| \equiv \left|(s_1)^2(\psi_2)^2(s_3)^2\right| \tag{8}$$

$$\equiv \left|(\psi_1')^2(\psi_2)^2(\psi_3')^2\right| \tag{9}$$

$$\equiv \left|(\phi_L)^2(\phi_R)^2(\frac{\phi_L^* + \phi_R^*}{2^{\frac{1}{2}}})\right| \tag{10}$$

$$\equiv (\Psi_{\mathrm{covalent}} + \Psi_{\mathrm{ionic}})/2^{½} \tag{11}$$

$$\Psi_{\mathrm{covalent}} = (\left|\phi_L^\alpha\phi_L^\beta\phi_R^\alpha\phi_R^\beta\phi_L^{*\alpha}\phi_R^{*\beta}\right| + \left|\phi_L^\alpha\phi_L^\beta\phi_R^\alpha\phi_R^\beta\phi_R^{*\alpha}\phi_L^{*\beta}\right|)/2^{\frac{1}{2}} \tag{12}$$

$$\Psi_{\mathrm{ionic}} = (\left|\phi_L^\alpha\phi_L^\beta\phi_R^\alpha\phi_R^\beta\phi_L^{*\alpha}\phi_L^{*\beta}\right| + \left|\phi_L^\alpha\phi_L^\beta\phi_R^\alpha\phi_R^\beta\phi_R^{*\alpha}\phi_R^{*\beta}\right|)/2^{\frac{1}{2}} \tag{13}$$

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[i] Although for completeness we have formulated the 6-electron wave-functions as Slater determinants (Section 3-7), this formulation is not required for the algebra of this chapter.

Because the identity $\psi_{ab}^{\alpha}\psi_{ab}^{\beta}\psi_{ab}^{*\alpha} \equiv -a^{\alpha}\psi_{ab}^{\beta}b^{\alpha}$ for the Pauling "3-electron bond" configuration (Section 3-6) arises when ψ_{ab} and ψ_{ab}^{*} are normalized excluding atomic orbital overlapping integrals, the $\Psi_{covalent}$ can be transformed further to give Eqn. (14) and then Eqn. (15).

$$\Psi_{covalent} = \left(\left|\overline{\pi}_1^{\alpha}\phi_L^{\beta}h_2^{\alpha}h_3^{\beta}\phi_R^{\alpha}\overline{\pi}_4^{*\beta}\right| + \left|\overline{\pi}_1^{\beta}\phi_L^{\alpha}h_2^{\beta}h_3^{\alpha}\phi_R^{\beta}\overline{\pi}_4^{*\alpha}\right|\right)/2^{\frac{1}{2}} \tag{14}$$

$$= \left\{\Psi_3 + \mu(\Psi_4 + \Psi_5) + \mu^2\Psi_6\right\}/\left(1+\mu^2\right) \tag{15}$$

In Eqn.(15), the $\Psi_3 - \Psi_6$ are the (S = 0 spin) bond-eigenfunctions or valence-bond structure functions for the six electrons that occupy the $\overline{\pi}_1$, h_2, h_3 and $\overline{\pi}_4$ atomic orbitals of the Lewis structures (**3**)-(**6**) of Section 7-1.

10-3 "Increased-Valence" Theory and Configuration Interaction for N_2O_4

Although it is not required for the "increased-valence" theory of the subsequent chapters, it is appropriate here to discuss aspects of configuration interaction (C.I.) theory for N_2O_4. In particular, we shall demonstrate that the $\Psi_{covalent}$ of Eqn. (12), which contributes equally with Ψ_{ionic} to the lowest-energy molecular orbital configuration $\Psi_1(MO)$ of Eqn. (8), is the primary component of the lower-energy C.I. wave-function obtained by linearly combining $\Psi_1(MO)$ with the $\Psi_2(MO)$ of Eqn. (16). This result is similar to that which pertains for the ground-state of H_2 (Section 3-3).

$$\Psi_2(MO) = \left|\psi_1^{\alpha}\psi_1^{\beta}\psi_2^{\alpha}\psi_2^{\beta}\psi_4^{\alpha}\psi_4^{\beta}\right| \tag{16}$$

Because the molecular orbital ψ_3 of Eqn. (8) is N-O antibonding (cf. Eqn. (7-5)), it is the highest-energy occupied orbital of $\Psi_1(MO)$. When two electrons are excited from ψ_3 into the vacant molecular orbital ψ_4 of Eqn. (7-6), (which is both N-O and N-N antibonding), the lowest-energy doubly-excited configuration $\Psi_2(MO)$ of Eqn. (16) is obtained.

It is now helpful to express the molecular orbital ψ_1 of Eqn. (16) in terms of the molecular orbitals ψ_1' and ψ_3' of Eqs. (3) and (4), in which the latter orbitals are defined in terms of the parameter μ. With ψ_1 defined in terms of λ according to Eqn. (7-3), we obtain Eqn. (17).

$$\psi_1 = \{(1+\lambda\mu)\psi_1' + (\mu-\lambda)\psi_3'\} / \{(1+\mu^2)\ (1+\lambda)\}^{\frac{1}{2}} \equiv x\psi_1' + y\psi_3' \tag{17}$$

By substituting Eqn. (17) into the $\Psi_2(\text{MO})$ of Eqn. (16) and then expanding $\Psi_2(\text{MO})$ in terms of configurations that involve the ψ_1', ψ_2, ψ_3' and ψ_4 orbitals, we obtain Eqn. (18),

$$\Psi_2(\text{MO}) = x^2\Psi_2'(\text{MO}) + 2^{1/2}xy\Psi_2^{*\prime}(\text{MO}) + y^2\Psi_2^{**\prime}(\text{MO}) \tag{18}$$

in which the Ψ_2, $\Psi_2^{*\prime}$ and $\Psi_2^{**\prime}$ are given by Eqs. (19), (21) and (23). By using techniques that are similar to those used to obtain Eqn. (11) from Eqn. (8), these three configurations may be transformed to give Eqs. (20), (22) and (24). In the latter configurations, the Ψ_{covalent} and Ψ_{ionic} are given by Eqs. (12) and (13), and the Ψ^* and Ψ^{**} configurations are obtained from the Ψ configurations by means of the excitations indicated in Eqn. (25).

$$\Psi_2(\text{MO}) = \left|\psi_1'^{\alpha}\psi_1'^{\beta}\psi_2^{\alpha}\psi_2^{\beta}\psi_4^{\alpha}\psi_4^{\beta}\right| \tag{19}$$

$$\equiv \left(-\Psi_{\text{covalent}} + \Psi_{\text{ionic}}\right)/2^{1/2} \tag{20}$$

$$\Psi_2{**}(\text{MO}) = (\left|\psi_1'^{\alpha}\psi_3'^{\beta}\psi_2^{\alpha}\psi_2^{\beta}\psi_4^{\alpha}\psi_4^{\beta}\right| + \left|\psi_3'^{\alpha}\psi_1'^{\beta}\psi_2^{\alpha}\psi_2^{\beta}\psi_4^{\alpha}\psi_4^{\beta}\right|) / 2^{\frac{1}{2}} \tag{21}$$

$$\equiv \left(-\Psi^*_{\text{covalent}} + \Psi^*_{\text{ionic}}\right)/2^{1/2} \tag{22}$$

$$\Psi_2^{**\prime}(\text{MO}) = \left|\psi_3'^{\alpha}\psi_3'^{\beta}\psi_2^{\alpha}\psi_2^{\beta}\psi_4^{\alpha}\psi_4^{\beta}\right| \tag{23}$$

$$\equiv (-\Psi^{**}_{\text{cov alent}} + \Psi^{**}_{\text{ionic}}) / 2^{\frac{1}{2}} \tag{24}$$

$$\begin{aligned} &\Psi^*_{\text{cov alent}} \text{ and } \Psi^*_{\text{ionic}} : \ \phi_L \to \phi_L^* \text{ or } \phi_R \to \phi_R^* \\ &\Psi^{**}_{\text{cov alent}} : \ \phi_L \to \phi_L^* \text{ and } \phi_R \to \phi_R^* \\ &\Psi^{**}_{\text{ionic}} : \ (\phi_L)^2 \to (\phi_L^*)^2 \text{ or } (\phi_R)^2 \to (\phi_R^*)^2 \end{aligned} \tag{25}$$

Configuration interaction is invoked by linearly combining $\Psi_1(\text{MO})$ with $\Psi_2(\text{MO})$, according to Eqn. (26).

$$\Psi(\text{CI}) = C_1\Psi_1(\text{MO}) + C_2\Psi_2(\text{MO}) \tag{26}$$

$$= \{(C_1 - x^2C_2)\Psi_{\text{covalent}} + (C_1 + x^2C_2)\Psi_{\text{ionic}}\}/2^{\frac{1}{2}}$$

$$+ C_2\{xy(-\Psi^*_{\text{covalent}} + \Psi^*_{\text{ionic}}) + y^2\left(-\Psi^{**}_{\text{covalent}} + \Psi^{**}_{\text{ionic}}\right)/2^{\frac{1}{2}}\} \tag{27}$$

The coefficients C_1 and C_2 are chosen so that the energy of this linear combination is a minimum, a necessary condition for which is that $\partial E/\partial C_1 = \partial E/\partial C_2 = 0$, where $E = (C_1^2H_{11} + C_2^2H_{22} + 2C_1C_2H_{12})/\left(C_1^2 + C_2^2\right)$. The integral $H_{12} = \int\Psi_1(\text{MO})\hat{H}\Psi_2(\text{MO})\text{d}\tau$ may be shown to be equivalent to $\iint \psi_3(1)\,\psi_4(2)\left(e^2/r_{12}\right)\psi_4(1)\,\psi_3(2)\,\text{d}v_1\text{d}v_2$, which is greater than zero. For a finite N-N internuclear separation (r(NN)) with $H_{22} > H_{11}$, it is easy to deduce that $|C_1| > |C_2|$ and that $C_1 > 0$ when $C_2 < 0$. By substituting Eqs. (11), (20), (22) and (24) into Ψ_{CI}, we obtain Eqn. (27), which indicates that Ψ_{covalent} for "increased-valence" structure (**4**) is the primary contributor to the lowest-energy linear combination of $\Psi_1(\text{MO})$ with $\Psi_2(\text{MO})$.

When r(NN) = ∞, $\Psi_1(\text{MO})$ and $\Psi_2(\text{MO})$ are degenerate and therefore $C_1 = -C_2 = 2^{-\frac{1}{2}}$. The parameters λ and μ are also equal for this distance, and therefore $x = 1$ and $y = 0$. The Ψ(CI) of Eqn. (27) then reduces to Ψ_{covalent}, i.e. this C.I. wave-function for N_2O_4 generates NO_2 radicals as dissociation products. The lowest-energy molecular orbital configuration, $\Psi_1(\text{MO})$ of Eqn. (11), generates both NO_2 radicals and NO_2^+ and NO_2^- ions as dissociation products, and therefore is unsatisfactory at large internuclear separations; cf. H_2 of Section 3-3.

There are four other S = 0 spin excited configurations that may be linearly combined with $\Psi_1(\text{MO})$ and $\Psi_2(\text{MO})$, but these are of less importance for the ground-state, i.e. the primary components of the "best" (lowest-energy) linear combination of the six S = 0 spin configurations are $\Psi_1(\text{MO})$ and $\Psi_2(\text{MO})$ with $|C_1| > |C_2|$ when r(NN) is finite.

In Sections 11-7, 11-9, 13-2, 13-8, 18-2 and 20-6, we shall discuss aspects of the bonding for some other molecular systems that, (as does N_2O_4), involve at least one 6-electron 4-centre bonding unit . For each of these systems, we shall use the "increased-valence" structure whose wave-function is the Ψ_{covalent} of the C.I. wave-function of the Eqn. (26) type for the 6-electron 4-centre bonding unit.

10-4 Conclusions

In Sections 7-1 and 10-1, we have shown how dimerization of Pauling "3-electron bond" structures for NO_2 leads to two equivalent types of valence-bond representations for the electron distribution in the N_2O_4 dimer. One of them, namely that of Section 7-1, involves resonance between four standard *cis* and *trans* Lewis structures, each with an N-N bond, and twelve "long-bond" Lewis structures. In Section 2-5, we have indicated that "long-bond" structures are usually omitted from elementary descriptions of the electronic structure of most molecules, but according to the electro-neutrality principle, such structures should often make important contributions to the ground-state resonance; this should be particularly the case when the standard structures carry atomic formal charges, and the "long-bond" structures do not. For N_2O_4 in Section 10-1, we have shown how we may summarize resonance between these two types of Lewis structures by spin-pairing the unpaired electrons of the Pauling "3-electron bond" structures for the NO_2 moieties. The resulting valence-bond structure is an "increased-valence" structure, which has two more electrons available for bonding than have any of the component Lewis structures. Because the two types of valence-bond representations for N_2O_4 are equivalent, each of them must provide a more stable representation of the electronic structure than does the use of only the familiar standard Lewis structures. However, as has been discussed in both Section 2-5(b) and Section 10-1, the "increased-valence" structures provide a more economical representation of the electron distribution, and therefore they are more easy to use to obtain qualitative information about bond properties. In the following chapters, we shall give our attention to the construction, types and uses of "increased-valence" structures for numerous other electron-rich systems. Most of these "increased-valence" structures have Pauling "3-electron bonds" as components.

References

1. R.D. Harcourt (a) Theor. Chim. Acta, **2,** 437 (1964); **4,** 202 (1966); (b) J. Mol. Struct., **9,** 221 (1971); (c) Aust. J. Chem., **32,** 933 (1979); (d) J. Amer. Chem. Soc., **102,** 5195 (1980); **103,** 5623 (1981).

Chapter 11 Pauling "3-Electron Bonds" and "Increased-Valence" Structures

We are now ready to examine in detail the incorporation of the Pauling "3-electron bond" structure $\dot{\mathbf{A}} \cdot \dot{\mathbf{B}}$ into the valence-bond structures for electron-rich molecules that involve 4-electron 3-centre and 6-electron 4-centre bonding units. To do this, we may use any of three alternative methods. In this Chapter, we shall discuss one of them. It involves the spin-pairing of the unpaired-electron of $\dot{\mathbf{A}} \cdot \dot{\mathbf{B}}$ with the unpaired electron of either an atom $\dot{\mathbf{Y}}$ or a second Pauling "3-electron bond" structure $\dot{\mathbf{C}} \cdot \dot{\mathbf{D}}$.

11-1 Pauling "3-Electron Bonds" and 4- Electron 3-Centre Bonding

To construct a valence-bond structure for a 4-electron 3-centre bonding unit, with a Pauling "3-electron bond" as a component, we commence by writing down the Pauling "3-electron bond" structure $\dot{\mathbf{A}} \cdot \dot{\mathbf{B}}$ with the electron spins indicated (× for s_z = +½ and o for s_z = -½ spin quantum numbers) as in structures (**1**) and (**2**) (Section 3-6).

$$\overset{\times}{\mathbf{A}}\,\mathrm{o}\,\overset{\times}{\mathbf{B}} \qquad \overset{\mathrm{o}}{\mathbf{A}}\,\times\,\overset{\mathrm{o}}{\mathbf{B}} \qquad \overset{\mathrm{o}}{\mathbf{Y}}\;\;\overset{\times}{\mathbf{A}}\,\mathrm{o}\,\overset{\times}{\mathbf{B}} \qquad \overset{\times}{\mathbf{Y}}\;\;\overset{\mathrm{o}}{\mathbf{A}}\,\times\,\overset{\mathrm{o}}{\mathbf{B}}$$

(1) **(2)** **(3)** **(4)**

We then introduce an atom **Y** with one unpaired-electron, whose spin is opposed to that of the electron located in an **A**-atom atomic orbital, to give the electron spin distributions of structures (**3**) and (**4**).

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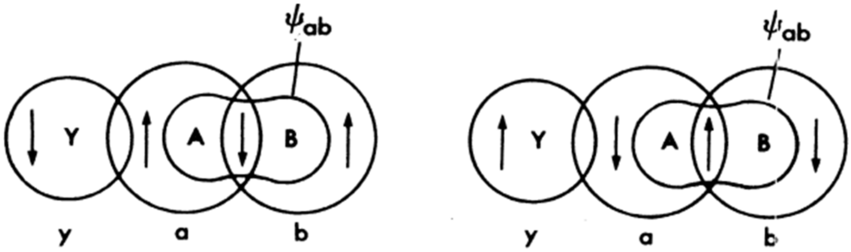
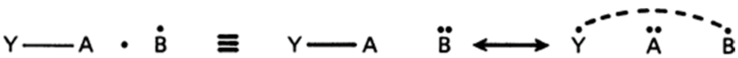


Figure 11-1: Spin-orbitals for electron distributions of structures (**3**) and (**4**).

Fig. 11-1 displays spin-orbitals for the electrons of structure (**3**) and (**4**), when the atomic orbitals are s orbitals. Figs. 1-5 and 2-4 display other sets of atomic orbitals that we are frequently likely to encounter.[i]

For the **A-B** bonding orbital $\psi_{ab} = a + kb$, which accommodates one electron, the bond parameter k is greater than zero.

If the y and a atomic orbitals of structures (**3**) and (**4**) overlap appreciably, we may represent as bonded together the **Y** and **A** atoms on which these atomic orbitals are centred, to give valence-bond structure (**5**).



(5) (6) (7)

Valence-bond structure (**5**) is equivalent to (the lower-energy) resonance between the electron spin structures (**3**) and (**4**). It is also equivalent to (the lower-energy) resonance between the Lewis structures (**6**) and (**7**), each of which has an electron-pair bond and a lone-pair of electrons. The latter equivalence arises because the Pauling "3-electron bond" configuration $(a)^1(\psi_{ab})^1(b)^1$ with $\psi_{ab} = a + kb$ is equivalent to $(a)^2(b)^1 + k(a)^1(b)^2$, i.e. the Pauling "3-electron bond" structure $\dot{\mathbf{A}} \cdot \dot{\mathbf{B}}$ is equivalent to the resonance of $\ddot{\mathbf{A}}\ \dot{\mathbf{B}} \leftrightarrow \dot{\mathbf{A}}\ \ddot{\mathbf{B}}$ (Section 3-6).

If we take account of the electron spins, then it follows that structure (**3**) summarizes (the lower-energy) resonance between structures (**8a**) and (**9a**), and structure (**4**) summarizes resonance between the same structures with the electron spins reversed, i.e. (**8b**) and (**9b**). The spin distributions of (**8a**) and (**8b**) pertain to the Lewis structure (**6**); those of (**9a**) and (**9b**) pertain to the Lewis structure (**7**).

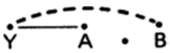
---

[i] As indicated already in Chapter 2, unless stated otherwise (see for example Chapter 23), the equivalent Lewis structure resonance theory assumes that electron-pair bond wavefunctions are of the Heitler-London atomic orbital type – for example $y(1)a(2) + a(1)y(2)$ and $y(1)b(2) + b(1)a(2)$ for structures (**6**) and (**7**). Atomic formal charges are not indicated in the generalized valence bond structures that involve the **Y**, **A**, **B**, **C** and **D** atoms.

$\overset{o}{\mathbf{Y}}\ \overset{x}{\mathbf{A}}\ \overset{ox}{\mathbf{B}}$	$\overset{x}{\mathbf{Y}}\ \overset{o}{\mathbf{A}}\ \overset{xo}{\mathbf{B}}$	$\overset{o}{\mathbf{Y}}\ \overset{xo}{\mathbf{A}}\ \overset{x}{\mathbf{B}}$	$\overset{x}{\mathbf{Y}}\ \overset{ox}{\mathbf{A}}\ \overset{o}{\mathbf{B}}$
(8a)	**(8b)**	**(9a)**	**(9b)**

In structure (**7**), we have indicated (cf. Sections 2-4 and 7-1) the presence of a "long bond" (or formal bond) between atoms **Y** and **B** by means of a pecked line (----). When **Y** and **B** are non-adjacent atoms, the y and b orbital overlap is very small, and therefore the **Y-B** bond is very weak (Section 2-4).

Because structure (**5**) summarizes resonance between (**6**) and (**7**), not all of the unpaired electron charge on **Y** is used to form the **Y-A** bond of (**5**); some of it is used to form the long weak **Y-B** bond. We could indicate this extra bonding in (**5**) by a pecked line, as is shown in **10**. However, since the **Y-B** bond will usually be very much weaker than the **Y-A** bond, in future we shall not indicate the **Y-B** bonding in structures of type (**5**).



(10)

We note also that structure (**7**) has no **Y-A** bond. Therefore, the **Y-A** bond-number (i.e. the number of electron-pair bonds) of structure (**5**) must be *fractional* and less than the value of unity that pertains to the **Y-A** single bond of the structure (**6**). This result is important, and as we shall find when we discuss some examples, it helps to provide a qualitative understanding of the properties of many bonds. *To distinguish the fractional **Y-A** bond of structure* (**5**) *from that of structure* (**6**)*, we have used a thin bond-line in structure* (**5**).

11-2 "Increased-Valence" or Electronic Hypervalence via Pauling "3-Electron Bonds"

In each of the Lewis structures (**6**) and (**7**), there are two bonding electrons, namely those that occupy the y and a, and y and b atomic orbitals, respectively. We shall now deduce that a maximum of three electrons can participate in bonding in structure (**5**). To do this, it is helpful to recall (Section 3-6) that the Pauling "3-electron bond" configuration $(a)^1(\psi_{ab})^1(b)^1$ for the valence-bond structure $\dot{\mathbf{A}}\cdot\dot{\mathbf{B}}$ is equivalent to the molecular orbital configuration $(\psi_{ab})^2(\psi^*_{ab})^1$, in which $\psi_{ab} = a + kb$ and $\psi^*_{ab} = k^*a - b$ are the **A-B** bonding and antibonding molecular orbitals. The one-electron bond of $\mathbf{\dot{A}} \cdot \mathbf{\dot{B}}$ ($\equiv \overset{x}{\mathbf{A}}\,\mathrm{o}\,\overset{x}{\mathbf{B}}$ **or** $\overset{o}{\mathbf{A}} \times \overset{o}{\mathbf{B}}$) is associated with the bonding ψ_{ab} electron whose spin is opposed to that of the unpaired antibonding ψ^*_{ab} electron. When the ψ^*_{ab} orbital of $(\psi_{ab})^2(\psi^*_{ab})^1$ overlaps with the singly-occupied y atomic orbital of a third atom **Y**, singlet spin-pairing of the two electrons that occupy these orbitals generates the fractional **Y-A** and **Y-B** bonding that arises in valence-bond structure (**5**). (The orbital occupations are displayed in Figure 11-2.) Therefore for k = k* = 1in the molecular orbitals $\psi_{\mathrm{ab}} = \mathrm{a} + k\mathrm{b}$ and $\psi^{*}_{\mathrm{ab}} = k^{*}\mathrm{a} - \mathrm{b}$, a total of three electrons can simultaneously participate[1] in **Y-A**, **Y-B** and **A-B** bonding in structure **5**. Because of the possible presence of an additional bonding electron, we have designated this valence-bond structure as an “*increased-valence*” structure[1]. When the ψ_{ab} bonding parameter k is chosen variationally, we may conclude that because an “increased-valence” structure summarizes resonance between several Lewis structures, it *must* have a lower energy than has any of the component Lewis structures.

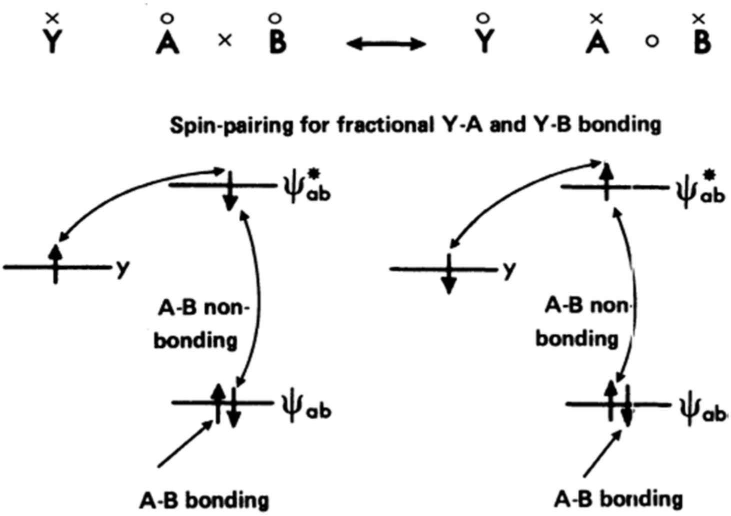
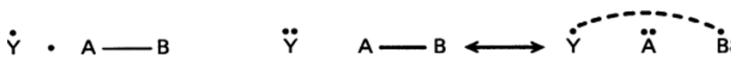


Figure 11.2: Orbital occupations and bonding properties for “increased-valence” structure $\mathbf{Y}-\mathbf{A}\cdot\dot{\mathbf{B}}$. The S = 0 spin wave-function for the spin-pairing is described in Section 15-1, but is not required here. Atomic orbital overlap integrals have been omitted from the normalization constants for ψ_{ab} and ψ^{*}_{ab}.

In most *elementary* accounts of valence, the Lewis “long-bond” structures have been usually omitted from consideration. The results of numerous calculations[2, 3] indicate that these structures can often have significant weights. When this is the case, “long-bond” structures should be included in the elementary valence-bond description of the molecule’s electronic structure. “Increased-valence” structures provide a simple way of including them, together with the more familiar standard Lewis structures (Section 2-2) such as (**6**) with electron-pair bonds located between pairs of adjacent atoms only.

For 4-electron 3-centre bonding units, the "increased-valence" structure (**11**) can also be constructed by spin-pairing the unpaired electron of atom **B** with the antibonding **Y-A** electron of the Pauling "3-electron bond" structure $\dot{\mathrm{Y}}\cdot\dot{\mathbf{A}}$. This "increased-valence" structure is equivalent to resonance between the "long-bond" and standard Lewis structures (**7**) and (**12**), and will participate in resonance with structure (**5**). We may therefore write (**5**) ↔ (**11**) ≡ (**6**) ↔ (**7**) ↔ (**12**), thereby including all of the Lewis electron-pair bond structures in the resonance description for the 4-electron 3-centre bonding unit. Alternatively, we may write either (**5**) ↔ (**12**) or (**6**) ↔ (**11**) to obtain the same result.

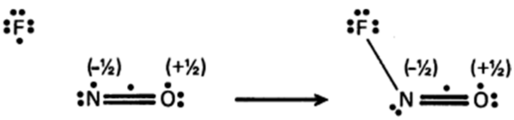


(11) (12) (7)

We shall now use "increased-valence" structures, with Pauling "3-electron bonds" as components, to discuss the electronic structures for a number of molecules that have NO, OO, SS, SO or NO_2 linkages. Bond-lengths for them are reported in Tables 11-1 to 11-4.

11-3 Nitrosyl Halides

The length of the N-O bond of FNO is 1.136 Å, which is similar to the length of 1.150 Å for the free NO molecule. This observation suggests that we might obtain a suitable valence-bond structure for FNO by bonding a fluorine atom to the Pauling "3-electron bond" structure **13** (Section 4-5) for NO.



(13) (14)

Table 11-1: Bond lengths (Å) for some nitrosyl and nitro compounds.

	r(N-O)	*r*(N-X)		*r*(N-O)	*r*(N-X)
NO[a]	1.150		O_2NNO_2 [j]	1.190	1.782
FNO[b]	1.136	1.512	$O'NNO_2$ [k]	1.142 (NO′)	1.864
ClNO[c]	1.139	1.975		1.202, 1.217	(NO)
BrNO[d]	1.146	2.140	FNO_2 [l]	1.180	1.467
HNO[e]	1.209	1.090	$ClNO_2$ [m]	1.202	1.840
CH_3NO [f]	1.211	1.480	CF_3NO_2 [n]	1.21	1.56
CF_3NO [g]	1.197	1.546	CCl_3NO_2 [o]	1.21	1.59
NO_2^- [h]	1.236		CH_3NO_2 [p]	1.224	1.489
NO_2 [i]	1.193				

References: (a) K.P. Huber and G. Herzberg, Molecular Spectra and Molecular Structure, Vol. 4 (Van Nostrand Reinhold, 1979). (b) K.S. Buckton, A.C. Legon and D.J. Millen, Trans. Faraday Soc., **65,** 1975 (1969). (c) D.J. Millen and J. Pannell, J. Chem. Soc., 1322 (1961). (d) D.J. Millen and D. Mitra, Trans. Faraday Soc., **66,** 2408 (1970). (e) J.F. Ogilvie, J. Mol. Struct. **31,** 407 (1976). (f) P.M. Turner and A.P. Cox, J. Chem. Soc., Faraday II, **74,** 533 (1978). (g) S.H. Bauer and A.L. Andreessen, J. Phys. Chem., **76,** 3099 (1972). (h) G.B. Carpenter, Acta. Cryst., **8,** 852 (1955). (I) G.R. Bird, J.C. Baird, A.W. Jache, J.A. Hodgeson, R.F. Curl, A.C. Kunkle, J.W. Bransford, J. Rastrup-Andersen and J. Rosenthal, J. Chem. Phys., **40,** 3378 (1964). (j) B.W. McClelland, G. Gundersen and K. Hedberg, J. Chem. Phys. **56,** 4541 (1972). (k) A.M. Brittain, P.A. Cox and R.L. Kuczkowski, Trans. Faraday Soc., **65,** 1963 (1969). (I) A.C. Legon and D.J. Millen, J. Chem. Soc. A., 1736 (1968). (m) D.J. Millen and K.M. Sinnott, J. Chem. Soc., 350 (1958). (n) I.L. Karle and J. Karle, J. Chem. Phys., **36,** 1969 (1962). (o) W.M. Barss, J. Chem. Phys., **27,** 1260 (1957). (p) A.P. Cox and S. Waring, J. Chem. Soc. Faraday II **68,** 1060 (1972).

Table 11-2: Bond-lengths (Å) for some molecules with O-O linkages.

	r(O-O)	*r*(O-X)		*r*(O-O)	*r*(O-X)
O_2 [a]	1.207		CF_3OOCl [f]	1.447	1.699 (O-Cl)
FOOF[b]	1.217	1.575			1.372 (O-C
HOOH[c, d]	1.475	0.950	CF_3OOF [f]	1.366	1.449 (O-F)
	1.452	0.965			1.419 (O-C)
CF_3OOCF_3 [e]	1.419	1.399	HO_2 [g, h]	1.335	0.977
CF_3OOH [f]	1.447	0.974 (O-H)		1.329	0.975
		1.376 (O-C)	O_3 [i]	1.272	

References: (a) Ref. (a) of Table 11-1. (b) R.H. Jackson, J. Chem. Soc. 4585 (1962). (c) A.L. Redington, W.B. Olson and P.C. Cross, J.Chem. Phys., **36,** 1311 (1962). (d) G. Khachkuruzov and I.W. Przherolskii, Opt. Spectrosk., **36,** 172 (1974). (e) C.J. Marsden, L.S. Bartell and F.P. Diodati, J. Mol. Struct. **39,** 253 (1977). (f) C.J. Marsden, D.D. DesMarteau and L.S. Bartell, Inorg. Chem., **16,** 2359 (1977). (g) Y. Beers and C.J. Howard, J. Chem. Phys., **64,** 1541 (1976). (h) R.P. Uckett, P.A. Freedman and W.J. Jones, Mol. Phys., **37,** 403 (1979). (I) J.-C. Depannemaecker and J. Bellet, J. Mol. Spectr., **66,** 106 (1977).

Table 11-3 Bond-lengths (Å) for some molecules with S-S linkages.

	r(S-S)	r(S-X)		r(S-S)	r(S-X)
S_2 (a)	1.889		HSSH(e)	2.057	1.327
FSSF(b)	1.888	1.635	CH_3SSCH_3 (f, g)	2.023	1.806
ClSSCl(c, d)	1.931	2.057		2.029	1.816
	1.950	2.055	CF_3SSCF_3 (h)	2.030	1.835
F_2SS (b)	1.860	1.598	SF_4 (i,j)		1.545, 1.542 (eq)
					1.646, 1.643 (ax)

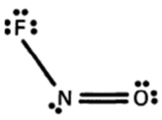
References: (a) Ref. (a) of Table 11-1. (b) R.L. Kuczkowski, J. Amer. Chem. Soc., **86,** 3617 (1964). (c) B. Beagley, G.H. Ekersley, D.P. Brown and D. Tomlinson, Trans. Faraday Soc., **65,** 2300 (1969). (d) C.J. Marsden, R.D. Brown and P.D. Godfrey, J. Chem. Soc. Chem. Comm. 399 (1979). (e) G. Winnewisser, M. Winnewisser and W. Gordy, J. Chem. Phys., **49,** 3465 (1968). (f) B. Beagley and K.T. McAloon, Trans. Farad. Soc., **67,** 3216 (1971). (g) A. Yokozeki and S.H. Bauer, J. Phys. Chem., **80,** 618 (1976). (h) C.J. Marsden and B. Beagley, J. Chem. Soc. Faraday Trans **2**, 77, 2213 (1981).. (I) W.M. Tolles and W.D. Gwinn, J. Chem. Phys. **36,** 1119 (1962); (j) K. Kimura and S.H. Bauer, J. Chem. Phys. **39,** 3172 (1963).

Table 11-4 Bond-lengths (Å) for some molecules with S-O linkages.

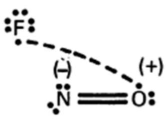
	r(S-O)	r(S-X)		r(S-O)	r(S-X)
SO(a)	1.481		HSO(e)	1.494	1.389
F_2SO (b)	1.413	1.585	SO_2 (f)	1.431	
FSO(c)	1.452	1.602	S_2O (g)	1.464	1.882
Cl_2SO (d)	1.443	2.077	OSSO(h)	1.458	2.025
			CH_2SO (i)	1.469	1.610

References: (a) Ref. (a) of Table 11-1. (b) N.J.D. Lucas and J.G. Smith, J. Molec. Spectr., **43,** 327 (1972); (c) Y. Endo, S. Saito and E. Hirota, J. Chem. Phys. **74**, 1568 (1981)., (d) I. Hargittai, Acta Chem. Acad. Sci. Hung. **59,** 351 (1969). (e) N. Ohashi, M. Kakimota and S. Saito, J. Mol. Spectr. to be published. (f) S. Saito, J. Mol. Spectr., **30,** 1 (1969). (g) E. Tiemann, J. Hœft, F.J. Lovas and D.R. Johnson, J. Chem. Phys., **60,** 5000 (1974). (h) F.J. Lovas, E. Tiemann and D.R. Johnson, J. Chem. Phys., **60,** 5005 (1974). (I) R.E. Penn and R.J. Olsen, J.Mol. Spectr., **61,** 21 (1976).

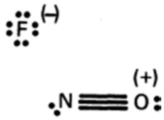
To obtain “increased-valence” structure (**14**), we have spin-paired the nitrogen odd-electron charge of structure (**13**) with a corresponding fraction of the fluorine unpaired electron. Because (**5**) ≡ (**6**) ↔ (**7**), valence-bond structure (**14**)is equivalent to resonance between the standard and “long-bond” Lewis structures (**15**) and (**16**). The “long-bond” structure has no N-F bond, and therefore, the N-F bond-number of (**14**) is *less* than unity. This effect, together with the presence of a “bent” N-F σ bond (Fig. 1-5) is primarily responsible for the N-F bond lengthening.



(15)



(16)



(17)

We may construct similar types of "increased-valence" structures for ClNO and BrNO; each of these molecules has a long nitrogen-halogen bond, and an N-O bond-length similar to that of free NO. (The N-Cl and N-Br bond-lengths of 1.98 Å and 2.14 Å are longer than Pauling's estimates of 1.73 Å and 1.86 Å for the lengths of N-Cl and N-Br single bonds[4]).

The more familiar valence-bond explanation of the bond properties for FNO involves resonance between the standard Lewis structures (**15**) and (**17**). In Chapters 12 and 14, we shall also use these valence-bond structures to generate the "increased-valence" structure (**14**).

It may be noted that the N-O bond-length for each of the nitrosyl halides is slightly shorter than that of free NO, and resonance between "increased-valence" structure (**14**) and the standard Lewis structure (**17**) can account for this observation. If resonance between only the standard Lewis structures (**15**) and (**17**) is used to represent the electronic structure, the shortening of the N-O bond can only be accommodated if the weight for (**17**) is larger than it is for (**15**). The electroneutrality principle suggests that this should not be the case, and this is supported by the results of valence-bond calculations[5], which give a substantially larger weight for structure (**15**). For structures (**15**), (**16**) and (**17**), Roso has calculated coefficients of 0.73, 0.19 and 0.13 for their bond-eigenfunctions in a valence-bond study of the 4-electron 3-centre bonding for FNO. These bond-eigenfunction coefficients suggest that structure (**15**), with zero formal charges on all atoms, must have a rather larger weight than has (**17**)[i].

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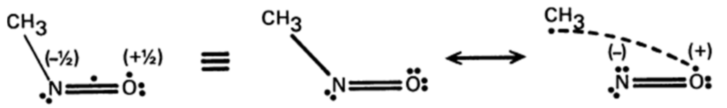
[i] Roso's bond-eigenfunction coefficients that we report here and in other sections, were calculated using non-empirical valence-bond procedures. For the electrons that were included explicitly in the bond-eigenfunction configurations, all integrals that arise in the valence-bond calculations were evaluated using STO-5G atomic orbitals. The number of electrons that could be included in the bond-eigenfunction configurations depended on the size of the molecule. For FNO, the 1s electrons were omitted, whereas all of the electrons were included for the HNO calculation (Section 11-3). In Section 11-10, the bond eigenfunction coefficients for FNO_2 were calculated by including only some of the valence-shell electrons in the bond-eigenfunction configurations, namely those electrons whose locations vary in the valence-bond structures of Fig. 11-8. Similar types of calculations were made for the $\pi + \bar{\pi}$ -electrons of CH_2N_2 (Section 22-4). Except for HNO, we have reported here only the bond-eigenfunction coefficients for the valence-bond structures that are explicitly discussed in the text. It should be noted that because the bond-eigenfunctions are not orthogonal in these calculations, the valence-bond weights are not equal to the squares of the bond-eigenfunction coefficients. However, the magnitudes of these coefficients should provide a qualitative guide to the relative importance of certain valence-bond structures for the ground-state resonance description of a molecule. The results of Roso's studies are in accord with the expectations of the electroneutrality principle. See Ref. 33 for the results of more-recent *ab-initio* valence-bond

11-4 CH_3NO and HNO

The N-O bond-length of 1.21 Å for CH_3NO is similar to Pauling's estimate of 1.20 Å for an N-O double bond, and 0.06 Å longer than that for free NO. The C-N bond-length of 1.48 Å is similar to the C-N single-bond length of 1.47 Å for CH_3NH_2. The "increased-valence" structure (**18**), which can be obtained by spin-pairing the odd-electron of CH_3 with that of NO, does not account for these properties. According to structure (**18**), the N-O and C-N bonds should be respectively shorter than a double bond, and longer than a single bond. Because structure (**18**) summarizes resonance between structures (**19**) and (**20**), the bond-lengths imply that (**20**) makes little contribution to resonance, and that (**19**) alone provides a satisfactory representation of the electronic structure for CH_3NO.



(18) (19) (20)

(21) (22)

For HNO, the N-O bond-length of 1.21 Å is also similar to that of a double-bond. However, the N-H length of 1.09 Å is 0.07 Å longer than the N-H single bonds of NH_3. Neither the "increased-valence" structure (**21**), nor the standard Lewis structure (**22**) can account for the lengths of both bonds simultaneously. But the similarity of the N–O bond-lengths of both CH_3NO and HNO to those of double-bonds suggests that CH_3- and H-substituents do not bring out the "increased-valence" aspects of bonding to a significant extent, i.e. they do not lead to much development of a Pauling "3-electron bond" in a 4-electron 3-centre bonding unit for a neutral molecule[ii]. This hypothesis will receive some further

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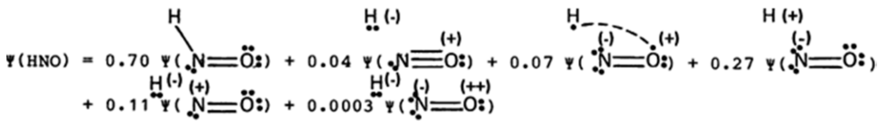
calculations for (a) FNO and FNO_2 and (b) *asym* N_2O_3. They give similar types of conclusions for both FNO (with the N-F nitrogen atomic orbital oriented as in Figure 1-5) and FNO_2.

ii This conclusion must have its origins partly in the different magnitude of the atomic orbital overlap Integral for N–F (σ) single bonds compared with those for N–H and N–CH_3 single bonds. For illustrative purposes here we shall assume that the nitrogen and carbon orbitals are respectively sp^2 and sp^3 hybridized, and that the fluorine and hydrogen orbitals are 2pσ and 1s. The resulting Slater orbital overlap integrals are then 0.3_2, 0.5_2 and 0.6_1 for the N–F, N–H and N–CH_3 bonds. With approximate molecular orbital theory for 4-electron 3-centre bonding units (Section 14-2), the much larger N–H and N–C overlap integrals must raise the empirical support in Sections 11-4 and 11-5. Another way to say this is that the contribution of the "long-bond" structure (such as structure (**20**)) to the ground-state resonance is small. Roso[5] has calculated the following valence-bond wave-function for HNO:

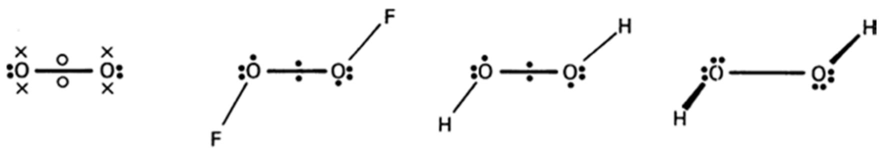


The coefficient of 0.07 for the "long-bond" structure provides theoretical support for the unimportance of this structure.

As we have found for the nitrosyl halides, if a hydrogen atom or CH_3 is replaced by the more-electronegative halogen atoms, the Pauling "3-electron bond" of NO in the nitrosyl compound can be stabilized. For CF_3NO, the electronegativity of CF_3 should be intermediate between those of CH_3 and F. Therefore, some stabilization of the Pauling "3-electron bond" for this molecule may occur. The "increased-valence" structure **18** for CF_3NO (with CF_3 replacing CH_3) implies that the C-N bond is longer than a single-bond, and that the N-O bond should be shorter than those of CH_3NO and HNO. Both of these inferences are in agreement with the observed bond-lengths of Table 11-1.

11-5 Some Dioxygenyl Compounds

The ($S = S_z = 1$ spin) valence-bond structure for the ground-state of molecular oxygen is (**23**), with two Pauling "3-electron bonds" (Section 4-3). By spin-pairing the two unpaired electrons with those of two fluorine or two hydrogen atoms, we obtain "increased-valence" structures (**24**) and (**25**) for F_2O_2 and H_2O_2. These valence-bond structures indicate O-O bond properties which are similar to that of free O_2 and long, weak O-F and O-H bonds.



(23) (24) (25) (26)

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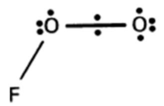
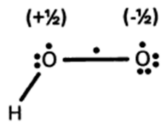
energies of the antibonding σ^*_{NH} and σ^*_{NC} orbitals relative to that of the σ^*_{NF} orbital, i.e. the latter orbital is more accessible for the oxygen $2p\bar{\pi}$ electrons of FNO. The greater electronegativity of F relative to CH_3 and H will also re-enforce the greater tendency for the oxygen $2p\bar{\pi}$ electrons of FNO to delocalize. Similar considerations are also appropriate for F_2O_2 vs H_2O_2 (Section 11-4), F_2S_2 vs H_2S_2 (Section 11-5) and for many related systems.

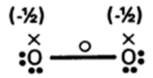
For F_2O_2, structure (**24**) is a suitable valence-bond structure; the O-O bond-lengths of O_2 and F_2O_2 in Table 11-2 are similar, and the O-F bond-lengths of 1.575 Å are much longer than the 1.42 Å for the single bonds of F_2O. However, the O-H bond-lengths of H_2O_2 are almost identical with those of the single bonds of H_2O (0.96 Å), and the O-O bond-length is similar to that of the single bond of O_2^{2-} (1.49 Å), whose valence-bond structure was derived in Section 4-2. The Lewis structure (**26**) for H_2O_2 accounts for these properties adequately, to lend support to the hypothesis that hydrogen atoms bring out little "increased-valence" aspects of bonding, i.e. that they do not stabilize significantly Pauling "3-electron bonds" in 4-electron 3-centre bonding units for neutral molecules.



(27)



(28)

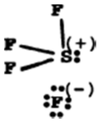
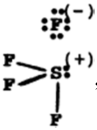


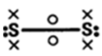
(29)

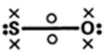
The radicals FO_2 and HO_2 are also known. By using the above considerations, we suggest that suitable valence-bond structures for them are (**27**) and (**28**), which we obtain by bonding an F atom to structure (**23**), and protonating the O_2^- "3-electron bond" structure (**29**) (Section 4-3). The results of some force constant calculations[6] indicate that the O-O bond of FO_2 is similar in strength to those of O_2 and F_2O_2, whereas the O-O bond of HO_2 resembles that of O_2^-. Valence-bond structures (**27**) and (**28**) show these relationships. For HO_2, the hydrogen atom is not able to stabilize appreciably the development of a Pauling "3-electron bond" for the 4-electron 3-centre bonding unit, and the O-O and H-O bond-lengths of 1.335 and 0.977 Å reflect this effect.

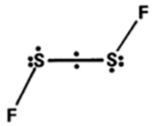
For the ROOR′ series of Table 11-2, increasing stabilization of the O-O Pauling "3-electron bond" as one passes from H to CF_3 to F accounts for the observed shortening of the O-O bond for the series HOOH, CF_3OOH, CF_3OOCF_3, CF_3OOF and FOOF. As the O-O bond-length decreases, the O-H, O-C and O-F lengths should increase according to the above "increased-valence" considerations. Lengthening of the latter bonds is observed to occur in a regular manner.

11-6 Some S-O and S-S Compounds

The ($S = S_z = 1$ spin) valence-bond structures for the ground-states of S_2 and SO are (**30**) and (**31**) (Section 4-6). From them, we may obtain the "increased-valence" structures (**32**), (**33**) and (**34**) for two isomers of F_2S_2, and for F_2SO. For both F_2S_2 isomers, these "increased-valence" structures imply that the S-S bonds should have lengths that are similar to those for free S_2, and that the S-F bonds are longer than single bonds; this they are found to be; see Table 11-3. (We have assumed that the two equatorial bonds of SF_4, with lengths of 1.54 Å are single-bonds; the standard Lewis structures, namely  and , show this to be the case.) On the other hand, the reported bond-lengths for H_2S_2 and $(CH_3)_2S_2$ indicate that these molecules have S-S single bonds, with the hydrogen and methyl radicals unable to stabilize the Pauling "3-electron bonds" of S_2.


(30)


(31)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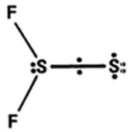
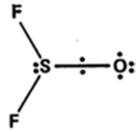
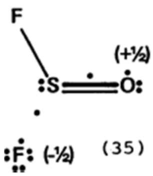
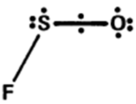
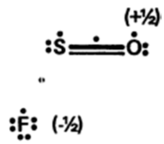

(33)


(34)

From "increased-valence" structure **(34)** for F_2SO, we would predict that the S-F bonds should be longer than the single-bond length of 1.54 Å, and that the S-O length should be similar to that of free SO. Although lengthening of the S-F bonds is observed, the S-O bond-length of 1.41 Å is shorter than the 1.48 Å for free SO. Possibly this shortening is due to a significant contribution of "increased-valence" structure **(35)** to resonance with (**34**); in structure (**35**), the S-O bond-number + bond-order (maximum value = 2.5) exceeds the value of 2 that occurs in (**31**). Similarly, for FSO, "increased-valence" structure (**36**) will participate in resonance with "increased-valence" structure (**37**), from which it may be deduced that the S-F and S-O bond-lengths for this radical are respectively longer than a single bond, and shorter than that of free SO. The experimental lengths of 1.602 and 1.452 Å are in accord with this deduction.


(35)


(36)


(37)

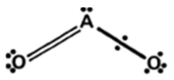
The above theory is also appropriate for Cl_2SO, whose S-Cl and S-O bond-lengths of 2.077 Å and 1.443 Å are respectively longer than the S-Cl single-bond length of 2.014 Å for CH_3SCl, and shorter than that for free SO.

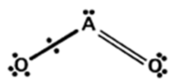
For HSO, a valence-bond structure similar to (**36**), with H replacing F, accounts simultaneously for the observations that the S-O length of 1.494 Å is similar to the 1.481 Å for free SO, and that the S-H length of 1.389 Å is longer than the single-bond length of 1.336 Å for H_2S. However, on the basis of the discussion in Section 11-4 for HO_2, it would be expected that the H-S bond length for HSO would be similar to those for HS and H_2S, and that the S-O bond-length would be appreciably longer than that of free SO.

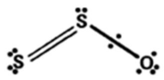
11-7 O_3, SO_2, S_2O and NO_2^-

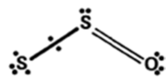
In Sections 11-2 to 11-5, atomic orbitals for the "increased-valence" bonding units are of the $\sigma + \bar{\pi}$ (Fig. 1-5) type. The $\mathbf{Y} — \mathbf{A}$ bonds are (fractional) σ-bonds. We shall now describe some examples of "increased-valence" structures that involve $\mathbf{Y} — \mathbf{A}$ π-bonds as well as σ-bonds in the "increased-valence" bonding units. For 4-electron 3-centre π-bonding, the orbital overlap is displayed in Fig. 2-4.

Oxygen and sulphur atoms ($:\dot{\underset{\cdot\cdot}{O}}\cdot$ and $:\dot{\underset{\cdot\cdot}{S}}\cdot$) have two unpaired electrons in their ground-states. By spin-pairing these electrons with those of the Pauling "3-electron bond" structures (**23**), (**30**) and (**31**) for the ground-states of O_2, SO and S_2, we obtain the "increased-valence" structures (**38**)-(**41**) for O_3, SO_2 and S_2O. In structures (**38**) and (**39**) the A-atom is either oxygen or sulphur. Since the two terminal oxygen atoms are symmetrically equivalent, these two valence-bond structures are of equal importance for a resonance description of O_3 and SO_2.

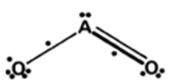

(38)

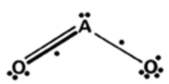

(39)

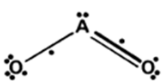

(40)

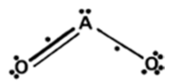

(41)

Each of the structures (**38**)-(**41**) has two "increased-valence" bonding units, which may be rearranged to obtain "increased-valence" structures such as (**42**)-(**45**), for O_3 and SO_2. These structures participate in resonance with (**38**) and (**39**). The presence of formal charges in structures (**42**)-(**45**) suggests that they make a smaller contribution to the ground-state resonance than do structures (**38**)-(**41**). Therefore, for simplicity here and elsewhere in this book, we shall usually give consideration only to what we assume to be the most important of the "increased-valence" structures, i.e. those that involve the smallest formal charge separations (when the formal charges are allocated using the assumption that bonding electrons are shared equally by pairs of adjacent atoms).

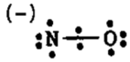

(-½) (+½)
(42)


(+½) (-½)
(43)


(-½) (+½)
(44)

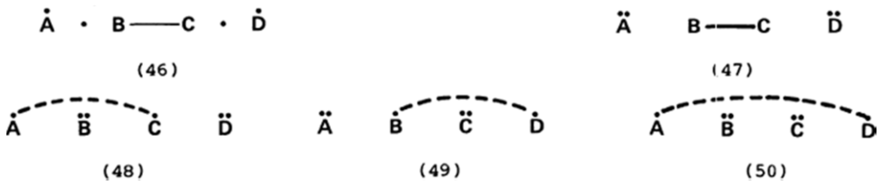

(+½) (-½)
(45)

Each of the "increased-valence" structures (**38**) and (**39**) has an O-O double bond similar to that of structure (**23**) for O_2, and a fractional $O = O$ bond with a bond-number less than 2. Thus, resonance between (**38**) and (**39**) implies that, on the average, less than four electrons are involved in bonding between each pair of adjacent oxygen atoms. Consequently, it is not surprising that the bond-lengths of 1.278 Å for O_3 are longer than the 1.207 Å for the double bond of O_2. However, resonance between structures (**38**) and (**39**) for SO_2 (with $\mathbf{A} \equiv S$) does not account for the observed shortening of its S-O lengths (1.431 Å) relative to the 1.481 Å for free SO.

The nitrite anion, NO_2^-, is isoelectronic with O_3, and its N-O bond-lengths of 1.24 Å are about 0.04 Å longer than a "normal" N-O double bond. Resonance between the "increased-valence" structures (**38**) and (**39**), in which atom A is a nitrogen atom, reflects this observation. These structures may also be obtained by spin-pairing the two unpaired electrons that are present for the ground-states of O and NO^-. The anion NO^- is isoelectronic with O_2, and therefore, its ground-state valence-bond structure  has two Pauling "3-electron bonds".

11-8 Pauling "3-Electron Bonds" and 6-Electron 4-Centre Bonding: N_2O_2, Cl_2O_2, S_2O_2 and $S_2I_4^{2+}$

In Fig. 11-3, the orbital occupations and electron spins are displayed for two equivalent Pauling "3-electron bond" structures $\dot{\mathbf{A}}\cdot\dot{\mathbf{B}}$ and $\dot{\mathbf{C}}\cdot\dot{\mathbf{D}}$. When the atomic orbitals of these two structures overlap, spin-pairing of their (antibonding) unpaired-electrons generates the "increased-valence" structure (**46**), for which a total of four electrons can participate in fractional **A–B, A–C**, **A–D**, **B–C, B–D** and **C–D** bonding[7].



Only two bonding electrons are present in the standard Lewis structure (**47**). Because $\dot{\mathbf{A}}\cdot\dot{\mathbf{B}} \equiv \ddot{\mathbf{A}}\,\dot{\mathbf{B}} \leftrightarrow \dot{\mathbf{A}}\,\ddot{\mathbf{B}}$ and $\dot{\mathbf{C}}\cdot\dot{\mathbf{D}} \equiv \ddot{\mathbf{C}}\,\dot{\mathbf{D}} \leftrightarrow \dot{\mathbf{C}}\,\ddot{\mathbf{D}}$, it may be deduced that "increased-valence" structure (**46**) is equivalent to resonance between the standard Lewis structure (**47)** and the "long-bond" Lewis structures (**48**), (**49**) and (**50**). Because no **B-C** bond is present in each of the latter three structures, the **B-C** bond-number for (**46**) is less than unity. Therefore, the **B-C** bond for structure (**46**) will be longer and weaker than is that for a "normal" **B-C** electron-pair bond, (as in structure (**47)**), with a bond-number of unity.

The discussion above is of course a generalization of that described previously in Section 10-1 for N_2O_4. It is appropriate for all molecules that involve extended 6-electron 4-centre bonding units, i.e. for molecules that have one or more sets of 6 electrons distributed amongst 4 overlapping atomic orbitals (a, b, c and d located around four atomic centres). These orbitals may be either π, or σ (Fig. 2-6) or $\sigma + \bar{\pi}$ (Fig. 1-5), or σ + δ (Fig. 8-2) or σ (Fig. 2-6) in character. Each of NO and ClO has a Pauling "3-electron bond" in its ground-state valence-bond structure (Sections 4-5 and 4-7), and dimers of these radicals are known to be

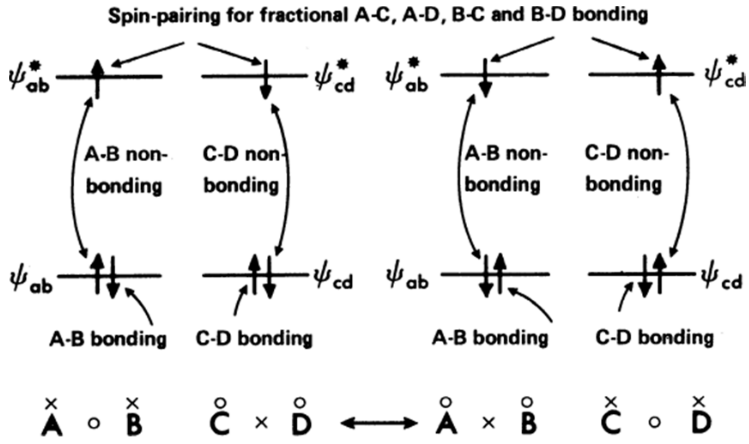
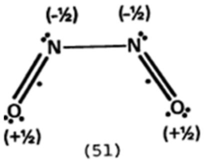
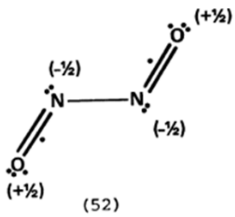
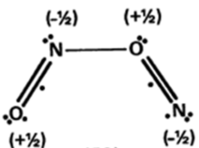


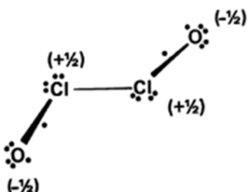
Figure 11-3: Orbital occupations and bonding properties for "increased-valence" structure $\dot{\mathbf{A}}\cdot\mathbf{B}$——$\mathbf{C}\cdot\dot{\mathbf{D}}$.

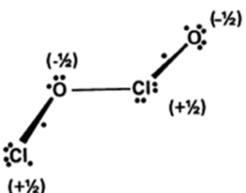
formed, with weak **B-C** type bonds. If dimerization is assumed to involve primarily the spin-pairing of the antibonding π*-electrons of two monomers in a $\sigma + \bar{\pi}$ manner, then "increased-valence" structures such as (**51**)-(**56**)

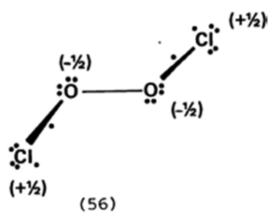

(51)


(52)


(53)

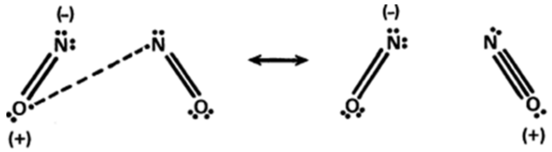

(54)

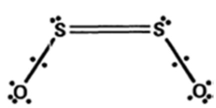

(55)


(56)

are obtained. These structures have **B-C** bond-numbers that are less than unity. However the results of valence-bond calculations[8] for N_2O_2 show that the orientations of the nitrogen atomic orbitals, as in Fig. 1-5 to give strong nitrogen lone-pair-lone-pair repulsions, rather than the fractionality of the N-N σ-bond, is primarily responsible for the existence of the long, weak N-N bond.

Both *cis* and *trans* conformers for ONNO are known[9], with *cis* more stable than *trans*. The additional stability of the *cis* conformer is associated with *cis* O-O overlap[10]; in valence-bond theory, this occurs primarily via the oxygen $2p\bar{\pi}$-orbitals (Fig. 1-5; cf. N_2O_4 in Section 7-3). The stabilization energy for covalent-ionic resonance of the type **(57)** ↔ (**58**) is *cis* O-O overlap dependent (Section 7-3)) and leads to the development of a Pauling "3-electron bond" between the oxygen atoms. The covalent structure (**57**) is one of the contributing forms (of type (**48**)) to the "increased-valence" structure (**51**).



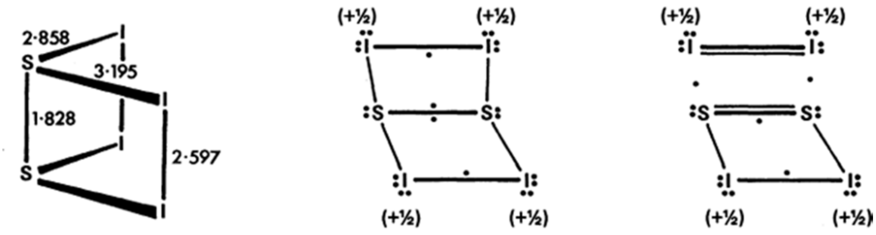


(57) (58) (59)

Dinerman and Ewing[11] have shown that the N-O stretching frequencies for gaseous NO and *cis* ONNO are very similar (1848 and 1860 cm^{-1}) and obtained a small dissociation energy of 11 kJ mol^{-1} for N_2O_2 (cf. 250 kJ mol^{-1} for N_2H_4, Section 7-1) . Ab-initio molecular orbital[10] estimates of the N-N bond-lengths for the *cis* and *trans* dimers are 1.768 Å and 1.686 Å. The N-N and N-O bond-lengths and the ONN bond-angles for the *cis* isomer in the gas phase have been estimated[9] to be approximately 1.75 Å, 1.15 Å and 90°. Molecular beam electron resonance spectroscopy[12] of the gaseous *cis* isomer give 2.33 (12) Å, 1.15 (1) Å, and 95 (5)° respectively for these lengths and angles. For the molecular crystal[13, 14], the N-N length of 2.18 Å is very long (cf. 1.45 Å for N_2H_4, Section 7-1). The ONON isomer has been characterized[9, 15], with a weak N-O bond linking the NO moieties.

Three Cl_2O_2 isomers have been characterized[16]. The lowest-energy isomer is Cl_2OO[16]. For the ClOOCl isomer, the Cl-O and O-O bond-lengths[17] of 1.7044 Å and 1.4259 Å imply that "increased-valence" structure (**56**) is not a suitable valence-bond structure for this isomer, and that the Cl_2O_2 analogue of the F_2O_2 increased-valence structure (**24**) is more (but not entirely) appropriate. For the ClOClO isomer, two sets of bond lengths have been reported in Ref. 18. Their average values are 1.50 Å (ClO), 1.73 Å (OCl) and 1.71 Å (ClO). Increased-valence structure (**55**) does not accommodate the 1.71 Å length. Essentially "increased-valence" descriptions of the bonding for Cl_2O_2 have been provided by Linnett[19].

The geometry for a *cis* dimer of SO has been reported (Table 11-4), with S-S and S-O bond-lengths of 2.025 and 1.458 A. The SO monomer, with two Pauling "3-electron bonds" in its valence-bond structure (**31**), has a bond-length of 1.481 Å. On dimerization, "increased-valence" structure (**59**), with fractional S-S σ- and π-bonds, is obtained. Inspection of structures (**31**) and (**59**) makes clear why the SO bond-lengths for the monomer and dimer are similar, and why the S-S bond for the dimer (with an S-S bond-number < 2 in structure (**59**)) is appreciably longer than the length of 1.89 Å for the double-bond of S_2.



(a) (b) (c)

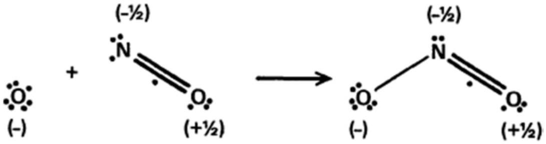
Figure 11-4: Bond-lengths and "increased-valence" structures for $S_2I_4^{2+}$.

The geometry (Fig. 11-4**a**) for the cation $S_2I_4^{2+}$ has been reported[20]. A convenient "increased-valence" structure, namely (**b**) of Fig. 11-4, can be constructed by spin-pairing the antibonding π_x^* and π_y^* electrons of ground-state S_2 with the unpaired-electrons for two I_2^+ radicals. On the basis of this structure, it would be predicted that the S-S and I-I bond lengths would be similar to the 1.89 and 2.56 Å for free S_2 and I_2^+. The observed shortening of the S-S bond and lengthening of the I-I bonds imply that other types of valence-bond structures such as (**c**), and its mirror image structure participate significantly in resonance with structure (**b**). In each $S_2I_2^+$ component of these structures, there is an "increased-valence" representation for a cyclic 6-electron 4-centre bonding unit. All structures account for the observation that the S-I bond-lengths are much longer than the estimate of 2.37 Å for a "normal" S-I single bond.

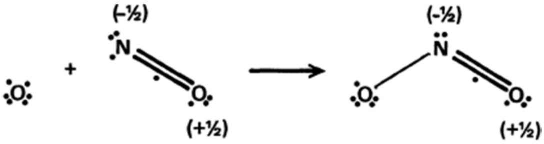
11-9 NO_2, NO_2^-, ClO_2, SO_2^- and SO_3

We shall now demonstrate that to obtain suitable "increased-valence" structures for some molecules, it is necessary either to use an excited state for the component diatomic system, or to re-organize the electron distribution of the "increased-valence" structure which is obtained using the diatomic ground-state.

In Section 11-7, we constructed suitable "increased-valence" structures for NO_2^- by bonding together O with NO^-. By singlet spin-pairing the unpaired electrons of O^- and NO, and O and NO, we obtain "increased-valence" structures (**60**) and (**61**) for NO_2^- and NO_2.



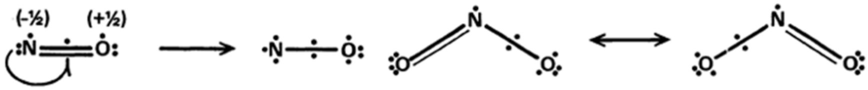
(60)



(61)

These “increased-valence” structures, together with their mirror images, indicate that the N-O properties for both systems should be very similar. However, the measured lengths of 1.24 Å (NO_2^-) and 1.19 Å (NO_2) differ significantly. Electron spin resonance studies[22] of NO_2 indicate appreciable unpaired-electron charge (about 1/2 electron) located in a nitrogen orbital (Section 6-1). “Increased-valence” structure (**61**) locates the unpaired electron solely on the oxygen atom. We may conclude that structures (**60**) and (**61**) give unsatisfactory representations of the electronic structures of NO_2^- and NO_2. However, if we use an excited state for NO, we can generate a more suitable valence-bond structure for NO_2.

The valence-bond structure (**62**) for the NO ground-state, can form only one (fractional) bond with a second oxygen atom by using its unpaired electron. We can increase the valence of the nitrogen atom by promoting a nitrogen (primarily) 2s electron into the antibonding NO π* orbital which is vacant in (**62**). This $s_N \rightarrow \pi^*_{NO}$ promotion generates the valence-bond structure (**63**), with two Pauling “3-electron bonds”.



(62) (63) (64) (65)

By bonding structure (**63**) for excited state NO to an oxygen atom ($:\dot{\underset{\cdot\cdot}{O}}\cdot$) in its ground-state, “increased-valence” structures (**64**) and (**65**) are obtained for NO_2. Resonance between these structures generates fractional odd-electron charge on each atom and, when compared with (**38**) ↔ (**39**) for NO_2^-, this resonance accounts for the observed shortening of the N-O bonds of NO_2 relative to those of NO_2^-.

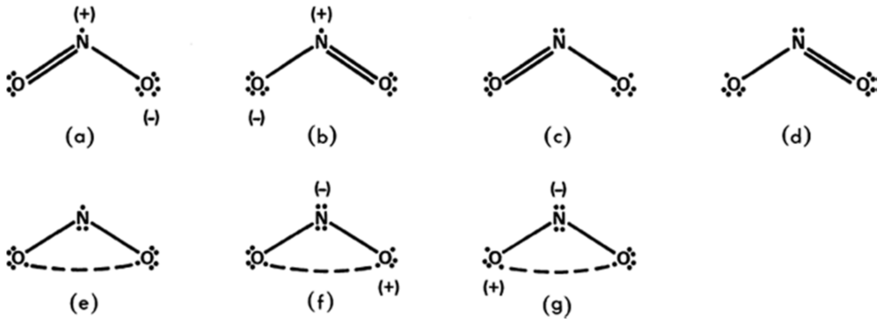


Figure 11-5: Component valence-bond structures for NO_2 "increased-valence" structures (**64**) and (**65**).

Resonance between "increased-valence" structures (**64**) and (**65**) is equivalent to resonance between the Lewis structures (**a**)-(**g**) of Fig. 11-5.

Structures (**a**)-(**d**) are the standard Lewis structures (**1**)-(**4**) of Section 6-1, and each of (**e**), (**f**) and (**g**) is a "long-bond" Lewis structure. The absence of formal charges for structure **e** would suggest that it could make an important contribution to the ground-state resonance.

In Fig. 11-6, we use an alternative method to construct "increased-valence" structures (**38**) and (**39**) for NO_2^-, and (**64**) and (**65**) for NO_2. It involves the delocalization of non-bonding electrons of "increased-valence" structures (**60**) and (**61**) into bonding orbitals (Chapter 12), and simultaneously, the transfer of a bonding electron into an atomic orbital. Similar types of electronic reorganizations are also displayed in Fig. 11-6 for ClO_2, SO_2^- and SO_3, when they are formed from O + ClO, O^- + SO and 2O + SO. For each of these latter structures, the formal charge separations are the smallest that are in accord with the presence of the maximum number of one-electron bonds and fractional electron-pair bonds.

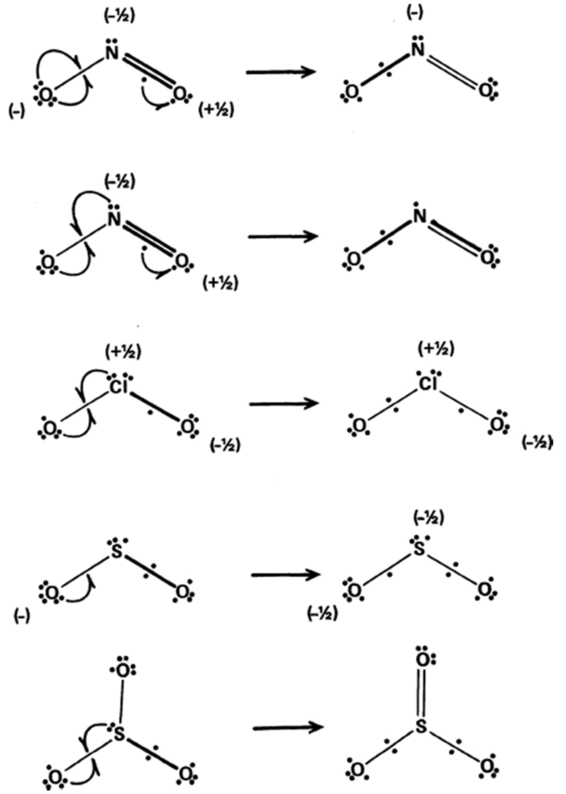
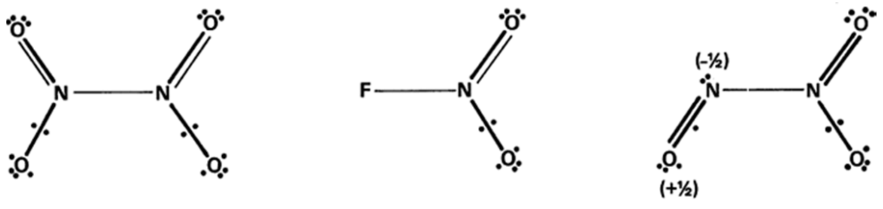


Figure 11-6: Construction of "increased-valence structures for NO_2^-, NO_2, ClO_2, SO_2^- and SO_3 from NO + O^-, NO + O, ClO + O, SO + O^- and SO + O + O. :O and O: are equivalent valence-bond locations for the oxygen lone-pair $2p\bar{\pi}$ electrons, here (for NO_2^- and NO_2), and elsewhere..

11-10 N_2O_4, N_2O_3 and FNO_2

In Sections 7-1 and 7-2 we have provided Lewis valence-bond and molecular orbital explanations for the existence of a long, weak N-N bond for N_2O_4. The N-N and N-F bond-lengths for N_2O_3 and FNO_2 are also longer than single bonds (Table 11-1).

By using the NO and NO_2 valence-bond structures (**62**) and (**64**) of Section 11-9, together with the reactions NO_2 + NO_2, NO_2 + NO_2 and F + NO_2, we can construct the "increased-valence" structures (**66**)-(**68**)



(66) (67) (68)

for N_2O_4, N_2O_3 and FNO_2. It is easy to deduce that "increased-valence" structure (**66**) for N_2O_4 summarizes resonance between 16 Lewis octet structures, namely those of Fig. 11-7 and their mirror images.

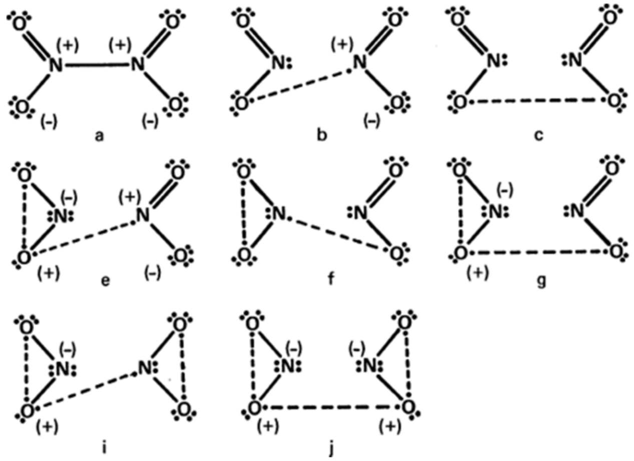


Figure 11-7: Component octet *cis* Lewis structures[24] for N_2O_4 "increased-valence" structure (**66**). Equivalent mirror-image *cis* structures are not displayed. There are also octet *trans* Lewis structures (cf. structure (**7**) of Chapter 7) that participate in resonance with the octet *cis* Lewis structures. As well the *cis* "increased-valence" structure (**66**), there is a mirror-image *cis* "increased-valence" structure and two *trans* "increased-valence" structures. Resonance between these four "increased-valence" structures is equivalent to resonance between the octet Lewis structures.

Of these latter structures, eleven do not have N-N electron-pair bonds, and the absence of formal charges for some of them suggests that they make important contributions to the ground-state resonance description of the electronic structure. Consequently, the N-N bond-number for the "increased-valence" structure (**66**) is rather less than unity, which implies that the N-N bond for N_2O_4 is longer than a single bond. The lengthenings of the N-F and N-N bonds for FNO_2 and N_2O_3 may similarly be deduced from an examination of "increased-valence" structures (**67**) and (**68**).

"Increased-valence" structure (**67**) for FNO_2 summarizes resonance between the Lewis octet structures of Fig. 11-8.

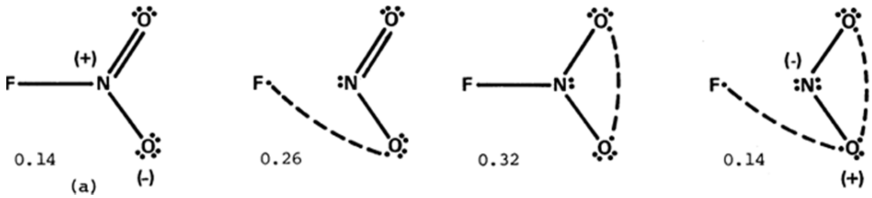


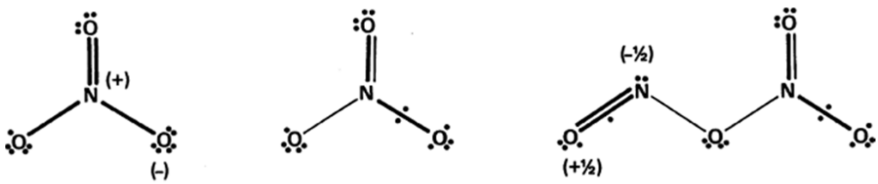
Figure 11-8: Component octet Lewis structures for FNO_2 "increased-valence" structure (**67**), together with bond-eigenfunction coefficients[25].

Two of these structures carry zero formal charges on all atoms, and involve a "long" O-F or O-O bond. Roso's bond-eigenfunction coefficients for all structures are reported in the Figure, and they imply that these "long-bond" structures may be more important than is the standard Lewis structure **a**.

For each of N_2O_4, N_2O_3 and FNO_2, the N-O bond-lengths of Table 11-1 for the nitro-linkages are similar to the N-O double-bond length of 1.20 Å. Resonance between "increased-valence" structures of types (**66**)-(**68**) indicates why this similarity exists better than does resonance between the standard Lewis structures (e.g. type **a** for each of Figs. 11-7 and 11-8).

11-11 *sym* NO_3 and *asym* N_2O_4

In Section 6-5, we have given consideration to a valence-bond structure of type (**69**) for *sym* NO_3. An "increased-valence" structure for this radical may be obtained by spin-pairing the odd-electron of NO_2 with an unpaired electron of an oxygen atom in its ground-state, when the NO_2 is represented by an "increased-valence" structure of type (**64**). The resulting "increased-valence" structure (**70**) for *sym* NO_3 has two more bonding electrons than has the Lewis structure (**69**), and therefore it is more stable. Because it does not involve formal charge separation, increased-valence structure (**70**) is in accord with the requirements of the electroneutrality principle. The location of the odd-electron in an oxygen $\overline{\pi}$-electron atomic orbital in these valence-bond structures is in accord with the results of electron spin resonance measurements and molecular orbital considerations[26].



(69) (70) (71)

Fateley et al.[27] have identified an *asym* N_2O_4 isomer $ONONO_2$ in a nitrogen matrix, and have assigned infra-red frequencies of 1654 cm^{-1} and 1290 cm^{-1} to the asymmetric and symmetric stretches of the nitro (NO_2) linkage. These frequencies may be compared with 1748 cm^{-1} and 1261 cm^{-1} for the *sym* N_2O_4 (O_2NNO_2) isomer[28] in a nitrogen matrix. (The gas-phase frequencies[29] for the latter isomer are 1758 cm^{-1} and 1264 cm^{-1}.) An 1829 cm^{-1} frequency for *asym* N_2O_4 is similar to the 1876 cm^{-1} frequency for the N-O stretch of free NO, and both are rather larger than the 1562 cm^{-1} and 1564 cm^{-1} stretching frequencies for the N-O double bonds[30] of HNO and CH_3NO. "Increased-valence" structures of type (**71**), which may be generated by spin-pairing the odd electrons of NO and NO_3 with the valence-bond structures (**62**) and (**70**), are in accord with these observations.

Spin-pairing of the odd electrons of "increased-valence" structures of type (**64**) for two NO_2 molecules, *cis* and *trans* "increased-valence" structures can be constructed for *asym* N_2O_4, as well as those of type (**66**) for *sym* N_2O_4.

The peroxy O_2NO isomer of NO_3 has been identified[31] as one of the products of the gas phase reactions NO + O_2 and NO + O_3. "Increased-valence" structures for the *cis* and *trans* isomers may be obtained by spin-pairing the unpaired electron of structure (**62**) for NO with one of the unpaired electrons of structure (**23**) for O_2, as described in Ref. 32.

11-12 Conclusions

By starting with Pauling "3-electron bond" structures for one or more diatomic systems, we have found that it is possible to construct "increased-valence" structures for polyatomic molecules. Often, use of the ground-states of the diatomic systems leads quickly to suitable polyatomic valence-bond structures. To obtain a suitable "increased-valence" structure for NO_2, we needed to proceed through an excited state of NO. This is also the case for various other molecules. However, valence-bond structures for excited states for diatomic systems might not always be easy to construct. Fortunately, it is possible to circumvent this problem by generating "increased-valence" structures from familiar standard Lewis structures for polyatomic molecules. In the following chapters, we shall describe how this may be done.

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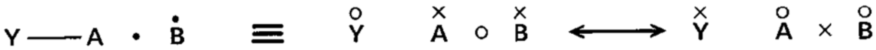
Chapter 12 "Increased-Valence" Structures Constructed from Lewis Structures: Delocalization of a Lone-Pair Electron into a Vacant Bonding Orbital

For diamagnetic polyatomic molecules, it is easy to write down standard Lewis structures that have electron-pair bonds and lone-pairs of electrons. It is then also easy to generate "increased-valence" structures from them. To do this, we must delocalize one or more lone-pair electrons into *either* two-centre bonding orbitals *or* two-centre antibonding orbitals, both types of orbitals being vacant in the standard Lewis structures. In this chapter, we shall describe these delocalizations into bonding orbitals.

In Section 11-1, we demonstrated that "increased-valence" structure (**1**) involves the electron spin distributions of structures (**2**) and (**3**).



(1) (2) (3)

The wave-functions for the $\overset{\mathrm{x}}{\mathbf{A}}\;\mathbf{o}\;\overset{\mathrm{x}}{\mathbf{B}}$ and $\overset{\mathrm{o}}{\mathbf{A}}\times\overset{\mathrm{o}}{\mathbf{B}}$ components of structures (**2**) and (**3**) utilize the orbitals a, $\psi_{ab} = \mathrm{a} + k\mathrm{b}$ and b, in which a and b are overlapping atomic orbitals that are centred on atoms **A** and **B** (Section 3-6). The s_z spin quantum numbers for the electrons that occupy these orbitals have values of $+\frac{1}{2}$, $-\frac{1}{2}$, and $+\frac{1}{2}$, and $-\frac{1}{2}$, $+\frac{1}{2}$ and $-\frac{1}{2}$. We may obtain the valence-bond structures $\overset{\mathrm{x}}{\mathbf{A}}\;\mathbf{o}\;\overset{\mathrm{x}}{\mathbf{B}}$ and $\overset{\mathrm{o}}{\mathbf{A}}\times\overset{\mathrm{o}}{\mathbf{B}}$ by starting with the electron arrangements of

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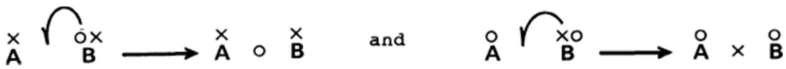
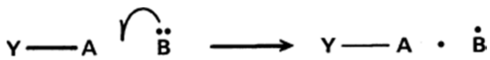
$\overset{\mathrm{x}}{\mathbf{A}}\ \overset{\mathrm{ox}}{\mathbf{B}}$ and $\overset{\mathrm{o}}{\mathbf{A}}\ \overset{\mathrm{xo}}{\mathbf{B}}$

and then delocalizing an $s_z = +\frac{1}{2}(\mathrm{x})$ or $s_z = -\frac{1}{2}(\mathrm{o})$ electron of **B** into an **A-B** bonding molecular orbital. Thus, we may write



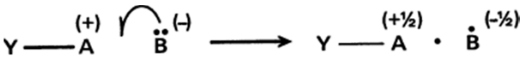
in which we have transferred one electron from the atomic orbital b into the bonding molecular orbital $\psi_{ab} = \mathrm{a} + k\mathrm{b}$. To indicate a one electron-transfer we have used a "fishhook" or "curly arrow"[1], with a single barb[1-3], i.e.

These considerations imply that we may generate the "increased-valence" structure (**1**) from the standard (or Kekulé-type) Lewis structure (**4**) by delocalizing a **B** electron of this structure into a vacant **A-B** bonding orbital, i.e. by writing



(4) (1)

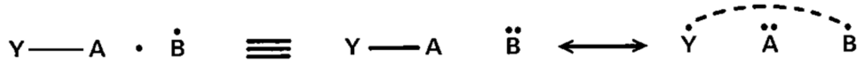
Whenever the a and b atomic orbitals overlap, the delocalization of (**4**) must *always* occur to some extent. It will be helped considerably if atoms **A** and **B** carry formal positive and negative charges, respectively. The delocalization will then reduce the magnitudes of these formal charges. Thus, if after the delocalization, the **A-B** bonding electron is shared equally by the two atoms, then the **A** and **B** formal charges become $+\frac{1}{2}$ and $-\frac{1}{2}$, i.e.



(5) (6)

In general, the electron of the **A-B** bond will be shared unequally by the **A** and **B** atoms, and the resulting formal charges will not be ½-integer in magnitude. Our example here is illustrative of formal charge reduction. However (in accord with what has been done in the previous chapters) for illustrative purposes only, formal charges are assigned on the assumption that bonding electrons are shared equally by a pair of adjacent atoms; see also Section 2-5(b).

Even if **A** and **B** carry no formal charges in structure (**4**), it is energetically advantageous to delocalize the **B** electron into the vacant **A-B** bonding orbital. By doing so, we increase the number of electrons that can participate in the overall **Y-A**, **Y-B** and **A-B** bonding. We have shown in Section 11-1 that structure (**1**) summarizes resonance between the standard Lewis structure (**4**) and the "long-bond" Lewis structure (**7**), and therefore *any* **B** electron delocalization into an **A-B** bonding orbital will stabilize structure (**4**) by means of its resonance with structure (**7**).



(1) (4) (7)

When describing the ground-states of neutral molecules, it is desirable that the formal charges be small in magnitude, i.e. less than unity. This requirement should be particularly appropriate when atoms **A** and **B** have fairly similar neutral atom electronegativities.

In Chapter 11, we have found that fluorine atoms could stabilize appreciably the Pauling “3-electron bond(s)” of NO, O_2, SO and S_2, and that “increased-valence” structures (**9**) and (**11**) are suitable valence-bond structures for FNO and F_2O_2. Therefore, if we write down the standard Lewis structures (**8**) and (**10**), the fluorine atom(s) must induce appreciable delocalization of oxygen lone-pair electron(s) into the N-O and O-O bonding orbitals. We have indicated these delocalizations in structures (**8**) and (**10**). On the other hand, hydrogen atoms do not generate appreciable stabilization of Pauling “3-electron bonds” (Sections 11-3 and 11-4) of 4-electron 3-centre bonding units in neutral molecules, and similar oxygen delocalizations for HNO and H_2O_2 must occur only to a very small extent. We have found that the standard Lewis structures (**12**) and (**13**) alone are adequate simple representations of the electronic structures of these molecules.

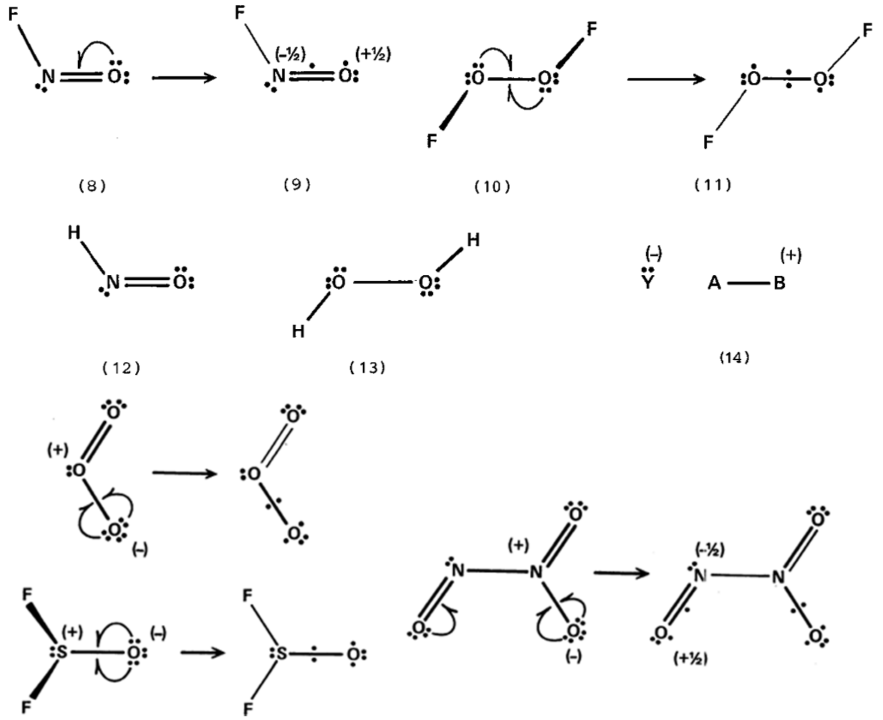


Figure 12-1: Generation of “increased-valence” structures from standard Lewis structures by delocalizing lone-pair electrons into vacant bonding orbitals.

In Fig. 12-1, we show how to use the standard Lewis structures to construct some of the “increased-valence” structures that we have considered previously in Chapter 11. For each molecule, one or more lone-pair electrons have been delocalized into vacant 2-centre bonding orbitals. This technique for generating “increased-valence” structures (and thereby stabilizing the Lewis structure) can be used whenever the arrangement of electrons shown in structure (**4**) occurs in a Lewis valence- bond structure. This must surely be the case for thousands of molecular systems!

The question may be asked: “How will such a delocalization reduce the magnitudes of the formal charges for a standard Lewis structure of type (**14**)?”. Delocalization of a **Y** electron into a **Y-A** bonding molecular orbital will not reduce the magnitude of the formal charge on **B**. To obtain this effect, it is necessary to delocalize a **Y** electron of structure (**14**) into an **A-B** *antibonding* molecular orbital. This procedure will be described in Chapter 14. However, in Chapter 13, we shall use the technique described in the present chapter (namely of delocalizing non-bonding electrons into bonding molecular orbitals) to construct “increased-valence” structures for various types of *N*-centre bonding units.

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Chapter 13 "Increased-Valence" Structures for *N*-Centre Bonding Units

The technique described in Chapter 12 for constructing "increased-valence" structures, namely that of delocalizing one or more non-bonding electrons of a standard Lewis structure into adjacent bonding orbitals, is quite general and easily applied. We shall now use this method to construct "increased-valence" structures for numerous molecular systems that involve 6-electron 5-centre, 8-electron 6-cent re and longer *N*-centre bonding units, as well as for some molecules with 4-electron 3- centre and 6-electron 4-centre bonding units. In general, we shall find that only one or two "increased-valence" structures are required in order to make deductions concerning bond lengths that are in qualitative accord with the measured lengths, i.e. for the systems considered, "increased-valence" structures provide easily derived and economical representations of their electronic structures.

13-1 N_2O and some Isoelectronic Molecules and Ions with 4-Electron 3-Centre Bonding Units

In Fig. 2-10 we have displayed four "increased-valence" structures for N_2O, namely (**I**)-(**IV**) of Fig. 13-1, here. They may be generated from the standard Lewis structures (**1**)-(**4**) of Fig. 2-8 by delocalizing non-bonding π- and $\bar{\pi}-$electrons from the terminal nitrogen and oxygen atoms into adjacent N-N and N-O π- and $\bar{\pi}-$bonding orbitals, as is done in Fig. 13-1.

In Section 2-5, we have used the electroneutrality principle to deduce that (**I**) should be the most important of the four "increased-valence" structures, and have then deduced from (**I**) that the N-N and N-O bond-lengths for N_2O should be respectively longer than an N-N triple bond, and similar to an N-O double bond. The bond-lengths reported in Table 13-1 are in accord with this deduction.

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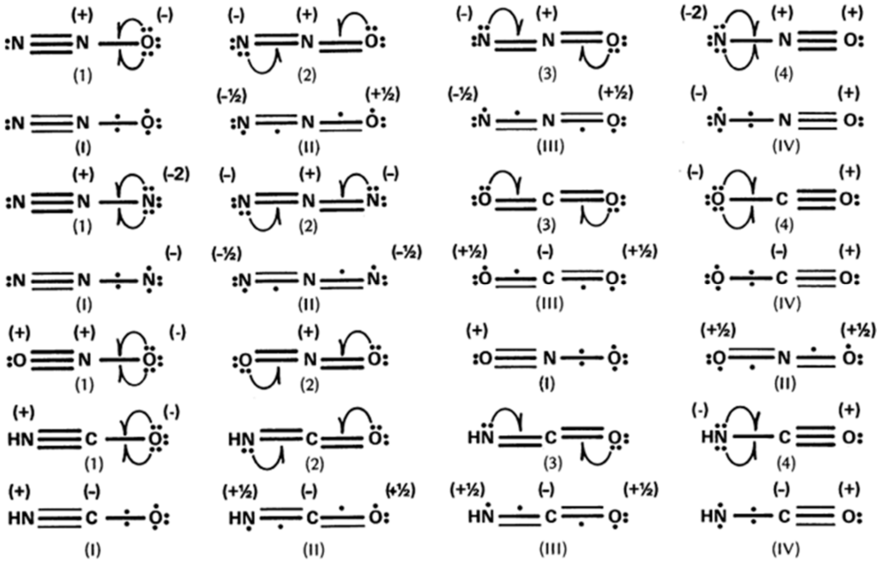
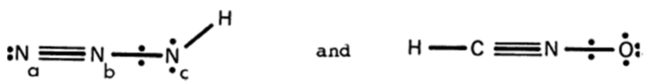


Figure 13-1: Standard Lewis and "increased-valence" structures for N_2O, N_3^-, CO_2, NO_2^+ and HNCO. For N_3^-, CO_2, and NO_2^+, the symmetrically-equivalent structures are not displayed.

Table 13-1: Bond-lengths[1-7] (Å) for some isoelectronic systems with 16 valence-shell electrons. See also Ref. 8. Estimates of standard triple and double bond lengths are[9]: $C \equiv N$, 1.15 Å; $N \equiv N$, 1.10 Å; $C = N$, 1.27 Å; $N = N$, 1.24 Å; $C = O$, 1.21 Å; $N = O$, 1.20 Å.

	N-N or C-N	N-O, C-O or N-NH
N_2O	1.129	1.188
HN_3	1.133	1.237
N_3^-	1.176	
HCNO	1.161	1.207
NO_2^+		1.153
CO_2		1.162
HNCO	1.207	1.171

For HN_3 and HCNO, which are isoelectronic with N_2O, the standard Lewis and "increased-valence" structures are similar to those for N_2O, except for the replacement of the O and terminal N of N_2O with N-H and H-C, respectively. From the "increased-valence" structures of type (**I**), namely

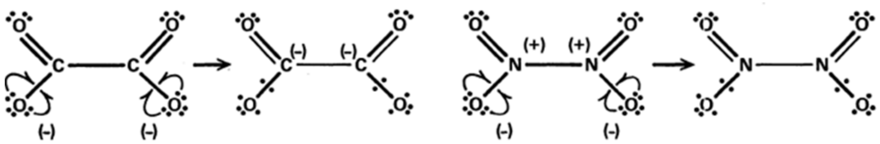


we may deduce that the $N_a - N_b$ and C-N bonds should be longer than triple bonds, and that the $N_b - N_c$ and N-O bond-lengths should be similar to those of double bonds. With the possible exception of the C-N bond for HCNO, the bond-lengths reported in Table 13-1 are in accord with these deductions.

The symmetrical triatomic species N_3^-, NO_2^+ and CO_2 are also isoelectronic with N_2O. Their standard Lewis and "increased-valence" structures are displayed in Fig. 13-1. For each of these systems, resonance between the four "increased-valence" structures indicates more clearly than does resonance between the standard Lewis structures that the N-N, N-O and C-O bond-lengths of 1.18 Å, 1.15 Å and 1.16 Å are shorter than those of double-bonds (see Table 13-1). The smaller formal charges for "increased-valence" structures (**II**) and (**III**) suggest that these are the most important of the four "increased-valence" structures, and inspection of them alone makes clear why the bond-lengths are shorter than double-bonds. Similar types of "increased-valence" structures should also be the primary structures for HNCO. Inspection of them in Fig. 13-1 leads to the conclusion that the C-N and C-O bonds are both shorter than double bonds, and the bond-lengths reported in Table 13-1 support this conclusion.

13-2 N_2O_4, $C_2O_4^{2-}$ and $(RNO)_2$, with 6-Electron 4-Centre Bonding Units

To generate the "increased-valence" structures for NO_2^+ and CO_2, we have delocalized oxygen non-bonding π- and $\bar{\pi}-$electrons into the adjacent N-O and C-O bonding π- and $\bar{\pi}-$orbitals. However, because these delocalizations lead to the formation of a negative formal charge on the carbon atom of CO_2, they should be less extensive than are those that occur for NO_2^+. Similarly, for $C_2O_4^{2-}$ the delocalizations of the (O^-) oxygen π- and $\bar{\pi}-$electrons for the standard Lewis structures of type (**1**) should be less extensive than they are for (**3**) for N_2O_4.



(1) (2) (3) (4)

In the resulting "increased-valence" structures (**2**) and (**4**), the carbon atoms carry formal negative charges, whereas the nitrogen atoms are uncharged. One consequence of a reduced degree of π_O and $\bar{\pi}_O$ electron delocalization for $C_2O_4^{2-}$ is that the C-O bond orders are smaller than are the N-O bond-orders for N_2O_4. If we use

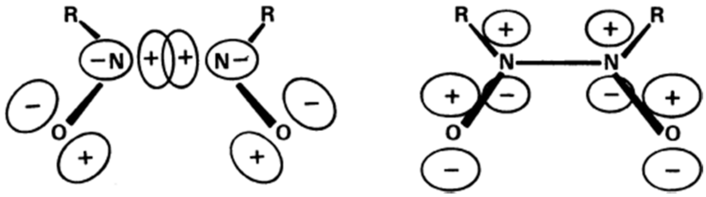
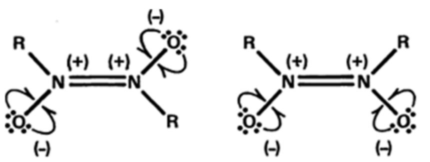


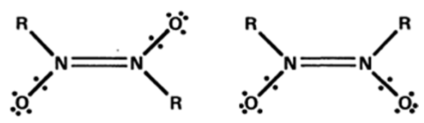
Figure 13-2: Atomic orbitals for 6-electron 4-centre bonding units of $(RNO)_2$.

this result when we compare structures (**2**) and (**4**), we can account[10] for the observation that the C-O bond-lengths[11] of 1.26 Å for $C_2O_4^{2-}$ are longer than a C-O double bond (1.21 Å), whereas the N-O bond- lengths[12] of 1.19 Å for N_2O_4 are similar to the double-bond length of 1.20 Å. The smaller extent of $\overline{\pi}_O$ electron delocalization for $C_2O_4^{2-}$ also generates a C-C σ-bond number for structure (**2**) that is larger than the N-N σ-bond number for structure (**4**). This accounts for the observation that the C-C bond-length of 1.57 Å[11] for $C_2O_4^{2-}$ is substantially shorter than the N-N bond-length of 1.78 Å[12] for N_2O_4; see also Section 7-4.

For the C-nitroso dimers $(RNO)_2$ of Table 13-2, the lengths of the N-N and N-O bonds are both longer than those of double-bonds. The standard Lewis structures of (**5**) may be used to generate the "increased-valence" structures of (**6**) by delocalizing the oxygen π- and $\overline{\pi}$ – electrons into bonding N-O orbitals. The "increased-valence" structures, with zero formal charges on all atoms, imply that only the N-N bond should be longer than a double bond. However, because the overlap integral for the N-N σ-bond (0.6_5) is larger than the 0.3 for the corresponding bond of N_2O_4, the $\overline{\pi}$ – electron delocalization must occur to a much smaller extent for $(RNO)_2$ than it does for N_2O_4. Therefore the N-O h_N-$\overline{\pi}_O$ bond order for $(RNO)_2$ does not reach the maximum value of 0.5 that obtains for structure (**6**) when zero formal charges are present. This reduced N-O bond-order leads to the lengthening of the N-O bonds for $(RNO)_2$ relative to the essentially N-O double-bond lengths for N_2O_4.



(5)



(6)

Table 13-2: Bond-lengths for dimeric nitroso and structurally similar compounds[13].

	bond length Å [a]				
compound names	C-N	N-N	N-O	geometry	Ref [e]
cis-Azobenzene dioxide	1.454 (5)	1.321 (5)	1.268 (4)	*cis*	present work
(Nitrosobenzene dimer)	1.463 (5)		1.261 (4)		
trans-2.2-Dicarboxy-azobenzene dioxide	1.460 (3)	1.308 (3)	1.267 (3)	*trans*	present work
(2-Nitrosobenzoic acid dimer) Perfluoroazobenzene dioxide	1.439 (6)	1.324 (5)	1.267 (6)	*cis*	41
(Pentafluoronitrosobenzene dimer)	1.439 (6)		1.267 (6)		
1, 8-Dinitrosonaphthalene	1.430 (6)	1.376 (5)	1.276 (6)	*cis*	25
(Internal dimer)	1.439 (6)		1.256 (5)		
Nitrosocyclohexane	1.488 (6)	1.319 (6)	1.272 (6)	*trans*	19
2-Nitronitrosoethane	1.470 (4)[b]	1.304 (6)	1.262 (4)[c]	*trans*	18
Azoxyanisole	1.496 (5)	1.218 (5)	1.279 (4)	*trans*	42
Azobenzene [d]	1.433 (3)	1.243 (3)		*trans*	43
p.p'-Dichloroazobenzene	1.433 (5)	1.252 (5)		*trans*	44

[a] Estimated standard deviations are given in parentheses.

[b] The C-N bond involving the nitroso group.

[c] The N-O bond of the nitroso group.

[d] Two unique molecules are present in the unit cell, one of which is disordered. The data presented are from the nondisordered molecule. The estimated standard deviations may be severely underestimated.

[e] See Ref. 13 for details of these references.

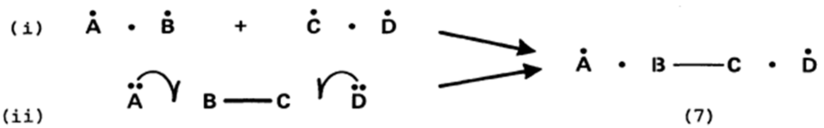
13-3 Comments on 6-Electron 4-Centre Bonding Units

Two "increased-valence" bonding units of the general type (**7**) are present in the "increased-valence" structures of (**6**); one for the six π-electrons and one for six $\bar{\pi} + \sigma -$ electrons The relevant atomic orbitals are displayed in Fig. 13-2 for the *cis* isomer. The latter type of "increased-valence" bonding unit is also present in structures (**2**) and (**4**) for the six $\bar{\pi} + \sigma -$ electrons of $C_2O_4^{2-}$ and N_2O_4. In this chapter and the previous chapters, we have introduced two techniques that may be used to generate (**7**), namely

(i) To bond together two Pauling "3-electron bond" structures $\dot{\mathbf{A}} \cdot \dot{\mathbf{B}}$ and $\dot{\mathbf{C}} \cdot \dot{\mathbf{D}}$ (with antiparallel spins for the two antibonding odd-electrons), and

(ii) To delocalize non-bonding $\mathbf{\ddot{A}}$ and $\mathbf{\ddot{D}}$ electrons of the standard Lewis structure $\mathbf{\ddot{A}}$ **B—C** $\mathbf{\ddot{D}}$ into the adjacent A-B and C-D bonding orbitals.

Thus, we may write



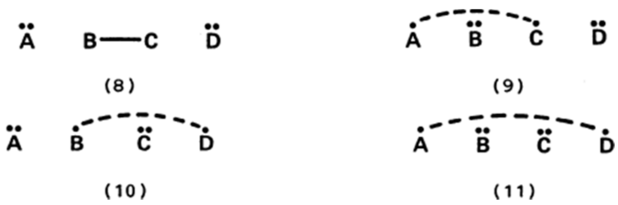
(7)

“Increased-valence” structure (**7**) may be generated whenever 6-electron 4-centre bonding can occur, i.e. whenever six electrons are distributed amongst four overlapping atomic orbitals. For the special case that **A** and **D**, and **B** and **C** are pairs of equivalent atoms (and therefore a and d, and b and c are pairs of equivalent atomic orbitals), the 4-centre molecular orbitals are given by Eqn. (1),

$$
\begin{aligned}
\psi_1 &= \{a + d + \lambda(b + c)\} / (2 + 2\lambda^2)^{\frac{1}{2}} \\
\psi_2 &= \{a - d + \mu(b - c)\} / (2 + 2\mu^2)^{\frac{1}{2}} \\
\psi_3 &= \{\lambda(a + d) - (b + c)\} / (2 + 2\lambda^2)^{\frac{1}{2}} \\
\psi_4 &= \{\mu(a - d) - (b - c)\} / (2 + 2\mu^2)^{\frac{1}{2}}
\end{aligned}
\qquad (1)
$$

in which λ and μ are parameters, both > 0. If atomic orbital overlap integrals are omitted from the normalizing constants and the orthogonality relationships, then the molecular orbitals of Eqn. (1) are normalized orthogonal. The mobile σ-electron molecular orbitals of Eqs. 7-3 to 7-6 for N_2O_4 are particular examples of these orbitals.

To construct the molecular orbitals of Eqn. (1), we have assumed that the atomic orbitals are oriented so that all overlap integrals between adjacent atomic orbitals are > 0, as occurs for the orbitals of Fig. 13-2, for example. Therefore, ψ_4 is **A-B**, **B-C** and **C-D** antibonding, and so it must be the highest-energy molecular orbital. The lowest-energy molecular orbital configuration for the six electrons is then $(\psi_1)^2(\psi_2)^2(\psi_3)^2$. In Section 10-2, we have deduced that this configuration may be expressed as $\Psi_{\text{covalent}} + \Psi_{\text{ionic}}$, and that Ψ_{covalent} is the wave-function for the mobile σ-electrons of “increased-valence” structure (**7**). It is easy to demonstrate that (**7**) summarizes resonance between the standard and “long-bond” Lewis structures (**8**)-(**11**); this is a result that we have obtained previously from the discussion of the bonding for N_2O_4 and N_2O_2 in Sections 10-1 and 11-7.



13-4 Cyclic 6-Electron 4-Centre Bonding Units

A number of cyclic molecules and ions, for example $(SN)_2$ and Se_4^{2+}, have six π-electrons distributed amongst four pπ-atomic orbitals. The standard Lewis structures for Se_4^{2+} are displayed in Fig. 13-3(a).

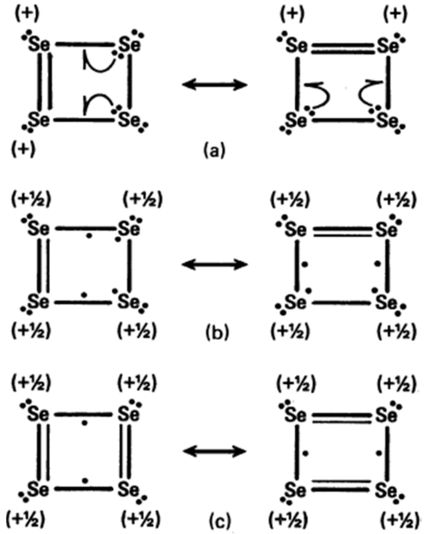
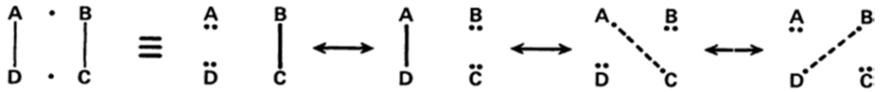
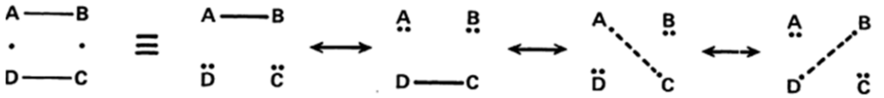


Figure 13-3: Standard Lewis and "increased-valence" structures for Se_4^{2+}. Mirror-image structures are not displayed for (a) and (b).

By delocalizing non- bonding π-electrons into the adjacent Se-Se π bonding-orbitals, we may generate the "increased-valence" structures of (**b**), each of which has an "increased-valence" bonding unit of type (**7**) for the six π-electrons. However, because the atoms of (**b**) that correspond to the **A** and **D** atoms of structure (**7**) are adjacent, their atomic orbitals can overlap well. Therefore, we shall represent these atoms as bonded together, to form the type (**c**) "increased-valence" structures. Either of the structures of (**c**) involves a cyclic "increased-valence" bonding unit of type (**12**) or (**13**), each of which summarizes resonance between four Lewis structures. These latter structures are similar to structures (**8**)-(**11**), except that the "long-bond" structure (**11**) is replaced by a standard structure.



(12)



(13)

The Se-Se bond lengths[14] of 2.28 Å for Se_4^{2+} are shorter than the estimate of 2.34 Å for an Se-Se single bond, and resonance between either the four standard Lewis structures of type (**a**) or the two "increased-valence" structures of type (**c**) accounts for this observation. However, the "increased-valence" representation does this in a more economical manner.

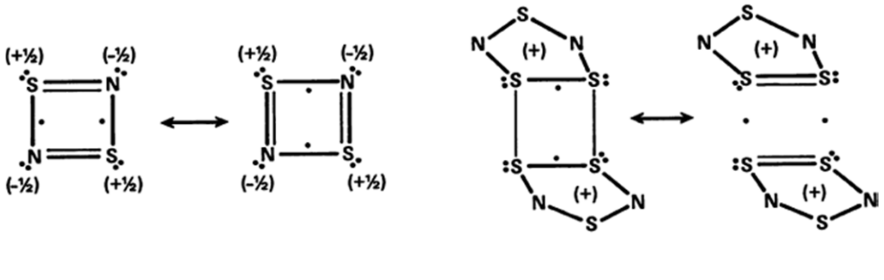
The molecular orbitals for the π-electrons are given by Eqn. (13-1), with $\mu = \lambda = 1$. For systems such as Se_4^{2+} with D_{4h} symmetry, the molecular orbitals ψ_2 and ψ_3 are degenerate, as are the excited configurations $\Psi_2(\mathrm{MO}) = (\psi_1)^2(\psi_2)^2(\psi_4)^2$ and $\Psi_3(\mathrm{MO}) = (\psi_1)^2(\psi_3)^2(\psi_4)^2$. These configurations may be linearly combined[15], with $\Psi_1(\mathrm{MO}) = (\psi_1)^2(\psi_2)^2(\psi_3)^2$ to generate the configuration interaction wave-function of Eqn. (2),

$$\Psi(\mathrm{CI}) = C_1\Psi_1(\mathrm{MO}) + C_2(\Psi_2(\mathrm{MO}) + \Psi_3(\mathrm{MO})) \tag{2}$$

with $C_2 < 0$ when $C_1 > 0$ in the lowest-energy linear combination (cf. Section 10-3). This C.I. wave-function may be transformed[15] (cf. Section 10-2) and expressed as

$$\Psi(\mathrm{CI}) = (C_1 - C_2)(\Psi_{\text{covalent}} + \Psi'_{\text{covalent}}) + (C_1 + C_2)(\Psi_{\text{ionic}} + \Psi'_{\text{ionic}}) \tag{3}$$

in which Ψ_{covalent} and Ψ'_{covalent} are the wave-functions for "increased-valence" structures (**12**) and (**13**). Because $C_1 > 0$ when $C_2 < 0$, these structures must represent the primary valence-bond structures for cyclic 6-electron 4-centre bonding units with D_{4h} symmetry. The same result is true for systems such as $(SN)_2$ with C_{2h} symmetry, for which the "increased-valence" structures are those of (**14**), and for the S_4 linkage of the $S_3N_2^+$ dimer[15]. The latter species has D_{2h} symmetry for the S_4 linkage; overlap considerations[15] for it suggest that "increased-valence" structure (**15**) has a larger weight than has structure (**16**). The bond-number for each of the intermoiety S-S bonds of structure (**15**) is 0.25 (cf. Section 7-1), and the length of 3.03 Å for these bonds is ~ 1 Å longer than a "normal" S-S single bond[16].

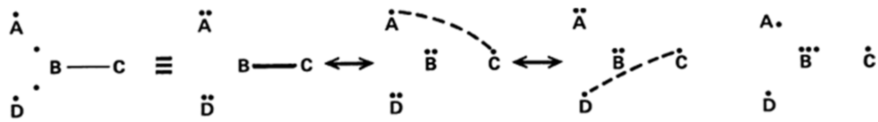


(14) (15) (16)

The bonding for $S_2I_4^{2+}$ has been described in Section 11-7; each $S_2I_2^+$ component has a cyclic 6-electron 4-centre bonding unit. For such bonding units, the concomitant bonding has also been designated as a 2-electron 4-centre bond[16, 17].

13-5 Branching 6-Electron 4-Centre Bonding Units

If an atom A is sp^2 hybridized to form three coplanar σ-bonds, it is often possible to find numerous molecules that have Lewis valence-bond arrangements of type (**17**) of Fig. 13-4 for six electrons that occupy four overlapping atomic orbitals. This bonding unit pertains for the π-electrons of $(NH_2)_2CO$, for example. For this molecule, the standard Lewis structures are structures (**1**)-(**3**) of Fig. 13-5.



(17) (18) (19) (20) (21)

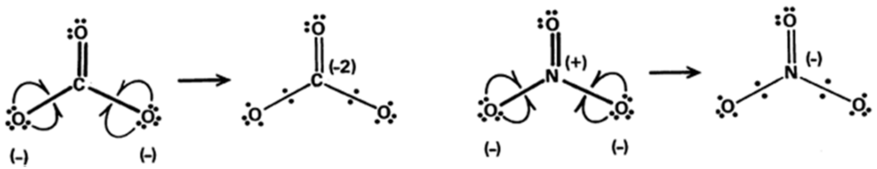


Figure 13-4: Standard Lewis and "increased-valence" structures for CO_3^{2-} and NO_3^-.

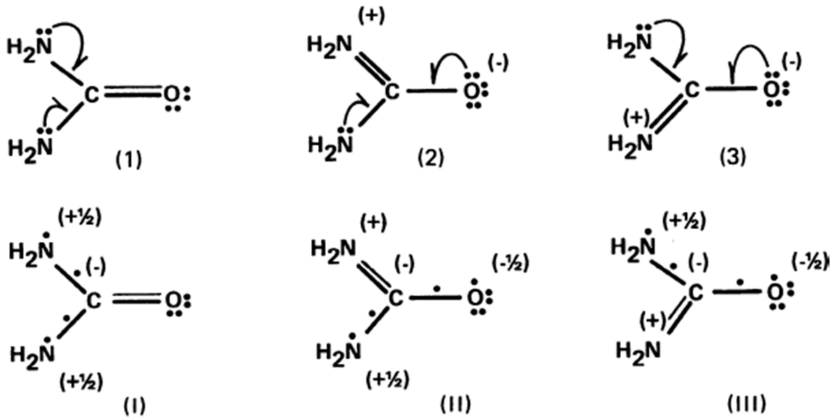


Figure 13-5: Standard Lewis and "increased-valence" structures for $(NH_2)_2CO$.

Resonance between these three structures is usually invoked to explain why the C-N and C-O bond-lengths[18] of 1.34 Å and 1.27 Å are respectively shorter than the C-N single-bond length of 1.47 Å and longer than the C-O double-bond length of 1.21 Å. An alternative explanation may be obtained by consideration of the "increased-valence" structures (**I**)-(**III**) of Fig. 13-5, which may be generated from the standard Lewis structures by means of the π-electron delocalizations that are indicated. The formal charges for the "increased-valence" structures suggest that (**I**) should be the most important of these structures, and it alone indicates that the C-O bond-number and C-N bond-orders are respectively less than two and greater than unity.

Each of the "increased-valence" structures of Fig. 13-4 involves an "increased-valence" bonding unit of type (**17**) for the six π-electrons. It summarizes[10] resonance between the standard Lewis structure (**18**) and the two "long-bond" Lewis structures (**19**) and (**20**). (Because structure (**21**) involves three electrons located in the **A**-atom atomic orbital, this structure cannot be included in the Lewis structure resonance scheme.)

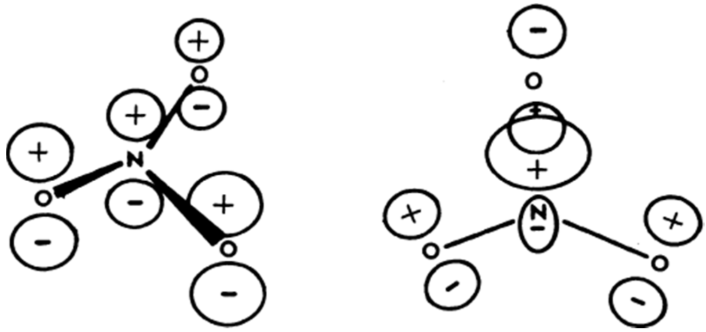


Figure 13-6: Atomic orbitals involved in the formation of 6-electron 4-centre bonding units for the valence-bond structures of Figure 13-5.

"Increased-valence" bonding units of type (**17**) also obtain for the NO_3^- and CO_3^{2-} anions, which are isoelectronic with $(NH_2)_2CO$. Each of their standard Lewis structures are displayed in Fig. 13-5 has valence-bond arrangements of type (**18**) for the six π-electrons and for sets of four $\overline{\pi}$ + two N-O or C-O σ-electrons. The relevant atomic orbitals are displayed in Fig. 13-6.

Therefore, when we generate the "increased-valence" structures of Fig. 13-5 (by delocalizing the oxygen π- and $\overline{\pi}$−electrons into N-O or C-O bonding orbitals), two "increased-valence" bonding units of type (**17**) will be formed. Because the N^+ for the standard Lewis structures of NO_3^- is more electronegative than the C for CO_3^{2-}, the delocalizations of the oxygen π- and $\overline{\pi}$−electrons for NO_3^- will be more appreciable than they are for CO_3^{2-} (cf. N_2O_4 and $C_2O_4^{2-}$ Section 13-2). Therefore, the N-O bond-orders will be larger than the C-O bond-orders, and this is reflected in the bond-lengths. The N-O lengths of 1.22 Å for NO_3^- (as in $NaNO_3$)[19] are only 0.02 Å longer than the N-O double-bond length of 1.20 Å, whereas for CO_3^{2-}, C-O lengths of 1.28 Å[20] are 0.07 Å longer than a double bond. Because of the symmetry of the anions, each of three "increased-valence" structures will contribute equally to the resonance, and therefore, no economy is obtained by using the "increased-valence" structures instead of the standard Lewis structures to describe the electronic structure. However, resonance between the three standard Lewis structures does not indicate why the C-O and N-O bond-orders should differ, and why the N-O bond-lengths for NO_3^- are so similar to those of double bonds.

It is to be noted that for NO_3^-, only two of the four delocalizations in Figure 13-5 are needed to obtain an "increased-valence" structure with a zero formal charge on the nitrogen atom. Using a one-electron delocalization from each of the π_O and $\overline{\pi}_O$ atomic orbitals of one O^-, the resulting "increased-valence" structure is the same as that obtained via the $NO_2 + O^- \rightarrow NO_3^-$ reaction, using an NO_2 "increased-valence" structure of type (**64**) or (**65**) in Section 11-8 (cf. also NO_2 + $O \rightarrow NO_3$ to give the NO_3 "increased-valence" structure (**70**) of Section 11-10).

13-6 6-Electron 5-Centre Bonding Units: C_3O_2, Succinimide, and Pyrrole

The phenomenon of 6-electron 5-centre bonding[21] is conveniently introduced by consideration of the π-electron distribution for linear C_3O_2. The standard Lewis structures (**22**)-(**25**) (together with the mirror image structures for structures (**22**)-(**24**)) reveal that this molecule has two sets of six π-electrons (π and $\overline{\pi}$ or π_x and π_y), each of which is distributed amongst five overlapping atomic orbitals. The orbitals are displayed in Fig. 13-7 for one set of electrons.

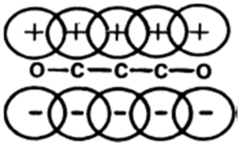


Figure 13-7: 2pπ atomic orbitals for C_3O_2.

For each set of π-electrons, the standard Lewis structures are of the general types (**26**)-(**28**), with two electron-pair bonds and a lone-pair of electrons. The C-C and C-O bond lengths[22] of 1.28 Å and 1.16 Å may be compared with[23] 1.34 Å for $\mathbf{H_2C=CH_2}$ (with sp^2 hybridized carbon atoms) and 1.13 Å for $\mathbf{:\overset{(-)}{C}\equiv\overset{(+)}{O}:}$. Resonance between structures of types (**22**)-(**25**) is sometimes used to rationalize the bond-length variations. However, a more economical valence-bond representation of the electronic structure, which also accounts for the observed lengths, may be obtained as follows.

$$\mathbf{:\ddot{O}=C=C=\underset{..}{O}:}$$

(**22**)

$$\mathbf{\overset{(+)}{:O}\equiv C-\overset{(-)}{\ddot{C}}=C=\underset{..}{O}:}$$

(**23**)

$$\mathbf{\overset{(+)}{:O}\equiv C-C\equiv C-\overset{(-)}{\underset{..}{\ddot{O}}}:}$$

(**24**)

$$\mathbf{\overset{(+)}{:O}\equiv C-\overset{(-2)}{\underset{..}{\ddot{C}}}-C\equiv\overset{(+)}{O}:}$$

(**25**)

$$\mathbf{\ddot{Y}\quad A-B\quad C-D}$$

(**26**)

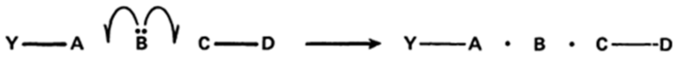
$$\mathbf{Y-A\quad B-C\quad \ddot{D}}$$

(**27**)

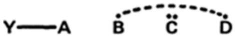
$$\mathbf{Y-A\quad \ddot{B}\quad C-D}$$

(**28**)

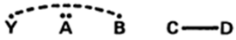
Commencing with the standard Lewis structure (**28**), we may delocalize both of the non-bonding **B** electrons into the adjacent **A-B** and **B-C** bonding orbitals to form two 1-electron bonds. The resulting "increased-valence" structure (**29**) summarizes resonance between structure (**28**) and the "long-bond" structures (**30**)-(**32**). When this type of delocalization is applied to the C^{2-} π and $\overline{\pi}$ electrons of (**25**), "increased-valence" structure (**33**) is obtained, which summarizes resonance between (**25**) *and* 13 "long- bond" structures. Inspection of (**33**) indicates that the C-C bond-lengths should be similar to those of double bonds with s-p hybriddization[24] for the carbon σ-orbitals (1.30 Å), and that the C-O lengths should be longer than the 1.13 Å for free carbon monoxide ($\mathbf{:\overset{(-)}{C}\equiv\overset{(+)}{O}:}$)[25].



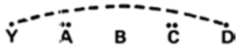
(28) (29)



(30)

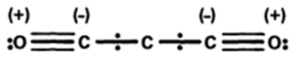


(31)



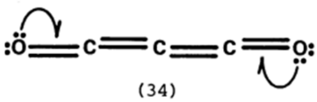
(32)

(25)

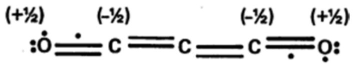


(33)

In structure (**29**) all adjacent atoms are represented as bonded together simultaneously, and two fractional electron-pair bonds are present. From each of the structures (**26**) and (**27**), it is also possible to generate an "increased-valence" structure for a 4-electron 3-centre bonding unit by delocalizing a non-bonding **Y** or **D** electron into the adjacent **Y-A** or **C-D** bonding orbitals. When this type of delocalization is applied to the C_3O_2 structures of types (**22**)-(**24**), numerous "increased-valence" structures are obtained, each of which will participate in resonance with "increased-valence" structure (**33**). For example, the oxygen π and $\bar{\pi}$ delocalizations displayed in structure (**34**) generate structure (**35**). These latter types of "increased-valence" structures involve fewer electrons in bonding than does structure (**33**).

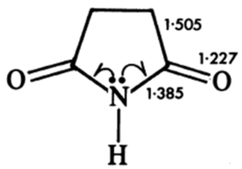


(34)

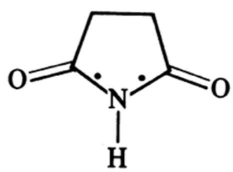


(35)

Molecules such as succinimide and pyrrole also provide a 6-electron 5-centre bonding unit for the π-electrons. For succinimide with the geometry[26] reported in the Lewis structure (**36**), the "increased-valence" structure (**37**) accounts immediately for the observed lengthenings and shortening of the C-O and C-N bonds relative to the standard double and single-bond lengths of 1.21 Å and 1.47 Å.

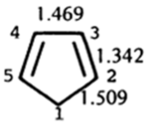


(36)

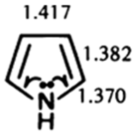


(37)

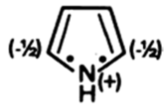
For pyrrole, it is of interest to compare the C-C bond-lengths[27] of the Lewis structure (**39**) with the corresponding bonds for cyclopentadiene in structure (**38**)[28]. Thus, the C_2-C_3 and C_4-C_5 bonds are longer in pyrrole, whereas the C_3-C_4 bond is shorter. The bond properties that are implied by "increased-valence" structure (**40**) are in accord with these observations. Although it is concealed, there is some C_3-C_4 π-bonding in (**40**); this bonding arises because (**40**) ≡ (**39**) ⟷ (**41**) ⟷ (**42**) ⟷ (**43**), and structure (**43**) has a C_3-C_4 π-bond. "Increased-valence" structure (**40**) also involves some C-N π-bonding, and the C-N bonds of pyrrole are shorter than the standard single-bond length of 1.47 Å.



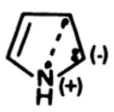
(38)



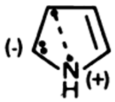
(39)



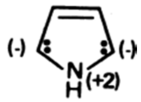
(40)



(41)

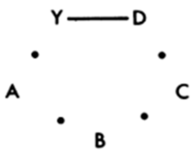


(42)



(43)

The π-electrons of pyrrole form a cyclic 6-electron 5-centre bonding unit, in which the **Y** and **D** atoms are adjacent in the generalized Lewis structures (**26**)-(**32**). The **Y-D** bond of structure (**32**) then becomes a normal electron-pair bond, as it is in structure (**43**). Another type of cyclic "increased-valence" structure can also be constructed, namely structure (**44**) (as in the pyrrole structures (**45**) and (**46**)). "Increased-valence" structure (**44**) should be more stable than (**29**), but we shall not pursue this matter here. To obtain structures (**45**) and (**46**), it is necessary to write down the non-octet structures (**47**) and (**48**), and then to delocalize the non-bonding π-electrons into the adjacent bonding orbitals.



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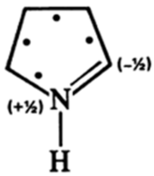

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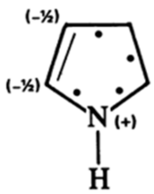

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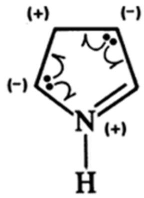

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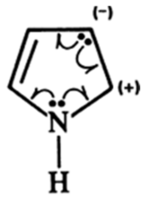
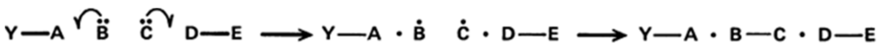


(48)

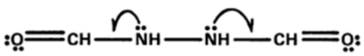
13-7 8-Electron 6-Centre Bonding Unites: Diformylhydrazine, N-alkyl sydnones and Dehydrodithizone

For molecules that involve a set of eight electrons distributed amongst six overlapping atomic orbitals, three types of "increased-valence" bonding units may be relevant for descriptions of their electronic structures. One of them, namely structure (**51**), may be obtained either by bonding together the "increased-valence" structures for two 4-electron 3-centre bonding units, namely those of structure (**50**), or by writing down the standard Lewis structure (**49**), and then delocalizing a non-bonding electron from each of the **B** and **C** atoms into the adjacent **A-B** and **C-D** bonding orbitals. "Increased-valence" structure (**50**) is thereby generated by these delocalizations; it leads to the formation of structure (**51**) when the fractional odd-electron charges on the **B** and **C** atoms are singlet spin-paired.

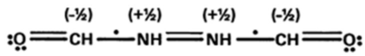


(49) (50) (51)

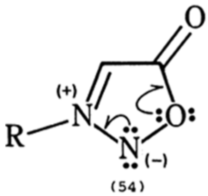
This procedure may be used to generate "increased-valence" structure (**53**) for diformylhydrazine from the standard Lewis structure (**52**). From structure (**53**), it may be deduced that each of the N-N, N-C and C-O bond-lengths should be intermediate in length between those for single and double bonds (N—N 1.45 Å; N=N, 1.24 Å; N–C, 1.47 Å; N=C, 1.27 Å; C–O, 1.43 Å; C=O, 1.21 Å), and the measured bond-lengths[29] (N-N = 1.383 Å, N-C = 1.333 Å and C-O = 1.234 Å) show that this is the case.



(52)



(53)



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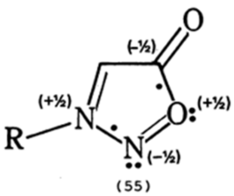
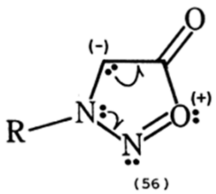
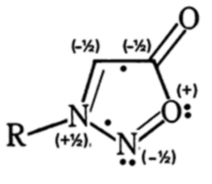


(55)



(56)



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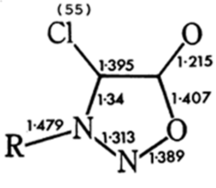

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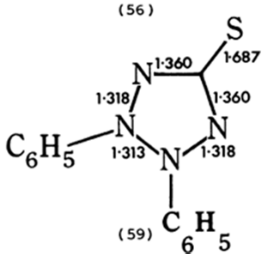
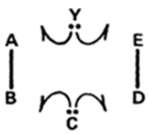


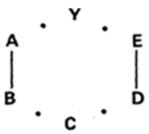
(59)

Diformylhydrazine has eight π-electrons, as have the N-alkyl sydnones. For the sydnones, there are eight standard Lewis structures, each of which involves formal charge separation. Two of them, namely (**54**) and (**56**), may be used to generate "increased-valence" structures (**55**) and (**57**), each of which has an "increased-valence" representation of type (**51**) for the π-electrons. The experimental bond-lengths[30, 31] displayed in (**58**) indicate that the five bonds of the heterocyclic ring have partial double bond character if the standard N-N, C-N, N-O, C-O and C-C bond-lengths are assumed to be 1.45 Å, 1.47 Å, 1.44 Å, 1.43 Å and (for sp^2 hybridized carbon) 1.51 Å. Resonance between structures (**55**) and (**57**) accounts for this observation. However, the exocyclic C-O bond-length of 1.215 Å is that of a C-O double bond (1.21 Å), whereas both "increased-valence" structures imply that it should be a little longer.

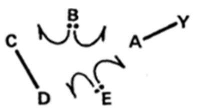
Other types of "increased-valence" structures may be constructed for 8-electron 6-centre bonding units. Two of them, namely structures (**61**) and (**63**) may be generated from the standard Lewis structures (**60**) and (**62**) by means of the delocalizations indicated. For dehydrodithizone, the electron arrangement in structure (**63**) is present for the π-electrons in "increased-valence" structure (**65**). The bond-lengths[32] are displayed in (**59**), and all of them are intermediate in length between those for single and double bonds. "Increased-valence" structure (**65**) (which is derived from the standard Lewis structure (**64**)), indicates the presence of partial double bond character for all bonds. Use of "increased-valence" structure (**65**) provides a more economical representation of this effect; if only standard Lewis structures are used, three of them are required to provide partial double-bond character for each of the six bonds.



(60)



(61)



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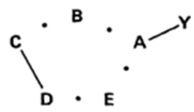

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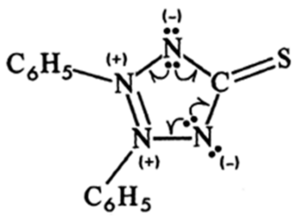

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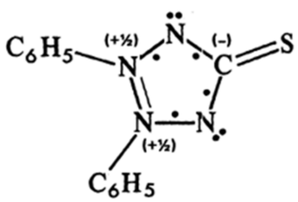


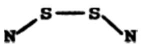
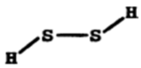
(65)

13-8 "Increased-Valence" Structures for Longer *N*-Centre Bonding Units

Fairly obviously, it is possible to extend the length of an "increased-valence" bonding unit in order to describe many instances of *N*-centre bonding. To demonstrate this, we shall examine three systems with S-N bonds.

13-8 (a) $S_4N_3^+$: 10-electron 7-centre bonding

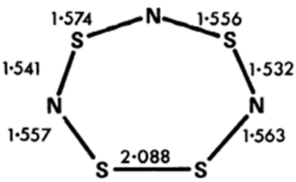
The $S_4N_3^+$ cation is planar and cyclic with the geometry[33, 34] of (**66**). Planar $S_4N_3^+$ has ten π-electrons distributed amongst seven overlapping pπ-atomic orbitals. The S-N bond-lengths are all shorter than the estimate of 1.67 Å for the length of an S-N single-bond[35]. From the standard Lewis structure (**67**), we may generate "increased-valence" structure (**68**), which involves a 10-electron 7-centre "increased-valence" bonding unit of type (**69**), and indicates the presence of partial double-bond character for all of the S-N bonds. If only the standard Lewis structures are used to represent the electronic structure of $S_4N_3^+$, it is necessary to invoke resonance between structure (**67**) and four other Lewis structures that differ in the positions of the two S-N π-bonds. Therefore, the main qualitative features of the electronic structure may be described more economically by using the "increased-valence" structure (**68**) for $S_4N_3^+$. This "increased-valence" structure associates partial double-bond character with each of the S-N bonds, thereby accounting for the observed shortening of these bonds relative to the single-bond length. Partial double-bond character for the S-S bond is also present in structure (**68**), but the length of this bond (2.070, 2.088 Å) is longer rather than shorter than the standard single-bond length of 2.06 Å for H_2S_2. This lengthening may be a consequence of a combination of the following factors:

(a) The  linkage is planar, whereas  is non-planar. Hordvik[36] has listed numerous examples of molecules for which the S-S bond-length varies with dihedral angle. The straining of the S-S σ-bonds is associated[37] with the existence of the non-bonded repulsions (Section 3-10) in standard Lewis structures such as (**67**) (which is a component of structure (**68**)) for $S_4N_3^+$. Therefore, if the natural conformation around the S-S bond is non-planar, the additional strain that occurs when planarity is enforced must lengthen[38] the S-S σ-bond.

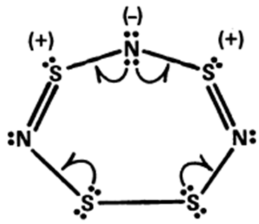
(b) For $S_4N_3^+NO_3^-$ and $S_4N_3^+Br^-$, lone-pair orbitals of the anions can overlap with the orbitals that form the S-S σ-bond of $S_4N_3^+$, to form 4-electron 3-centre or 6-electron 4-centre bonding units[39]. The "increased-valence" structures **X· · S—S** and **X· · S—S · ·X**, which are obtained by delocalizing a lone-pair **X:** electron from each **X:** of **X: S—S** and **X: S—S :X** into an **X-S** bonding orbital, have S-S σ-bond numbers that are less than unity.

If the S-S σ-bond of $S_4N_3^+$ is lengthened by either or both of (a) and (b), then the measured S-S lengths[33, 34] of 2.088 or 2.070 Å do not preclude the presence of some S-S π-bonding.

Similar considerations have also been used[38] to account for the lengthenings of the S-S bonds for the $S_3N_2^+$ derivatives (with planar $S_3N_2^+$ rings) listed in Table 13-3.



(66)



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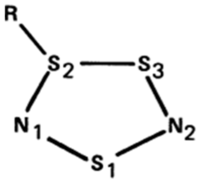

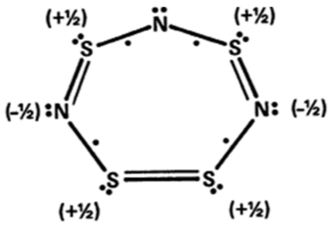

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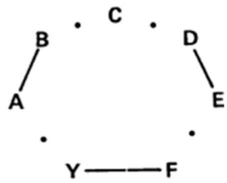


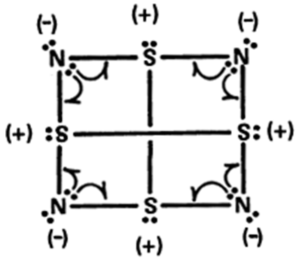
(69)

Table 13-3: Bond-lengths (Å) for S_3N_2 rings of $S_3N_2^+$ and derivatives[39-44].

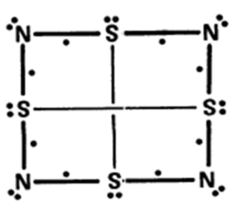
compound	$S_1 - N_1$	$S_1 - N_2$	$S_2 - N_1$	$S_3 - N_2$	$S_2 - S_3$
$S_3N_2^+$	1.575	1.555	1.617	1.602	2.141
$S_6N_4^{2+}$	1.569	1.569	1.605	1.605	2.154
$S_3N_2Cl^+$	1.617	1.543	1.581	1.615	2.136
$S_3N_2^-NSO_2F$	1.578	1.565	1.644	1.635	2.200
$S_3N_2^-NCOCF_3$	1.589	1.551	1.641	1.633	2.206
$S_3N_2^-NP_3N_3F_5$	1.573	1.540	1.647	1.528	2.220

13-8 (b) S_4N_4 : 12–electron 8–centre bonding

In Section 7-7, a molecular orbital explanation was provided for the existence of long S-S bonds (2.58 Å [45], cf. 2.06 Å for an S-S single-bond) in S_4N_4. It was suggested that one set of nitrogen lone- pair electrons of the standard Lewis structure (**70**) could delocalize appreciably into the antibonding S-S σ*-orbital, thereby reducing the S-S bond-order below the value of unity that pertains for structure (**70**). If these electrons are delocalized into the adjacent S-N bonding-orbitals, "increased-valence" structure (**71**) is obtained[21, 38] with S-S σ-bond numbers less than unity. This structure indicates that the S-S and S-N bonds should be respectively longer and shorter than single-bonds, and this they are found to be. The measured S-S and S-N bond-lengths are 2.58 Å and 1.62 Å, respectively, and the estimate of an S-N single-bond length[35] is 1.67 Å. A 12-electron 8-centre “increased-valence” bonding unit is present in “increased- valence” structure (**71**); it involves the eight nitrogen $\bar{\pi}$ – electrons and the four S-S σ-electrons of (**70**).



(70)

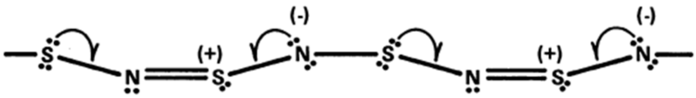


(71)

“Increased-valence” descriptions of the bonding for other cyclic S-N compounds are described in Refs. 21 and 38.

13-8 (c) $(SN)_x$: Polymerized Pauling “3-electron bonds” and Polymerized 6-Electron 4-Centre bonding units

The polymer $(SN)_x$ consists of layers of 2-dimensional chains of alternating sulphur and nitrogen atoms. Each sulphur and nitrogen atom contributes respectively two π-electrons and one π-electron to form a $2x$-centre π-electron bonding unit within a 2-dimensional chain. For such a chain, the standard Lewis structures are of type (**72**), from which we may generate the “increased- valence” structure (**74**)[21] via structure (**73**) and the delocalizations indicated in structure (**72**). Alternatively, we may also obtain (**74**) by writing down the “long- bond” structure (**75**) with zero formal charges on all atoms, and then proceed to structure (**74**) via structure (**76**) by delocalizing non-bonding sulphur electrons into adjacent S-N bonding π-orbitals. Examination of structure (**76**) shows that “increased-valence” structure (**74**) is constructed from polymerized Pauling “3-electron bond” structures for the S-N π-electrons. Alternatively, structure (**74**) may also be considered to involve the polymerization of the 6-electron 4-centre “increased-valence” structures for the π-electrons of structure (**73**). “Increased-valence” structure (**74**) involves partial double-bond character for each of the S-N bonds, which is in accord with the measured bond-lengths[46] of 1.59 Å and 1.63 Å.



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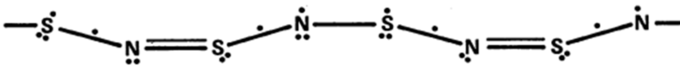

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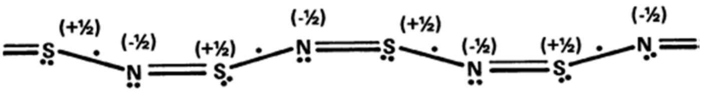

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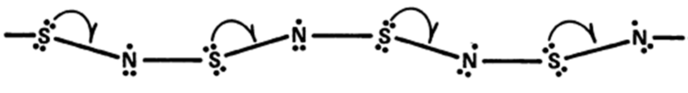

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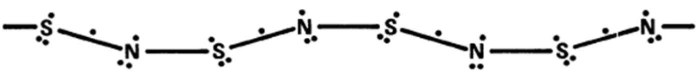
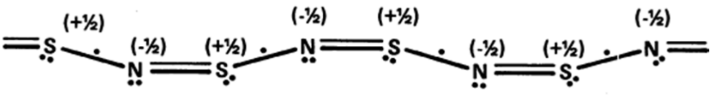


(76)

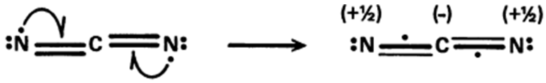


(74)

13-9 Paramagnetic "Increased-Valence" Structures

All "increased-valence" structures that we have described in this Chapter are appropriate when an even number of electrons is present in the *N*-centre bonding unit. Therefore, they can be constructed for diamagnetic $S = 0$ spin-states· When an odd number of electrons is involved in *N*-centre bonding, paramagnetic "increased- valence" bonding units are also possible. The smallest of them pertain for 3-electron 3-centre, 5-electron 4-centre and 7-electron 5-centre bonding. They are exemplified in the "increased-valence" structures for (**78**) for CN_2 and the bimolecular HO_3 and ONO_3 complexes that pertain for the $H + O_3 \rightarrow HO + O_2$

and $NO + O_3 \rightarrow NO_2 + O_2$ reactions. “Increased-valence” mechanisms for these reactions are described in Chapter 22. The general “increased-valence” structures for 5-electron 4-centre and 7-electron 5-centre bonding units are of types (**79**) and (**80**) respectively. They may be constructed by bonding the “increased-valence” structure $\mathbf{Y{-}A \cdot \dot{B}}$ to either an atom $\mathbf{\dot{C}}$ with one unpaired electron, or to the diatomic Pauling “3-electron bond” structure $\mathbf{\dot{C} \cdot \dot{D}}$, as is shown. Electron spin theory for (**79**) is described in Section 15-2. “Increased-valence” structure (**78**) for CN_2, which may be generated from the Lewis structure (**77**), involves no Pauling “3-electron bond”. It may be noted that 3-electron 3-centre bonding units are not electron-rich, but “increased-valence” structures can be constructed for them. A second example is provided by H_3, with the Lewis and “increased-valence” structures of (**81**) and (**82**).



(77) (78)

$$\mathrm{Y{-\!-}A \cdot \dot{B} \quad + \quad \dot{C} \longrightarrow Y{-\!-}A \cdot B{-\!-}C}$$

(79)

$$\mathbf{Y{-\!-}A \cdot \dot{B} \quad + \quad \dot{C} \cdot \dot{D} \;\rightarrow\; Y{-\!-}A \cdot B{-\!-}C \cdot \dot{D}}$$

(**80**)

$$\mathbf{H{-}H \quad \dot{H} \leftrightarrow \dot{H} \quad H{-}H \quad H{-}\overset{(-\frac{1}{2})}{H} \cdot \overset{(+\frac{1}{2})}{H} \leftrightarrow \overset{(+\frac{1}{2})}{H} \cdot \overset{(-\frac{1}{2})}{H}{-}H}$$

(81) (82)

It is easy to verify that “long-bond” structures are not components of “increased-valence” structures for 3-electron 3-centre bonding units. Further discussion of “increased-valence” structures for 3-electron 3-centre bonding units is provided in Chapter 25, Section 2.

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13-10Addendum Chapter 13

S_2N_2 Polymerization and Electron Conduction in the $(SN)_x$ Polymer

In Section 13-8(c), increased-valence structure (**74**) for the $(SN)_x$ polymer is derived from the Lewis structure (**72**). The derivation of structure (**74**) via S_2N_2 polymerization, and electron conduction in the $(SN)_x$ polymer, are displayed in Fig. 13-7.

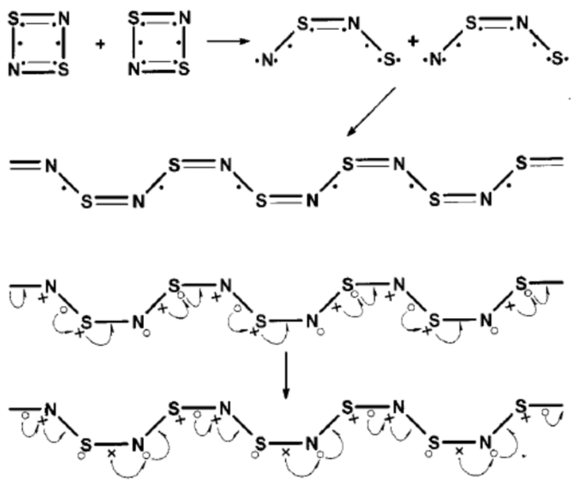

Figure 13-7: S_2N_2 polymerization and electron conduction in the $(SN)_x$ polymer[47-49] (with atomic formal charges omitted). Reproduced from Ref. 49 with permission from Wiley-VCH.

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See also Refs. 50-53 for further increased-valence studies of S_2N_2.
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Chapter 14 Delocalization of a Lone-Pair Electron into a Vacant Antibonding Orbital: "Increased-Valence" Structures, Molecular Orbital Theory and Atomic Valencies

Three related topics that involve diatomic antibonding orbitals will be discussed in this chapter. First, "increased-valence" structures for 4-electron 3-centre bonding units will be constructed by delocalizing a lone-pair electron on one atom into an antibonding orbital between a pair of adjacent atoms. Then the approximate 3-centre molecular orbital theory that arises from delocalization of lone-pair electrons into an antibonding orbital will be presented, with emphasis given to the relationship that exists between the "increased-valence" and the molecular orbital theory. Finally, by making particular use of the charge distribution for antibonding orbitals, expressions for atomic valencies will be deduced for "increased-valence" structures.

14-1 Delocalization of a Lone-Pair Electron into a Vacant Antibonding Orbital

The third method for generating "increased-valence" structures utilizes the molecular orbital description of the Pauling "3-electron bond" in terms of bonding and antibonding orbitals.

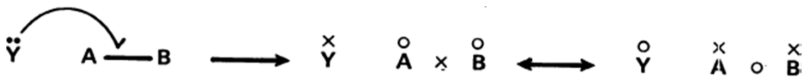
We shall commence our discussion by recalling that "increased-valence" structure (**1**) involves the electron spin distributions of structures (**2**) and (**3**).

(1) (2) (3)

R.D. Harcourt, *Bonding in Electron-Rich Molecules*,
Lecture Notes in Chemistry 90, DOI 10.1007/978-3-319-16676-6_14

In Section 3-6, we have demonstrated that a wave-function for a Pauling "3-electron bond" structure $\dot{\mathbf{A}} \cdot \dot{\mathbf{B}}$ can be expressed as either $(\psi_{ab})^2(\psi^*_{ab})^1$ or $(a)^1(\psi_{ab})^1(b)^1$, $(\equiv a^{\alpha}\psi^{\beta}_{ab}b^{\alpha}$ or $a^{\beta}\psi^{\alpha}_{ab}b^{\beta})$, in which $\psi_{ab} = a + kb$ and $\psi^*_{ab} = k^*a - b$ are bonding and antibonding molecular orbitals, and a and b are overlapping atomic orbitals. For the Pauling "3-electron bond" structures $\overset{\mathrm{o}}{\mathbf{A}} \times \overset{\mathrm{o}}{\mathbf{B}}$ and $\overset{\mathrm{x}}{\mathbf{A}}\ \mathrm{o}\ \overset{\mathrm{x}}{\mathbf{B}}$ of structures (**2**) and (**3**), the antibonding ψ^*_{ab} electron of the molecular orbital configuration $(\psi_{ab})^2(\psi^*_{ab})^1$ must have an s_z spin quantum number of –½ and +½, respectively.

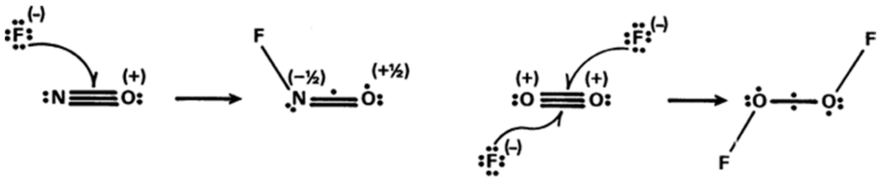
This equivalence that exists between $(\psi_{ab})^2(\psi^*_{ab})^1$ and $(a)^1(\psi_{ab})^1(b)^1$ indicates that we may obtain the electron distributions of spin structures (**2**) and (**3**) by writing down the standard Lewis structure (**4**), and then delocalizing one of the non-bonding $\ddot{\mathbf{Y}}$ electrons into the vacant antibonding **A-B** orbital of this structure. By doing this we are assuming here that the wave-function for the **A-B** bond of structure (**4**) is a doubly-occupied bonding molecular orbital with wave function $(\psi_{ab})^2$ (However, as discussed in the Chapter 3 Addendum, it is also appropriate when Coulson Fischer type orbitals a + k_1b and b + k_2a are used to formulate the wavefunction for the **A-B** electron-pair bond, for which the Heitler-London a(1)b(2) + b(1)a(2) and $(\psi_{ab})^2$ wavefunctions are special cases.) Thus, we may write



(**4**) (**2**) (**3**)

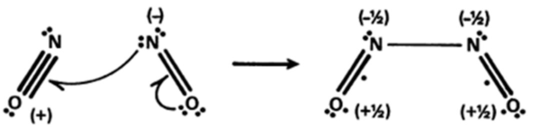
We now have a second method for generating an "increased-valence" structure from a standard Lewis structure. This technique, namely that of delocalizing a lone-pair electron into an antibonding orbital, is particularly suitable when the **Y** and **B** atoms of Lewis structure (**4**) carry formal negative and positive charges respectively. Atom **A** of structure (**4**) may carry either no formal charge, or a formal positive charge. The delocalization of a **Y** electron of structure (**4**) into the antibonding **A-B** orbital will then reduce the magnitudes of the formal charges and increase the number of electrons that participate in bonding.

To obtain suitable arrangements of formal charges in structure (**4**), it is often necessary to construct standard Lewis structures that exhibit considerable formal charge separation. Structures (**6**) and (**8**) are the primary "increased-valence" structures for FNO and F_2O_2 that are in qualitative accord with the observed bond-lengths (Sections 11-2 and 11-4). To generate them by using the present procedure, we need to commence with the standard Lewis structures (**5**) and (**7**), and then delocalize electrons from the F^- into vacant antibonding orbitals of NO^+ and O_2^{2+}.



(5) (6) (7) (8)

Other examples are shown in Fig. 14-1, where we have written down ionic standard Lewis structures for some of the molecules discussed in Chapter 11, and then generated "increased-valence" structures by using this technique alone. For some molecules, it is necessary to delocalize electrons into both bonding and antibonding orbitals simultaneously. For example, if we wish to generate the "increased-valence" structure (**10**) for N_2O_2 from the ionic Lewis structures of (**9**) for NO^- and NO^+, we must delocalize a nitrogen lone-pair electron of NO^- into an *antibonding* molecular orbital of NO^+, and also delocalize an oxygen electron of NO^- into the adjacent *bonding* molecular orbital. These delocalizations are indicated in structure **9**.



(9) (10)

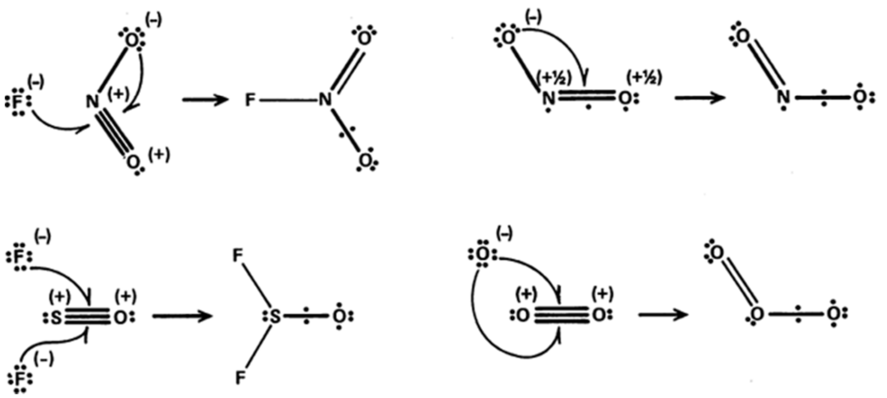
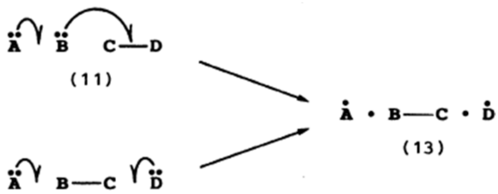


Figure 14-1: Generation of "increased-valence" structures for FNO_2, NO_2, F_2SO and O_3 from Lewis structures by delocalizing lone-pair electrons into vacant antibonding molecular orbitals. (In structure (**9**), an oxygen electron of the NO^- is delocalized into an O-N bonding molecular orbital.)

This type of combined delocalization can be used whenever one has Lewis structures of type (**11**) for 6-electron 4-centre bonding units. On the other hand, the Lewis structure (**12**) requires delocalization of **A** and **D** electrons into bonding **A-B** and **C-D** orbitals in order to generate the "increased-valence" structure (**13**).



(11) (12) (13)

In this chapter, we have used both Heitler-London and molecular orbital descriptions of electron-pair bonds on different occasions. For example, a doubly occupied bonding molecular orbital (namely $(\psi_{ab})^2$) has been used to describe the electron-pair **A-B** bond of the standard Lewis structure (**4**), but when we delocalize a **Y** electron of structure (**4**) into the antibonding **A-B** orbital (ψ^*_{ab}), the resulting wave-function (neglecting electron spin and indistinguishability)

$$(y)^1(\psi^*_{ab})^1(\psi_{ab})^2 \equiv \text{constant} \times (y)^1(a)^1(\psi_{ab})^1(b)^1$$

indicates that the (fractional) **Y-A** bond of "increased-valence" structure **1** must have a Heitler-London type wave-function arising from the $(y)^1(a)^1$ configuration.

If one wishes to use only Heitler-London wave-functions for all electron-pair bonds, as indicated above when considering Coulson-Fischer **A-B** orbitals, we can still speak of the delocalization of a **Y** electron of structure (**4**) into the antibonding **A-B** orbital. When this is done, we obtain Lewis structures (**14**) and (**15**), with configurations $(y)^1(a)^2(b)^1$ and $(y)^1(a)^1(b)^2$ that involve Heitler-London formulations of the wave-functions for the **Y-A** and "long" **Y-B** bonds. Resonance between structures (**14**) and (**15**) is equivalent to the utilization of "increased-valence" structure (**1**) (with a Heitler-London type wave-function for the fractional **Y-A** bond).

(14)

(15)

In Chapter 21, the theory of this section will be applied to Lewis acid-base reactions.

14-2 Approximate Molecular Orbital Theory for 4-Electron 3-Centre Bonding Units

An approximate 3-centre molecular orbital theory has been used frequently to describe non-symmetrical 4-electron 3-centre bonding units. It involves the construction of an (approximate) 3-centre molecular orbital by linearly combining the **Y** lone-pair orbital with the vacant antibonding **A-B** orbital of the Lewis structure (**4**). This gives a 3-centre molecular orbital formulation for the phenomenon of lone-pair delocalization into an antibonding orbital (cf. Sections 7-2 and 7-4 for 6-electron 4-centre bonding).

If the **A-B** bond of the standard Lewis structure (**4**) is described in terms of double occupation of the bonding molecular orbital ψ_{ab}, the wave-function[i] for this structure is given by Eqn. (1).

$$\Psi(\ddot{\mathbf{Y}} \quad \mathbf{A—B}) = (\mathbf{y})^2(\psi_{\mathbf{ab}})^2 \equiv \left|\mathbf{y}^{\alpha}\mathbf{y}^{\beta}\psi^{\alpha}_{\mathbf{ab}}\psi^{\beta}_{\mathbf{ab}}\right| \tag{1}$$

The vacant antibonding orbital ψ^{*}_{ab} overlaps with the doubly-occupied lone-pair orbital y. The approximate molecular orbitals of Eqn. (2) may then be constructed, which omit the overlap that also exists between y and the doubly-occupied ψ_{ab}.

$$\boldsymbol{\psi}_1 = c_1\mathbf{y} + c_2\boldsymbol{\psi}^{*}_{\mathbf{ab}}, \qquad \boldsymbol{\psi}_2 = c_2\mathbf{y} - c_1\boldsymbol{\psi}^{*}_{\mathbf{ab}} \tag{2}$$

$$\Psi_1(\mathrm{MO}) = (\psi_{ab})^2(\psi_1)^2 \equiv |\, \psi^{\alpha}_{ab}\psi^{\beta}_{ab}\psi^{\alpha}_{1}\psi^{\beta}_{1} \,| \tag{3}$$

The lowest-energy molecular orbital configuration is then given by Eqn. (3), and this type of configuration has been used either frequently or implied in qualitative molecular orbital descriptions of 4-electron 3-centre bonding units. Thus:

(a) To account for transition metal-ligand and ligand bond-properties, back-donation of t_{2g} electrons from the metal into the antibonding π^* orbitals of CO, CN^-, NO^+ and N_2 ligands is invoked[1–5].

(b) For some aliphatic chloro compounds that contain oxygen or fluorine atoms, Lucken[6] has described the interaction of a p-orbital of either of these atoms with the antibonding C-Cl σ^*-orbital.

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i Slater determinantal formulations for 4-electron 3-centre wave-functions are described in Section 15-1. Although they are not required for the algebra of this section, we have used them for the sake of completeness in Eqs. (1), (3), (4) and (8).

(c) Williams[7] has indicated that Lucken's theory might pertain to many saturated systems – for example, to account for the shortening of the C-F bonds and the lengthening of the C-H bond of CF_3H .

(d) Spratley and Pimentel[8] have described the relative extent of interaction of fluorine or hydrogen atomic orbitals with antibonding N-O or O-O π* orbitals of FNO, HNO, F_2O_2 and H_2O_2 .

(e) Pearson's[9] molecular orbital description of S_N2 reactions involves the interaction of a lone-pair orbital of the nucleophile **B** with the antibonding C-Cl σ* orbital of CH_3-Cl.

(f) Drago and Corden[10] have reviewed the spin-pairing model of the bonding of O_2 to Co(II), Cr(II), Mn(II) and Fe(II) complexes, with a ψ_1-type molecular orbital to describe the spin-pairing. The y and ψ^*_{ab} are the metal d, and an antibonding π^*_{OO} orbital of ground-state O_2.

We shall now relate this type of molecular orbital theory to the "increased-valence" theory of Section 14-1. A doubly-excited configuration $\Psi_2(MO)$ of Eqn. (4) can also be constructed, in which ψ_2 instead of ψ_1 is doubly-occupied.

$$\Psi_2(MO) = (\psi_{ab})^2(\psi_2)^2 \equiv \left|\psi^\alpha_{ab}\psi^\beta_{ab}\psi^\alpha_2\psi^\beta_2\right| \tag{4}$$

On substitution of the LCAO forms for ψ_1 and ψ_2 into Eqs. (3) and (4), we obtain

$$\mathbf{\Psi_1(MO)} = c_1^2\Psi(\ddot{\mathbf{Y}}\quad \mathbf{A—B}) + c_2^2\Psi(\mathbf{Y}\quad \ddot{\mathbf{A}}\quad \ddot{\mathbf{B}}) + c_1c_2\{\Psi(\overset{x}{\mathbf{Y}}\quad \overset{o}{\mathbf{A}}\,x\,\overset{o}{\mathbf{B}}) + \Psi(\overset{o}{\mathbf{Y}}\quad \overset{x}{\mathbf{A}}\,o\,\overset{x}{\mathbf{B}})\} \tag{5}$$

$$\mathbf{\Psi_2(MO)} = c_2^2\Psi(\ddot{\mathbf{Y}}\quad \mathbf{A—B}) + c_1^2\Psi(\mathbf{Y}\quad \ddot{\mathbf{A}}\quad \ddot{\mathbf{B}}) - c_1c_2\{\Psi(\overset{x}{\mathbf{Y}}\quad \overset{o}{\mathbf{A}}\,x\,\overset{o}{\mathbf{B}}) + \Psi(\overset{o}{\mathbf{Y}}\quad \overset{x}{\mathbf{A}}\,o\,\overset{x}{\mathbf{B}})\} \tag{6}$$

in which $\Psi\left(\ddot{\mathbf{Y}}\ \ \mathbf{A—B}\right)$ is given by Eqn. (1),

$$\Psi(\mathbf{Y}\quad \ddot{\mathbf{A}}\quad \ddot{\mathbf{B}}) = (\psi_{ab})^2(\psi^*_{ab})^2 \equiv \left|\psi^\alpha_{ab}\psi^\beta_{ab}\psi^{*\alpha}_{ab}\psi^{*\beta}_{ab}\right| \tag{7}$$

and

$$\Psi(\overset{x}{\mathbf{Y}}\quad \overset{o}{\mathbf{A}}\,x\,\overset{o}{\mathbf{B}}) + \Psi(\overset{o}{\mathbf{Y}}\quad \overset{x}{\mathbf{A}}\,o\,\overset{x}{\mathbf{B}}) = \left|\psi^\alpha_{ab}\psi^\beta_{ab}y^\alpha\psi^{*\beta}_{ab}\right| + \left|\psi^\alpha_{ab}\psi^\beta_{ab}\psi^{*\alpha}_{ab}y^\beta\right| \tag{8}$$

The lower-energy linear combination of $\Psi_1(\mathrm{MO})$ with $\Psi_2(\mathrm{MO})$ gives the configuration-interaction (Section 3-3) wave-function of Eqn. (9) with $|C_1|>|C_2|$ and $C_1 > 0$ when $C_2 < 0$.

$$\Psi(\mathrm{CI}) = C_1\Psi_1(\mathrm{MO}) + C_2\Psi_2(\mathrm{MO}) \tag{9}$$

If c_1 and c_2 in the molecular orbitals of Eqn. (2) have similar magnitudes, i.e. if y and ψ^*_{ab} have similar energies, then the primary component of Ψ(CI) will be given by Eqn. (8). Therefore, "increased-valence" structure (**1**) (which is equivalent to resonance between the Lewis structures (**2**) and (**3**)) is the primary valence-bond structure for this approximate molecular orbital scheme when configuration interaction is invoked.

It should be noted that because ψ_{ab} as well as ψ^*_{ab} overlaps with y, the canonical 3-centre molecular orbitals[11] are given by Eqn. (10) rather than Eqn. (2).

$$\psi_i = c_{i1}\mathrm{y} + c_{i2}\psi^*_{\mathrm{ab}} + c_{i3}\psi_{\mathrm{ab}} \, (i = 1-3) \tag{10}$$

14-3 Atomic Valencies for "Increased-Valence" Structures[12]

The (co)valence of an atom in a molecule corresponds to the number of covalent bonds formed by the atom. Inspection of the standard Lewis structure (**15**) reveals that the valencies for the **Y** and **A** atoms are both unity. Each atom contributes one electron to form the **Y-A** covalent bond. For "increased-valence" structure (**1**), the **A**-atom is involved in both **Y-A** and **A-B** bonding. These two components of the **A**-atom valence will be designated as V_{ay} and V_{ab}, with $V_{\mathrm{a}} = V_{\mathrm{ay}} + V_{\mathrm{ab}}$. We shall now show that V_{a} for "increased-valence" structure (**1**) can exceed unity when the molecular orbitals of Eqn. (11) are used to construct the Pauling "3-electron bond" configuration $(\psi_{\mathrm{ab}})^2(\psi^*_{\mathrm{ab}})^1$ for the **A-B** component of increased-valence structure (**1**). (Here, the atomic orbital overlap integral S_{ab} will be omitted from the molecular orbital normalization constants and orthogonality relationship. They are included in Ref. 13, thereby elaborating the expressions for the atomic valencies.)

$$\psi_{\mathrm{ab}} = (\mathrm{a} + k\mathrm{b})/(1+k^2)^{\frac{1}{2}}, \ \psi^*_{\mathrm{ab}} = (k\mathrm{a} - \mathrm{b})/(1+k_2)^{\frac{1}{2}} \tag{11}$$

To calculate V_{ay}, either of the following equivalent procedures may be used:

(a) The antibonding ψ^*_{ab} electron of valence-bond **1** is spin-paired with the y electron to generate fractional **Y-A** and **Y-B** bonding (Fig. 11-2). The valence

V_{ay} must therefore correspond to the **A**-atom odd-electron charge, which is calculated from the square of the coefficient of the a orbital in ψ^*_{ab}. We thereby obtain

$$V_{ay} = k^2/(1+k^2) \tag{12}$$

b) Because structure (**1**) is equivalent to resonance between Lewis structures (**14**) and (**15**), and (**14**) has no **Y-A** bond, V_{ay} must correspond to the weight for structure (**15**) in this resonance. In Section 3-11, we have deduced that

$$(\psi_{ab})^2(\psi^*_{ab})^1 \equiv \{(a)^2(b)^1 + k(a)^1(b)^2\}/(1+k_2)^{\frac{1}{2}} \tag{13}$$

from which it follows that

$$\Psi(\mathbf{Y{-}A \cdot \dot{B}}) \equiv \{\Psi(\mathbf{\dot{Y}\ \ddot{A}\ \dot{B}}) + k\Psi(\mathbf{Y{-}A\ \ddot{B}})\}/(1+k^2)^{\frac{1}{2}} \tag{14}$$

The weight for $\mathbf{Y{-}A\ \ddot{B}}$ is equal to the square of the coefficient of $\mathbf{\Psi(Y{-}A\ \ddot{B})}$ in Eqn. (14). This gives the V_{ay} of Eqn. (12). It also corresponds to the bond-number of the fractional **Y-A** bond in structure (**1**).

For the one-electron $\mathbf{A \cdot B}$ bond of structure (**1**), the valence V_{ab} must be such that for the Pauling "3-electron bond" configuration $(\psi_{ab})^2(\psi^*_{ab})^1$ the following correlation must exist between the a-orbital charge (P_{aa}) and V_{ab}:

Structure	$\mathbf{\ddot{A}\ \dot{B}}$	$\mathbf{\dot{A} \cdot \dot{B}}$	$\mathbf{\dot{A}\ \ddot{B}}$
k	0	1	∞
P_{aa}	2	1.5	1
V_{ab}	0	0.5	0

(For $k = 1$, the one-electron bond of $\mathbf{\dot{A} \cdot \dot{B}}$ is homopolar, and therefore $V_{ab} = 0.5$). We thereby obtain Eqn. (15)[12]

$$V_{ab} = -2(2-P_{aa})(1-P_{aa}) \tag{15}$$

For any value of *k,* the P_{aa} is given by $1+1/(1+k^2)$ (Table 3-3) and therefore

$$V_{ab} = 2k^2/(1+k^2)^2 \equiv 2P^2_{ab} \tag{16}$$

in which P_{ab} is the bond-order for the $\dot{\mathbf{A}} \cdot \dot{\mathbf{B}}$ component (Table 3-3) of "increased-valence" structure (**1**).

By summing V_{ay} and V_{ab} of Eqs. (12) and (16) the total **A**-atom valence of Eqn. (17) is obtained.

$$V_a = V_{ay} + V_{ab} = k^2/(1+k^2) + 2k^2/(1+k^2)^2 \tag{17}$$

For $1 < k < \infty$, $V_a > 1$ i.e. the **A**-atom valence for "increased-valence" structure (**1**) exceeds the value of unity that occurs in the standard Lewis structure (**15**).

Similar procedures may be used to deduce that the **B**-atom valence for structure (**1**) is given by Eqn. (18). .

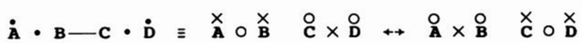
$$V_b = V_{by} + V_{ba} = 1/(1+k^2) + 2k^2/(1+k^2)^2 \tag{18}$$

Because the **Y**-atom valence for structure (**1**) (namely $V_y \equiv V_{ya} + V_{yb}$) must always equal unity, the sum of the atomic valencies for structure (**1**) is given by Eqn. (19).

$$V(\text{total}) = V_y + V_a + V_b = 2 + 4k^2/(1+k^2)^2 \tag{19}$$

V(total) has a maximum value of 3 when k = 1, which is in accord with the earlier deduction (Section 11-1) that a maximum of three electrons may simultaneously participate in fractional **Y-A**, **Y-B** and **A-B** bonding.

For "increased-valence" structure (**13**), the bonding and antibonding molecular orbitals for the Pauling "3-electron bond" components of structures (**16**) and (**17**) are given by Eqs. (11) and (20) when **A** and **D**, and **B** and **C** are pairs of equivalent atoms. We shall now use these orbitals to deduce that the **B** and **C** valencies of "increased-valence" structure (**13**) can exceed unity in value.



(13) (16) (17)

$$\psi_{cd} = (d + kc)/(1+k^2)^{1/2}, \quad \psi^*_{cd} = (kd - c)/(1+k^2)^{1/2} \tag{20}$$

With $(\psi_{ab})^2(\psi^*_{ab})^1 = (a)^2(b)^1 + k(a)^1(b)^2$ and $(\psi_{cd})^2(\psi^*_{cd})^1 = (c)^1(d)^2 + k(c)^2(d)^1$, it is easy to deduce that the normalized wave-function for "increased-valence" structure (**13**) is equivalent to that of Eqn. (21),

$$\Psi_{13} = \{\Psi_{12} + k(\Psi_{18} + \Psi_{19}) + k^2\Psi_{20}\}/(1+k^2) \tag{21}$$

in which $\Psi_{12}, \Psi_{18}, \Psi_{19}$ and Ψ_{20} are the wave-functions for Lewis structures (**12**) and (**18**)-(**20**) (cf. Eqn. (10-15)).

(12) (18) (19) (20)

By squaring the coefficient of Ψ_{12} in Eqn. (21), the weight (W_{12} of Eqn. (22))

$$W_{12} = V_{bc} = 1/\left(1+k^2\right)^2 \equiv N_{bc} \tag{22}$$

for Lewis structure (**12**) is obtained, which corresponds to the bond-number (N_{bc}) for the **B-C** bond of "increased-valence" structure (**13**), and hence to the valence V_{bc} in the latter structure. Similarly, the weights for Lewis structures (**18**)-(**20**) (Eqs. (23) and (24))

$$W_{18} = W_{19} = V_{bd} = V_{ac} = k^2/\left(1+k^2\right)^2 \tag{23}$$

$$W_{20} = V_{ad} = k^4/\left(1+k^2\right)^2 \tag{24}$$

give the valencies V_{bd}, V_{ac} and V_{ad} for "increased-valence" structure (**13**). When V_{bc} and V_{bd} are added, the **B**-atom odd-electron charge (c_b^{*2} of Eqn. (25))

$$V_{bc} + V_{bd} = 1/(1+k^2) \equiv c_b^{*2} \tag{25}$$

is obtained. The latter result shows how the fractional odd-electron charge of the **B**-atom is used for both **B-C** and **B-D** bonding; this has been noted previously in Section 7-1.

Within the Pauling "3-electron bonds" $\dot{\mathbf{A}} \cdot \dot{\mathbf{B}}$ and $\dot{\mathbf{C}} \cdot \dot{\mathbf{D}}$ of structure (**13**), the **B** and **C** valencies are given by Eqn. (26) (cf. (Eqn. (16)), in which P_{ab} and P_{cd} are the bond-orders for these bonds in "increased-valence" structure (**13**). The total **B**-atom valence, namely $V_b = V_{bc} + V_{bd} + V_{ba}$, is then equal to the V_b of Eqn. (18) for "increased-valence" structure (**1**). Therefore, V_b is greater than unity when $0 < k < 1$.

$$V_{ba} = V_{cd} = 2k^2/(1+k^2)^2 \equiv 2P_{ab}^2 = 2P_{cd}^2 \tag{26}$$

In Section 13-3, the delocalized molecular orbitals are given for symmetrical 6-electron 4-centre bonding units. When these are normalized excluding atomic orbital overlap integrals, and the parameter μ is set equal to k, the **B-C** bond-order

P_{bc} for the molecular orbital configuration $\Psi_1(\mathrm{MO}) = (\psi_1)^2(\psi_2)^2(\psi_3)^2$ is equivalent to the **B**-atom odd-electron charge of Eqn. (25) for "increased-valence" structure (**13**). The **B-C** bond-number for structure (**13**), namely the weight W_{12} of Eqn. (22), is equal to P_{bc}^2 for $\Psi_1(\mathrm{MO})$ when μ = *k*. For this value of μ, the **A-B** and **C-D** bond-orders for "increased-valence" structure (**13**) and $\Psi_1(\mathrm{MO})$ are identical, with each having a value of $k/(1+k^2)$.

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Addendum Chapter 14

1. Wiberg Valence for the A : B Electron-Pair Bond

The covalent-ionic resonance wavefunction for the **A:B** electron-pair bond can be expressed according to Eqs. (27) and (28).

$$\Psi(\mathbf{A{:}B}) = C_1\Psi\{\mathbf{A}^{\cdot}\!\!-\!\!^{\cdot}\mathbf{B}\} + C_2\Psi\{\mathbf{A{:}}^{(-)}\ \mathbf{B}^{(+)}\} + C_3\Psi\{\mathbf{A}^{(+)}\ \mathbf{{:}B}^{(-)}\} \tag{27}$$

$$= C_1\{\mathrm{a}(1)\mathrm{b}(2) + \mathrm{b}(1)\mathrm{a}(2)\} + C_2\{\mathrm{a}(1)\mathrm{a}(2)\} + C_3\{\mathrm{b}(1)\mathrm{b}(2)\} \tag{28}$$

For it, the Wiberg atomic valence ($V_{\mathrm{ab}} = V_{\mathrm{ba}} = P_{\mathrm{aa}}.P_{\mathrm{bb}}$)[13] for a diatomic electron-pair bond can be expressed[14] according to Eqs. (29) and (30).

$$V_{\mathrm{ab}} = 2C_1^{\,2}/D + 2C_1^{\,2}C_2^{\,2}/D^2 + 2C_1^{\,2}C_3^{\,2}/D^2 + 4C_2^{\,2}C_3^{\,2}/D^2 \tag{29}$$

$$= V_{\mathrm{ab}}(\mathrm{covalent})_{11} + V_{\mathrm{ab}}(\mathrm{covalent,ionic})_{12} + V_{\mathrm{ab}}(\mathrm{covalent,ionic})_{13} + V_{\mathrm{ab}}(\mathrm{ionic,ionic})_{2,3} \tag{30}$$

in which $D = 2C_1^{\,2} + C_2^{\,2} + C_3^{\,2}$.

The V_{ab} of Eqn. (28) could be considered to be a valence analogue of the covalent, covalent-ionic and ionic-ionic contributions to the charge-shift bonding formulation[15,16] of the binding energy for the electron-pair bond.

2. Concerted 2-Electron Delocalizations

Some concerted, 2-electron delocalization of the $\ddot{\mathbf{Y}}$ electrons into the antibonding molecular orbital $\varphi_{\mathrm{ab}}{}^{*} = k^{*}\mathrm{a} - \mathrm{b}$ of $\mathbf{A}:\mathbf{B}$, (in which the two electrons occupy the bonding molecular orbital $\varphi_{\mathrm{ab}} = \mathrm{a} + k\mathrm{b}$), is equivalent to the concerted delocalization of these electrons into the **Y-A** bonding molecular orbital $\varphi_{\mathrm{ya}} = \mathrm{y} + l\mathrm{a}$, i.e. the identity of Eqn. (1)

$$\left|(\mathrm{y} + \lambda\varphi_{\mathrm{ab}}{}^{*})^{\alpha}(\mathrm{y} + \lambda\varphi_{\mathrm{ab}}{}^{*})^{\beta}(\varphi_{\mathrm{ab}})^{\alpha}(\varphi_{\mathrm{ab}})^{\beta}\right| \equiv \left|(\varphi_{\mathrm{ya}})^{\alpha}(\varphi_{\mathrm{ya}})^{\beta}(\varphi_{\mathrm{ab}})^{\alpha}(\varphi_{\mathrm{ab}})^{\beta}\right| \tag{1}$$

obtains[17a], with $\lambda = kl/(1 + kk^{*})$. The associated valence-bond structure for $\left|(\varphi_{\mathrm{ya}})^{\alpha}(\varphi_{\mathrm{ya}})^{\beta}(\varphi_{\mathrm{ab}})^{\alpha}(\varphi_{\mathrm{ab}})^{\beta}\right|$ is $\mathbf{Y}:\mathbf{A}:\mathbf{B}$, in which the φ_{ya} and φ_{ab} orbitals are not orthogonal.

Similarly for a 3-electron 3-centre bonding unit with the wavefunction $\left|(\mathrm{y})^{\alpha}(\varphi_{\mathrm{ab}})^{\alpha}(\varphi_{\mathrm{ab}})^{\beta}\right|$ for the valence-bond structure $\dot{\mathbf{Y}}\ \ \mathbf{A}:\mathbf{B}$, the identity

$|(y + \lambda\varphi_{ab}{}^*)^{\alpha}(\varphi_{ab})^{\alpha}(\varphi_{ab})^{\beta}| \equiv |(\varphi_{ya})^{\alpha}(\varphi_{ab})^{\alpha}(\varphi_{ab})^{\beta}|$ pertains[17b], with $\lambda = kl/(1 + kk^*)$. The associated valence-bond structure for $|(\varphi_{ya})^{\alpha}(\varphi_{ab})^{\alpha}(\varphi_{ab})^{\beta}|$ is[17b] **Y • A : B**.

3. Additional References on Valence

Additional publications on valence for a variety of types of "increased-valence" and non-paired spatial orbital structures are those of Ref. 18.

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Chapter 15 Slater Determinants and Wave-Functions for "Increased-Valence" Structures

We will now extend the Slater determinant theory of Section 3-7 to construct wave-functions for "increased-valence" structures. Some of the theory for this Chapter will be used again in Chapters 20, 23 and 24.

15-1 "Increased-Valence" Wave-Functions for 4-Electron 3-Centre and 6- Electron 4- Centre Bonding Units

In Chapters 11, 12 and 14, we have indicated that the "increased-valence" structure (**1**)

(1) (2) (3)

(with y(1)a(2) + a(1)y(2) as the wavefunction for the fractional **Y-A** electron-pair bond) involves the electron spin distributions of structures (**2**) and (**3**), in which the **x** and **o** represent electrons with α and β spin wave-functions. Here, we shall construct Slater-determinantal wave-functions for (**2**) and (**3**), and hence for the "increased-valence" structure (**1**).

The wave-functions for the Pauling "3-electron bond" components $\overset{o}{\mathbf{A}} \times \overset{o}{\mathbf{B}}$ and $\overset{o}{\mathbf{A}} \times \overset{o}{\mathbf{B}}$ of the spin structures (**2**) and (**3**) are given by Eqs. (3-36) and (3-35). In structures (**2**) and (**3**), we have a fourth electron with spin wave-function α or β, which occupies the **Y**-atom atomic orbital y. Therefore, the wave-functions for spin structures (**2**) and (**3**) are given by the Slater determinants of Eqs. (1) and (2),

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$$\Psi(\overset{\times}{\mathbf{Y}}\quad \overset{\circ}{\mathbf{A}} \times \overset{\circ}{\mathbf{B}}) = |y^{\alpha}\,\psi^{\alpha}_{ab}\,\psi^{\beta}_{ab}\,\psi^{*\beta}_{ab}| = (1 + kk^{*})\,|y^{\alpha}\,a^{\beta}\,\psi^{\alpha}_{ab}\,b^{\beta}| \tag{1}$$

$$\Psi(\overset{\circ}{\mathbf{Y}}\quad \overset{\times}{\mathbf{A}} \circ \overset{\times}{\mathbf{B}}) = |y^{\beta}\,\psi^{\alpha}_{ab}\,\psi^{\beta}_{ab}\,\psi^{*\alpha}_{ab}| = -(1 + kk^{*})\,|y^{\beta}\,a^{\alpha}\,\psi^{\beta}_{ab}\,b^{\alpha}| \tag{2}$$

for which the identities of Eqs. (3-36) and (3-35) have been used.

Examination of Eqs. (1) and (2) shows that each of the spin structures (**2**) and (**3**) involves two singly-occupied orbitals, namely y and $\psi^{*}_{ab} = k^{*}a - b$. For bonding to occur between **Y** and **AB** because of overlap between y and ψ^{*}_{ab}, as it does in the “increased-valence” structure (**1**), it is necessary to spin-pair the two electrons that occupy these orbitals, thereby generating an S = 0 spin-state. By examination of the Heitler-London S = 0 spin wave-function of Eqn. (3-25), which also has two singly-occupied orbitals, it is seen that the appropriate wave-function for the S = 0 spin-pairings for structure (**1**) must involve the wave-function $|\ldots\, y^{\alpha}\psi^{*\beta}_{ab}| + |\ldots\, \psi^{*\alpha}_{ab}y^{\beta}|$ for the two singly occupied-orbitals of this structure.

By interchanging rows or columns of the Slater determinants of Eqs. (1) and (2), we may write

$$\Psi(\overset{\times}{\mathbf{Y}}\quad \overset{\circ}{\mathbf{A}} \times \overset{\circ}{\mathbf{B}}) = |\psi^{\alpha}_{ab}\,\psi^{\beta}_{ab}\,y^{\alpha}\,\psi^{*\beta}_{ab}| \tag{3}$$

$$\Psi(\overset{\circ}{\mathbf{Y}}\quad \overset{\times}{\mathbf{A}} \circ \overset{\times}{\mathbf{B}}) = -|\psi^{\alpha}_{ab}\,\psi^{\beta}_{ab}\,\psi^{*\alpha}_{ab}\,y^{\beta}| \tag{4}$$

in which we have grouped together the singly-occupied orbitals. The appropriate S = 0 spin wave-function for “increased-valence” structure (**1**) is therefore given by Eqs. (5) and (6).

$$\Psi(\mathbf{Y}\!-\!\!-\mathbf{A}\ \bullet\ \dot{\mathbf{B}}) = \Psi(\overset{\times}{\mathbf{Y}}\quad \overset{\circ}{\mathbf{A}} \times \overset{\circ}{\mathbf{B}}) - \Psi(\overset{\circ}{\mathbf{Y}}\quad \overset{\times}{\mathbf{A}} \circ \overset{\times}{\mathbf{B}})$$

$$= |\psi^{\alpha}_{ab}\,\psi^{\beta}_{ab}\,y^{\alpha}\,\psi^{*\beta}_{ab}| + |\psi^{\alpha}_{ab}\,\psi^{\beta}_{ab}\,\psi^{*\alpha}_{ab}\,y^{\beta}| \tag{5}$$

$$= (1 + kk^{*})\left(|y^{\alpha}\,a^{\beta}\,\psi^{\alpha}_{ab}\,b^{\beta}| + |y^{\beta}\,a^{\alpha}\,\psi^{\beta}_{ab}\,b^{\alpha}|\right) \tag{6}$$

It is important to realize that $\Psi(\mathbf{Y}\!-\!\!-\mathbf{A}\ \bullet\ \dot{\mathbf{B}})$ may be expressed as either Eqn. (5) or Eqn. (6). To relate directly to the valence-bond structure (**1**), Eqn. (6) is appropriate, but Eqn. (5) shows clearly that the “increased-valence” structure (**1**) involves the spin-pairing of two electrons, one of which occupies an atomic orbital on **Y**, and the other occupies the **A-B** antibonding molecular orbital.

Inspection of Eqn. (6) shows that a Heitler-London type wave-function has been used to construct the wave-function for the fractional **Y-A** bond of structure (**1**). If it is preferred to use bonding molecular orbitals to describe the wave-functions for all bonds, then we may construct the S = 0 spin wave-function of Eqn. (7)

$$\Psi(\mathbf{Y}\text{—}\mathbf{A}\ \bullet\ \dot{\mathbf{B}}) = |\psi_{ya}^{\alpha}\psi_{ya}^{\beta}\psi_{ab}^{\alpha}b^{\beta}| + |\psi_{ya}^{\alpha}\psi_{ya}^{\beta}b^{\alpha}\psi_{ab}^{\beta}| \tag{7}$$

for the four electrons of structure (**1**), in which $\psi_{ya} = y + \ell a$ and $\ell > 0$. The properties of Eqs. (**6**) and (**7**) are different, and on most occasions, we shall be implying the usage of Eqn. (6). Some further considerations of Eqn. (**7**), and elaborations of it (via the use of the orbitals $\phi = y + ka$ and $\phi' = y + k'a$ instead of doubly-occupied ψ_{ya}), will be provided in Chapters 20 and 23.

"Increased-valence" structure (**1**) is the fundamental "increased-valence" structure. Together with "increased-valence" structure (**4**),

$$\mathbf{Y}\text{—}\mathbf{A}\cdot\dot{\mathbf{B}} \qquad\qquad \dot{\mathbf{Y}}\cdot\mathbf{A}\text{—}\mathbf{B}$$
$$(\mathbf{1}) \qquad\qquad\qquad (\mathbf{4})$$

$$\dot{\mathbf{A}}\cdot\mathbf{B}\text{—}\mathbf{C}\cdot\dot{\mathbf{D}} \qquad\qquad \dot{\mathbf{A}}\cdot\dot{\mathbf{B}}\ \ \dot{\mathbf{C}}\cdot\dot{\mathbf{D}}$$
$$(\mathbf{5}) \qquad\qquad\qquad (\mathbf{6})$$

it is appropriate whenever four electrons can participate in 3-centre bonding. But as we have discussed in Chapter 13, it is possible to construct longer "increased-valence" structures that are appropriate for different types of N-centre bonding units, with $N \geq 4$. Here, we shall construct a Slater-determinantal wave-function for the 6-electron 4-centre "increased-valence" structure (**5**) (Section 12-3), which is obtained by spin-pairing the odd-electrons of the Pauling "3-electron bond" structures of structure (**6**). For the latter structures, the odd electrons occupy the antibonding ψ^{*}_{ab} and ψ^{*}_{cd} molecular orbitals, and the bonding molecular orbitals ψ_{ab} and ψ_{cd} are doubly occupied. When S = 0 spin-pairing of the odd-electrons of structure (**6**) occurs, the two singly-occupied antibonding orbitals will also pertain for the wave-function for structure (**5**). Consequently, the S = 0 spin wave-function for (**5**) is given by Eqn. (8).

$$\Psi(\dot{\mathbf{A}}\cdot\mathbf{B}\text{—}\mathbf{C}\cdot\dot{\mathbf{D}}) = |\psi_{\mathbf{ab}}^{\alpha}\psi_{\mathbf{ab}}^{\beta}\psi_{\mathbf{ab}}^{*\alpha}\psi_{\mathbf{cd}}^{*\beta}\psi_{\mathbf{cd}}^{\alpha}\psi_{\mathbf{cd}}^{\beta}| + |\psi_{\mathbf{ab}}^{\alpha}\psi_{\mathbf{ab}}^{\beta}\psi_{\mathbf{cd}}^{*\alpha}\psi_{\mathbf{ab}}^{*\beta}\psi_{\mathbf{cd}}^{\alpha}\psi_{\mathbf{cd}}^{\beta}| \tag{8}$$

Orbital-occupancy diagrams that correspond to the Slater determinants of Eqs. (5) and (8) are displayed in Figs. 11-2 and 11-3.

15-2 Spin Degeneracy and Wave-Functions for "Increased-Valence" Structures

Except for 4-electron 3-centre and 6-electron 4-centre "increased-valence" structures, all other "increased-valence" structures involve the spin-pairing of three or more odd electrons, i.e. in the "increased-valence" wave-function, three or more orbitals must be singly-occupied. This may be seen by examination of the "increased-valence" structures (**7**) and (**8**)

$$\begin{array}{cccc}
\mathbf{A{-}B{\cdot}C{-}D} \equiv \dot{\mathbf{A}}\ \ \dot{\mathbf{B}}{\cdot}\dot{\mathbf{C}}\ \ \dot{\mathbf{D}} & & \mathbf{Y{-}A{\cdot}B{-}C{\cdot}D{-}E} \equiv \dot{\mathbf{Y}}\ \ \dot{\mathbf{A}}{\cdot}\dot{\mathbf{B}}\ \ \dot{\mathbf{C}}{\cdot}\dot{\mathbf{D}}\ \ \dot{\mathbf{E}} \\
(7) \qquad a\ \ \psi^{*}_{ab}\ \ d & & (8) \qquad y\ \ \psi^{*}_{ab}\ \ \psi^{*}_{cd}\ \ e
\end{array}$$

for 5-electron 4-centre and 8-electron 6-centre bonding. These structures have been expressed in terms of their atomic and Pauling "3-electron bond" components, below which we have written the singly-occupied orbitals. When three or more orbitals of an atom or molecule are singly-occupied, the phenomenon of *spin degeneracy* arises, i.e. there exist two or more wave-functions with the same set of S and S_z spin quantum numbers. For each of the "increased-valence" structures (**7**) and (**8**), the spin degeneracy is two; there are two wave-functions with spin quantum numbers $S = S_z = ½$ for structure (**7**), and two wave-functions with $S = S_z = 0$ for structure (**8**). These wave-functions are given[i] by Eqs. (9)-(12), in which we have omitted all doubly-occupied orbitals from the Slater determinants.

$$\mathbf{\Psi_1(Y{-}A\cdot B{-}C)} = 2\,|\,y^{\alpha}\psi^{*\alpha}_{ab}c^{\beta}\,| - |\,y^{\alpha}\psi^{*\beta}_{ab}c^{\alpha}\,| - |\,y^{\beta}\psi^{*\alpha}_{ab}c^{\alpha}\,| \tag{9}$$

$$\mathbf{\Psi_2(Y{-}A\cdot B{-}C)} = |\,y^{\alpha}\psi^{*\beta}_{ab}c^{\alpha}\,| - |\,y^{\beta}\psi^{*\alpha}_{ab}c^{\alpha}\,| \tag{10}$$

$$\begin{aligned}\mathbf{\Psi_1(Y{-}A\cdot B{-}C\cdot D{-}E)} &= |\,y^{\alpha}\psi^{*\beta}_{ab}\psi^{*\alpha}_{cd}e^{\beta}\,| + |\,y^{\beta}\psi^{*\alpha}_{ab}\psi^{*\beta}_{cd}e^{\alpha}\,| \\ &\quad - |\,y^{\alpha}\psi^{*\beta}_{ab}\psi^{*\beta}_{cd}e^{\alpha}\,| - |\,y^{\beta}\psi^{*\alpha}_{ab}\psi^{*\alpha}_{cd}e^{\beta}\,|\end{aligned} \tag{11}$$

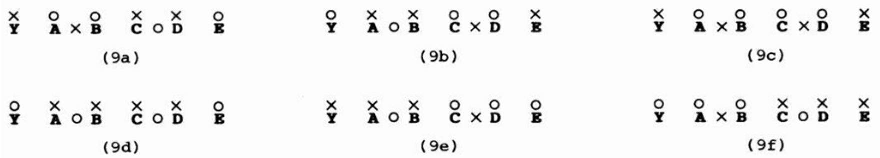
$$\begin{aligned}\mathbf{\Psi_2(Y{-}A\cdot B{-}C\cdot D{-}E)} &= |\,y^{\alpha}\psi^{*\beta}_{ab}\psi^{*\alpha}_{cd}e^{\beta}\,| + |\,y^{\beta}\psi^{*\alpha}_{ab}\psi^{*\beta}_{cd}e^{\alpha}\,| \\ &\quad - |\,y^{\alpha}\psi^{*\alpha}_{ab}\psi^{*\beta}_{cd}e^{\beta}\,| - |\,y^{\beta}\psi^{*\beta}_{ab}\psi^{*\alpha}_{cd}e^{\alpha}\,|\end{aligned} \tag{12}$$

In Eqs. (11) and (12), there are six types of Slater determinants. They generate different spin arrangements for the four singly-occupied orbitals, and lead to the

---

[i] The Ψ_1 and Ψ_2 of Eqs. (9) and (10) are orthogonal, whereas the Ψ_1 and Ψ_2 of Eqs. (11) and (12) are not orthogonal. An orthogonal set may of course be constructed from the latter pair of functions, but for our present purposes, it is more useful to use Eqs. (11) and (12).

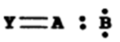
spin distributions of spin structure (**9**) for the eight electrons of "increased-valence" structure (**8**).



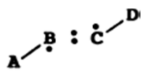
(9a) (9b) (9c) (9d) (9e) (9f)

Each of the spin structures (**9a**)-(**9f**) involves two one-electron **A-B** and **C-D** bonds, but they differ in the number of two-electron spin-pairings which can occur between pairs of adjacent atoms. Thus, each of (**9a**) and (**9b**) can lead to fractional **Y-A**, **B-C** and **D-E** spin-pairings; (**9c**) and (**9d**) generate **Y-A** and **D-E** spin-pairings, and (**9e**) and (**9f**) can only involve **B-C** spin pairing. We may construct any linear combination of Ψ_1 and Ψ_2, each of which generates some **Y-A**, **B-C** and **D-E** bonding (i.e. spin pairing). However, the special linear combination $\Psi_1 + \Psi_2$ gives equal possibility for the three spin-pairings to occur.

Similar types of wave-functions are also appropriate when two orthogonal sets of 4-electron 3-centre bonding units are present in the molecule, as occurs in the "increased-valence" structures (**10**) and (**11**)



(10)



(11)

(cf. "increased-valence" structures (**I**) and (**V**) of Section 2-5 (b) for N_2O and F_2O_2). For spin-pairing to occur only within a 4-electron 3-centre bonding unit, the appropriate S = 0 spin wave-functions have Slater determinants with the spin distribution of Eqn. (11) (i.e. αβαβ + βαβα – αββα – βααβ), in which the order of (singly-occupied) spatial orbitals in each determinant is y, ψ^*_{ab}, y′, and ψ'^*_{ab} for structure (**10**) and a, ψ^*_{bc}, d, and ψ'^*_{bc} for structure (**11**).

One of the "increased-valence" formulations of 1,3-dipolar cycloaddition reactions (Section 22-4) involves electronic reorganization of the general type (**12**) → (**13**)

(12) (13)

for a 6-electron 5-centre bonding unit. Four singly-occupied orbitals (y, ψ^*_{ab}, c and d) are involved, and the spin wave-functions are the analogues of Eqn. (11) for structure (**12**), and Eqn. (12) for structure (**13**); the order of spatial orbitals in each Slater determinant is y, ψ^*_{ab}, c and d. For the linear combination $\Psi = C_1\Psi_1 + C_2\Psi_2$, $|C_1| >> |C_2|$ near the commencement of the reaction and $|C_2| >> |C_1|$ near its conclusion.

In Table 15-1, we report the spin degeneracies for the S = 0 and S = ½ spin wave-functions for “increased-valence” structures with 4-12 electrons.

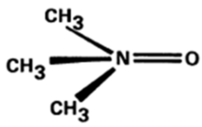
Table 15-1: Some “increased-valence” structures expressed in terms of their component “three-electron bonds”. n = number of electrons; n_u = number of unpaired electrons ; D = spin degeneracy for singlet (S = 0 spin) and doublet (S = ½ spin) states.

	n	n_u	D
$\dot{\mathbf{A}}\cdot\dot{\mathbf{B}}$	3	1	1
$\dot{\mathbf{Y}}\;\;\dot{\mathbf{A}}\cdot\dot{\mathbf{B}}$	4	2	1
$\dot{\mathbf{A}}\;\;\dot{\mathbf{B}}\cdot\dot{\mathbf{C}}\;\;\dot{\mathbf{D}}$	5	3	3
$\dot{\mathbf{A}}\cdot\dot{\mathbf{B}}\;\;\dot{\mathbf{C}}\cdot\dot{\mathbf{D}}$	6	2	1
$\dot{\mathbf{Y}}\cdot\dot{\mathbf{A}}\;\;\dot{\mathbf{B}}\cdot\dot{\mathbf{C}}\;\;\dot{\mathbf{D}}$	7	3	2
$\dot{\mathbf{Y}}\;\;\dot{\mathbf{A}}\cdot\dot{\mathbf{B}}\;\;\dot{\mathbf{C}}\cdot\dot{\mathbf{D}}\;\;\dot{\mathbf{E}}$	8	4	2
$\dot{\mathbf{Y}}\cdot\dot{\mathbf{A}}\;\;\dot{\mathbf{B}}\cdot\dot{\mathbf{C}}\;\;\dot{\mathbf{D}}\cdot\dot{\mathbf{E}}$	9	3	2
$\dot{\mathbf{Y}}\cdot\dot{\mathbf{A}}\;\;\dot{\mathbf{B}}\cdot\dot{\mathbf{C}}\;\;\dot{\mathbf{D}}\cdot\dot{\mathbf{E}}\;\;\dot{\mathbf{F}}$	10	4	2
$\dot{\mathbf{Y}}\;\;\dot{\mathbf{A}}\cdot\dot{\mathbf{B}}\;\;\dot{\mathbf{C}}\cdot\dot{\mathbf{D}}\;\;\dot{\mathbf{E}}\cdot\dot{\mathbf{F}}\;\;\dot{\mathbf{G}}$	11	5	5
$\dot{\mathbf{Y}}\cdot\dot{\mathbf{A}}\;\;\dot{\mathbf{B}}\cdot\dot{\mathbf{C}}\;\;\dot{\mathbf{D}}\cdot\dot{\mathbf{E}}\;\;\dot{\mathbf{F}}\cdot\dot{\mathbf{G}}$	12	4	2

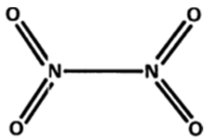
Chapter 16 Classical Valence-Bond Structures and Quinquevalent Nitrogen Atoms

For a number of electron-excess molecules that involve atoms of first-row elements (in particular, nitrogen atoms), an older type of "increased-valence" structure is sometimes used to represent their electronic structures. Since the 1860s and until the introduction of the Lewis-Langmuir octet theory, nitrogen atoms were often represented with valencies of 3 or 5 in valence-bond structures. For example, valence-bond structures for N_2O, Me_3NO, and N_2O_4 were written as structures (**1**)-(**3**).

(1)



(2)



(3)

Using structure (**1**) for N_2O, with an N-N triple bond and an N-O double bond, we would be let to predict that the bond-lengths are similar to the 1.10 Å and 1.21 Å for N_2 and $CH_3N{=}O$. The experimental lengths of 1.13 Å and 1.19 Å confirm this expectation (Section 2-3 (b)), and on this basis structure (**1**) is a suitable valence-bond structure for N_2O. But the Lewis theory, with electron-pair bonds, does not permit a valence of five for first-row atoms, provided that only the 2s and three 2p orbitals of these atoms are valence orbitals for bonding. Therefore, in the Lewis theory, the quinquevalent structures are replaced[3] by octet structures such as structures (**4**)-(**6**) for N_2O, and (**7**) and (**8**) (together with equivalent resonance forms) for Me_3NO and N_2O_4.

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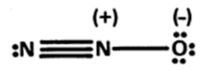
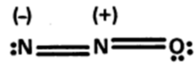
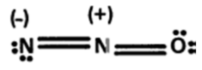
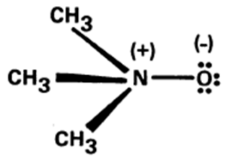
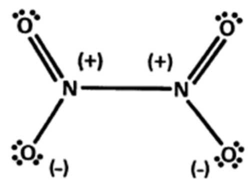

(4)


(5)


(6)


(7)

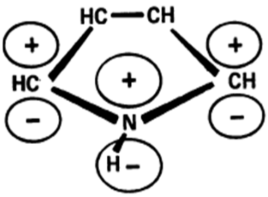

(8)

In these latter structures, the valencies of N^-, N, and N^+ are 2, 3 and 4, respectively. We may note that each of the structures (**1**), (**2**) and (**3**) seems to have one more bond than have the corresponding Lewis structures, and therefore we might also designate structures (**1**), (**2**) and (**3**) as "increased-valence" structures. Alternatively, we may say that the quinquevalent nitrogen atom has increased its valence relative to the maximum of four which is allowed in the Lewis theory. Sometimes, the valence-bond structures such as (**1**), (**2**) and (**3**) are designated as "classical valence structures", and we shall refer to them as such here.

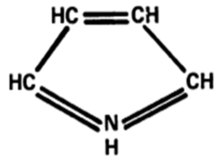
Although the use of octet structures such as (**5**)-(**8**) is extremely widespread, it is by no means universal[4, 5]. Sometimes, the classical valence structures are used to account for certain empirical information, and the quantum mechanical basis for them is not discussed, i.e. it is not suggested how the nitrogen atom forms five covalent bonds. However, there have been three major attempts to explain how a nitrogen atom (or other first-row atoms – in particular, a carbon atom) may acquire an apparent valence of five, and we shall describe them briefly here.

(a) The nitrogen ground-state configuration $2s^2\ 2p_x^1\ 2p_y^1\ 2p_z^1$ is promoted to either the $2s^1\ 2p_x^1\ 2p_y^1,\ 2p_z^1\ 3s^1$ or the $2s^1\ 2p_x^1\ 2p_y^1\ 2p_z^1\ 3d^1$ configuration[6, 8], both of which have five unpaired electrons. Because the $2s \rightarrow 3s$ and the $2s \rightarrow 3d$ promotion energies are large, this theory is usually considered to be unsatisfactory.

(b) By overlapping three of its four valence orbitals with three atomic orbitals on one or more adjacent atoms, the nitrogen atom can form three normal electron-pair bonds. The fourth nitrogen valence orbital then overlaps simultaneously with two atomic orbitals on adjacent atoms and thereby forms two non-orthogonal bond orbitals. In structure (**9**) we show the latter type of overlap for the nitrogen atom of pyrrole; the classical valence structure for this molecule is (**10**).



(9)



(10)

If in structure (**9**), y and b are the carbon $2p_z$ atomic orbitals, and a is the nitrogen $2p_z$ atomic orbital, then from them we may construct the two-centre bond-orbitals $\phi_L = y + ka$ and $\phi_R = b + ka$ with $k > 0$. We may locate the four N-C-N π-electrons of structure (**10**) into these two orbitals, to afford the bond-orbital configuration $(y + ka)^2(b + ka)^2$. It is satisfactory to do this, provided it is recognised that the two bond-orbitals are not orthogonal, and therefore, when they are both doubly occupied, they cannot represent two separate, independent C-N π-bonds. Therefore for this theory, the nitrogen atom does not have a true valence of five – it is only apparently quinquevalent.

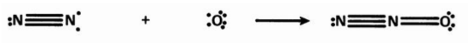
Bent[9] has used this type of "increased-valence" theory to describe the bonding for numerous molecules. It may be noted that (except for a multiplicative constant) the configuration $(y + ka)^2(b + ka)^2$ is equivalent to the delocalized molecular orbital configuration $(y + 2ka + b)^2(y - b)^2$, for which the delocalized molecular orbitals correspond to the bonding and non-bonding molecular orbitals of Section 2-3 (a). (The proof of this result is obtained by using the identity of Eqn. (3-17), namely if two electrons occupy orbitals ψ_1 and ψ_2 with the same spins, then $(\psi_1)^1(\psi_2)^1 \equiv -2(\psi_1 + \psi_2)^1(\psi_1 - \psi_2)^1)$). With this equivalence, the a-orbital valence is[13, 14] $V_a = P_{ay}^2 + P_{ab}^2 = 8k^2/(2k^2 + 1)^2$, which has a maximum value of unity when $k = 2^{-\frac{1}{2}}$. Consequently, using the C-N-C π-electron configuration $(y + 2ka + b)^2(y - b)^2$, the nitrogen atom of structure (**10**) remains quadrivalent[14], as it is in the Lewis octet structure.

This use of two non-orthogonal π-orbitals forms the basis of Paoloni's theory[4] of the quinquevalent nitrogen atom. Paoloni was not concerned with the construction of a wave-function for the quinquevalent nitrogen atom in a molecule, but only with indicating by means of the valence-bond structure that the two π-electrons of the pyrrolic nitrogen (tr, tr, tr, π^2) configuration ($tr = sp^2$) are involved in bonding to the adjacent carbon atoms.

(c) The third theory of nitrogen quinquevalence has an interesting history[15]. By using the molecular orbital configuration

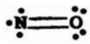
$$(\sigma 2s)^2(\sigma^* 2s)^1(\sigma 2p)^2(\pi_x)^2(\pi_x^*)^1(\pi_y)^2 \tag{1}$$

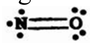
for an excited state of N_2, in 1944, Samuel[16] derived the valence-bond structure , which has two unpaired electrons. Samuel then paired these electrons with two unpaired electrons of an oxygen atom to form two N-O covalent bonds, i.e. he wrote

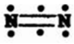
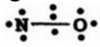


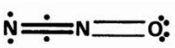
In 1945, Wheland[17] defended the Lewis structures (i.e structures (**4**)-(**6**)), and suggested that N_2O could be formed by combination of the excited NO configuration

$$(\sigma 2s)^2(\sigma 2s)^1(\sigma 2p)^2(\pi_x)^2(\pi_x^*)^1(\pi_y)^2(\pi_y^*)^1 \tag{2}$$

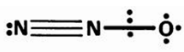
with a nitrogen atom. From this NO configuration, Wheland obtained the valence-bond structure $^{+}\cdot\dot{\mathrm{N}}\text{—}\ddot{\mathrm{O}}\!:^{-}$, which enabled him to retain the nitrogen quadrivalence in the Lewis structure (**4**). In another paper, Samuel implied that the excited NO configuration corresponded to the valence-bond structure , which generates nitrogen quinquevalence in the reaction

On replying to Wheland's paper, Samuel gave some additional justification for using the  valence-bond structure[18].

It seems now that both Samuel and Wheland held the widespread opinion that valence-bond structures for diamagnetic molecules must only have electron-pair bonds. Samuel and Wheland had attempted to transform the molecular orbital configurations for N_2 and NO so that they would obtain electron-pair bonds for N_2O. But neither worker used the correct procedure to obtain valence-bond structures from diatomic molecular orbital configurations with one or more singly-occupied anti-bonding molecular orbitals. The technique that should be used was developed by Linnett in 1956[19], and then by Green and Linnett in 1960[20], and it has formed the primary Pauling "3-electron bond" basis for the increased-valence theory we use in this book. When this theory is applied to the excited N_2 and NO configurations of Eqs. (1) and (2), we obtain the valence-bond structures  and , with two and three Pauling "3-electron bonds". When these structures are bonded to oxygen or nitrogen atoms, we obtain valence-bond structures (**11**) and (**12**) for N_2O.

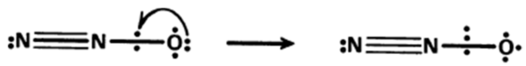


(11)



(12)

The valence-bond structure (**12**) is similar to the "increased-valence" structure (**13**) (cf. Figures 2-10 and 13-1), and it is possible to derive (**12**) from structure (**13**) by delocalizing an oxygen lone-pair electron into a bonding N-O orbital. To show this we write

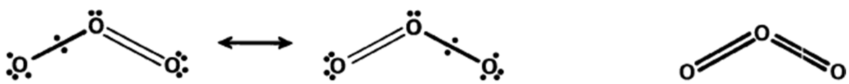


(13) (12)

(We note that the oxygen lone-pair electron of structure (**13**) that is delocalized occupies an atomic orbital which should be primarily 2s in character. Therefore, this electron must be strongly bound to the oxygen atom, and very little delocalization of it is expected to occur. Any delocalization of nitrogen or oxygen 2s lone-pair electrons has been ignored throughout this book.)

If we use valence-bond structures such as (**13**), which have both one-electron bonds and fractional electron-pair bonds, then we may give the following interpretation of the apparent nitrogen quinquevalence in structure (**1**). Let us assume that structures (**1**) and (**13**) are equivalent structures. It then follows that one of the two N-O bond-lines of structure (**1**) represents two N-O bonding electrons occupying two different spatial orbitals, i.e. this N-O bond-line in structure (**1**) is equivalent to the two one-electron N-O bonds in structure (**13**).

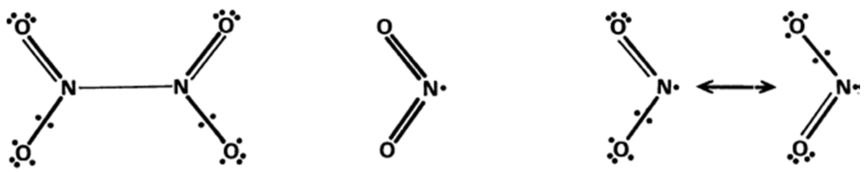
Because "increased-valence" structures such as (**13**) make clearer the nature of the spatial distributions of the electrons than do the classical valence structures such as (**1**), it would seem to be preferable to use the former types of valence-bond structures. They also have the advantage that they do not conceal the (spin-paired) diradical character, which is sometimes important for discussions of chemical reactivity. For example, O_3 reacts with univalent radicals such as hydrogen and chlorine atoms, and NO, to form $O_2 + HO$, ClO or NO_2. In Chapter 22, we shall find that the electronic reorganization that may occur as the reactions proceed is easily followed through by using "increased-valence" structure (**14**)



(14) (15)

rather than the classical valence bond structure (**15**). In structure (**14**), (fractional) odd-electron charge occupies an atomic orbital on a terminal oxygen atom, and this charge may be used to form a partial bond with the univalent radical.

In Section 13-2, we have generated "increased-valence" structure (**16**) from the standard Lewis structure (**8**) for N_2O_4. Each of the structures (**3**) and (**16**) has an *apparent* valence of 5 for each nitrogen atom[i], but structure (**16**) relates better to the experimental electronic structure than does structure (**3**). Thus, by inspection of structure (**3**), it is not possible to deduce that the N-N bond should be long and weak. Also, when the N-N bonds of structures (**3**) and (**16**) are broken, the NO_2 monomers of (**17**) and (**18**) are obtained, with their odd-electron located in a nitrogen atomic orbital of structure (**17**), but delocalized over the molecule in the structures of (**18**). Only the latter description is in accord with the results of electron spin resonance measurements[21].



(16) (17) (18)

For each of the "increased-valence" structures that we have described in this chapter, there is an *apparent violation* of the Lewis-Langmuir octet rule for some of the first-row atoms. However, because only the 2s and 2p orbitals are required for a minimal basis set description of the bonding, no real octet violation occurs in the molecular wave-function. Further, (with either Heitler-London atomic-orbital or 2-centre bond-orbital wavefunctions for nearest-neighbour electron-pair bonds, cf. Chapter 23), these structures summarize resonance between standard and "long-bond" Lewis structures, each of which obeys the octet rule. This latter result has been demonstrated in Section 11-9 for the N_2O_4 "increased-valence" structure (**16**), whose component octet structures are displayed in Fig. 11-5. Further comments on "apparent octet violation" for atoms of first-row and higher-row elements are provided in Refs. 14, 15, 22, 23 and 24.

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[i] Using the procedures described in Section 14-3, it may be deduced that the maximum nitrogen valence for structure (**16**) is 4.25, and that a total of 18 electrons participate in bonding between all pairs of atoms. Also, as indicated in the caption for Fig. 11-7, as well the *cis* "increased-valence" structure (**16**) here, there is a mirror-image *cis* "increased-valence" structure and two *trans* "increased-valence" structures. Resonance between these four "increased-valence" structures is equivalent to a restricted form of resonance between the 64 octet Lewis structures.

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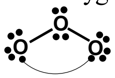
Addendum Chapter 16

Generalized valence bond perfect pairing (GVB/PP)[25] and spin-coupled valence bond (SCVB)[26] calculations for tri- and polyatomic molecules use multicentre, delocalized orbitals (i.e. 3-centre or many-centre orbitals) to accommodate the active space electrons. To quote Ref. 27: “The GVB/PP wavefunctions are antisymmetrized products of paired orbitals and represent a single valence bond structure. … The SC method is based on a single configuration in which each electron is described by a distinct orbital. The complete spin state is utilized.” For example, a 4-electron 3-centre SC wavefunction involves four non-orthogonal 3-centre orbitals and two $S = 0$ spin wavefunctions. For some of the molecules that have been studied[28] – for example CH_2NN and O_3 - the resulting SCVB structures have an apparent valence of five, as in $H_2C{=}N{\equiv}N$ for the central nitrogen and either four for the central oxygen atom (as in structure (15)) or two as in the singlet diradical structure ). See Refs. 29 and 30 for comparisons of valence bond structures obtained from SCVB calculations with increased-valence structures. The quinquevalent valence-bond structure (3) for symmetric N_2O_4 has been used in the GVB studies of Ref.31.

Use of classical quinquevalent valence-bond structures disguises the singlet diradical character that electron-rich systems possess.

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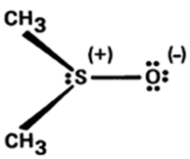
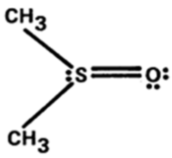
Chapter 17 Some Tetrahedral Molecules and $d_\pi - p_\pi$ Bonding for some Sulphur Compounds

17-1 d-Orbitals as Polarization and Hybridization Functions

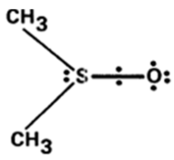
In Chapters 11 and 13, we have constructed valence-bond structures for several molecules that involve sulphur atoms. For them, it was assumed that only the valence-shell 3s and 3p orbitals need participate in bonding. Of course, atoms of the second-row of the periodic table may also utilize one or more 3d-orbitals as hybridization functions for bonding, i.e. such atoms may expand their valence shells. When this occurs, the associated Lewis-type valence-bond structures involve more electron-pair bonds than are present in the octet structures. For $(CH_3)_2SO$, structures (**1**) and (**2**)



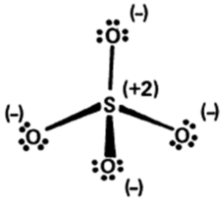
(1)



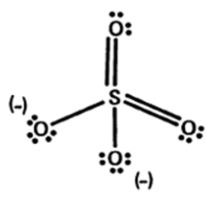
(2)



(3)



(4)



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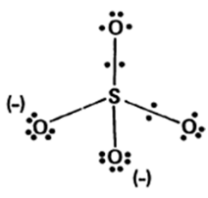

(6)

R.D. Harcourt, *Bonding in Electron-Rich Molecules*,
Lecture Notes in Chemistry 90, DOI 10.1007/978-3-319-16676-6_17

are examples of Lewis octet and Lewis expanded valence-shell structures. The "increased-valence" structure[i†] (**3**) does not involve the participation of sulphur 3d-orbitals as hybridization functions in bonding.

Structures (**2**) and (**3**) are obtained respectively by delocalizing oxygen π or/and $\bar{\pi}$ electrons of structure (**1**) into either a vacant sulphur 3d-orbital or into bonding S-O orbitals; the relevant (overlapping) atomic orbitals for the latter are a sulphur hybrid orbital of an adjacent S-C σ-bond and an oxygen π- or $\bar{\pi}$-orbital. In structure (**3**), 1-electron bonds replace the additional $d_\pi - p_\pi$ bond that is formed when the sulphur atom expands its valence shell in structure (**2**). Structures (**4**)-(**6**) are similar types of structures for SO_4^{2-}, with the sulphur atom for structure (**5**) utilizing two 3d-orbitals to form the two $d_\pi - p_\pi$ S-O bonds.

It is important to distinguish between the role of d-orbitals as hybridization functions and their role as polarization functions. For the former case, the d-orbital serves to "increase the number of distinct orbitals utilized in the wave-function"[1]. Thus, the octet and expanded valence-shell structures (**1**) and (**2**) have $C_1s^2p^3$, $V_3 + C_2sp^4$, V_3 and $C_1s^2p^3d$, $V_4 + C_2sp^4d$, V_4 valence-state configurations for the trivalent and quadrivalent sulphur atoms. For structures (**4**) and (**5**) the sulphur valence-state configurations are sp^3, V_4 and sp^3d^2, V_6. When a 3d-orbital participates as a polarization function, it "merely moderates the shape of pre-existing orthogonal hybrid atomic orbitals"[1]. For example, the three sulphur orbitals that form σ-bonds in the octet structure (**1**) may involve some 3d as well as 3s and 3p character; i.e. each orbital may be expressed as $c_1s + c_2p + c_3d$. The resulting valence-state configuration is then $C_1s^2p^3$, $V_3 + C_2sp^4$, $V_3 + C_3s^2p^2d$, $V_3 + C_4sp^3d$, V_3. Therefore, the utilization of 3d orbitals as polarization functions is not precluded for either the octet structures or "increased-valence" structures such as (**3**) and (**6**). Our concern here is to distinguish between this type of "increased-valence" structure, and those that utilize 3d orbitals as hybridization functions for $d_\pi - p_\pi$ bonding. We shall restrict our attention primarily to a consideration of the bonding for some sulphur compounds.

On the basis of some bond-length data, we shall suggest that expansion of the sulphur valence-shell to generate $d_\pi - p_\pi$ bonding is more likely to occur in either of the following situations:

(a) The **R** substituents of R_2SO are alkyl radicals. In Sections 11-3 and 11-4 we have concluded that H and alkyl substituents seem unable to stabilize appreciable development of Pauling "3-electron bonds" in 4-electron 3-centre bonding units of neutral molecules. The delocalization of oxygen π or $\bar{\pi}$ electrons

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[i] Relative to the octet Lewis octet structures (**1**) and (**4**), structures (**2**) and (**5**) as well as structures (**3**) and (**6**) exhibit "increased-valence", i.e. more electrons participate in bonding than does occur in structures (**1**) and (**4**). In this Chapter (and throughout this book), we refer to valence bond structures that involve one or more Pauling "3-electron bonds" as "increased-valence" structures.

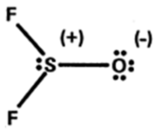
of structure (**1**) into the sulphur 3d-orbital to form structure (**2**) then helps reduce the magnitudes of the atomic formal charges.

(b) The sulphur (or other second-row) atom is involved in the formation of four electron pair σ-bonds in a standard octet structure – for example structure (**4**) for SO_4^{2-}. This is equivalent to saying that either the sulphur oxidation state (or number) is +6 or that the sulphur formal charge is +2 in the octet structure.

These hypotheses are speculative, and exceptions to them exist. Therefore, the discussion for some of this chapter should be viewed more as involving orientation, rather than as definitive accounts of the bonding. The role of 3d-orbitals in bonding for second-row atoms has been discussed by numerous workers – see for example Refs. 1-6 – and the reader is referred to them for further details.

17-2 F_2SO, F_2SS, and $(CH_3)_2SO$

In Section 11-5, "increased-valence" structures (**8**) and (**10**)



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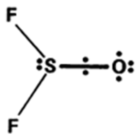

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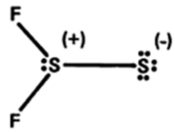

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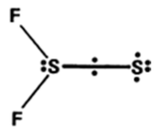

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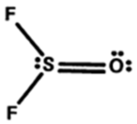

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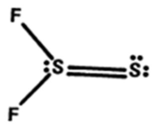


(12)

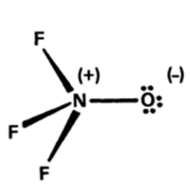
are generated from the standard octet Lewis structures (**7**) and (**9**) by delocalizing oxygen π- and $\bar{\pi}$-electrons into bonding S-O orbitals. Without the participation in bonding of a sulphur 3d orbitals as a hybridization function, these structures (together with structure (**35**) of Section 11-5 for F_2SO) account for (i) the shortening or the similarity of the S-O and S-S bond-lengths (1.41 Å and 1.86 Å) to those of double bonds (1.49 Å and 1.89 Å), and (ii) the lengthening of their S-F bonds (1.59 Å and 1.60 Å) relative to the estimate of 1.54 Å for the length of an S-F single-bond.

If it is assumed that an oxygen lone-pair electron delocalizes into a sulphur 3d orbital for either molecule, Lewis structures (**11**) and (**12**) are obtained. The latter structures have S-O double-bonds, but because they retain S-F single-bonds, they cannot account for the observed lengthening of the S-F bonds relative to those of single bonds.

In contrast to what is the case for F_2SO, the bond-lengths for isoelectronic $(CH_3)_2SO$ (C-S = 1.80 Å, S-O = 1.48 Å)[7] suggest that a sulphur 3d orbital does participate in S-O bonding as a hybridization function. The S-O bond-length is shorter than a single-bond (1.70 Å), but the C-S bond-lengths are essentially those of C-S single-bonds (cf. 1.82 Å for CH_3SH)[8]. Resonance between valence-bond structures (**1**) and (**2**), each of which has two C-S single-bonds, accounts for the observed bond-lengths. In Section 11-3, we have concluded that CH_3 groups cannot provide much stabilization of Pauling "3-electron bonds" for 4-electron 3-centre bonding units in neutral molecules, and therefore the delocalization of oxygen π and $\overline{\pi}$ electrons of structure (**1**) to generate "increased-valence" structure (**3**) must occur only to a small extent; otherwise the C-S bonds of $(CH_3)_2SO$ would be rather longer than single bonds.

17-3 F_3NO, $(CH_3)_3NO$, F_3SN, and FSN

Each of the tetrahedral AX_3Y molecules of this Section has 32 valence-shell electrons, as have the sulphones and AO_4 anions of Sections 17-4 and 17-5. Consideration of the bonding for these AX_3Y molecules provides some support for the hypothesis that fluorine atoms can stabilize Pauling "3-electron-bonds" in 4-electron 3-centre bonding units for neutral molecules, and that Lewis structures with expanded valence-shells for sulphur atoms could be appropriate if the sulphur atoms acquire +2 formal charges in the Lewis octet structures.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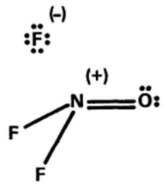
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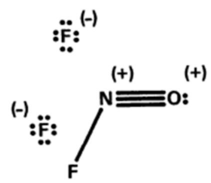
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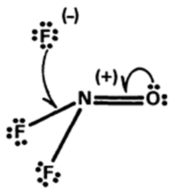
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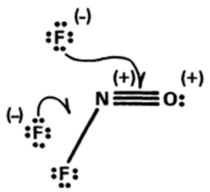
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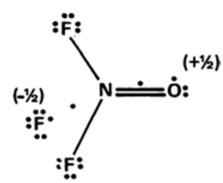
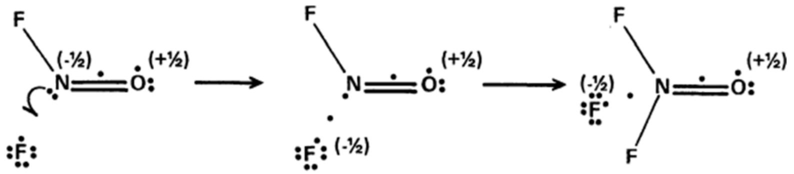

(16)

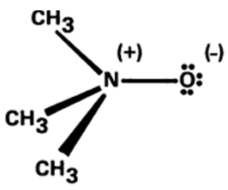
For F_3NO, the standard Lewis structures are of types (**13**)-(**15**). The N-F and N-O bond-lengths[9] of 1.432 Å and 1.159 Å for this molecule are respectively longer than the N-F bonds of NF_3 (1.37 Å) and similar to the bond-length (1.15 Å) for free NO with valence-bond structure $^{-\frac{1}{2}}\mathbf{:\dot{N} \doteq \dot{O}:}^{+\frac{1}{2}}$ (Section 4-5). Resonance between the six structures of types (**14**) and (**15**) can account qualitatively for these bond properties, but the formal charges of structures of type (**15**) suggest that their weight should be rather less than that of the type (**14**) structures. Alternatively, we may construct "increased-valence" structures of type (**16**) either via the delocalizations shown in structures (**14**) or (**15**), or from 3F + NO via FNO and F_2NO according to structures (**17**) → (**18**) → (**16**).

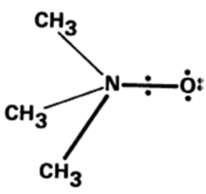


(17) (18) (16)

"Increased-valence" structures of type (**16**) have satisfactory arrangements of formal charges. The electronic structure of the N-O component is similar to that of free NO, and each N-F bond has a bond-number or bond-order which is less than unity. Therefore, resonance between the three equivalent structures of type (**16**) accounts for the nature of the observed bond-lengths.

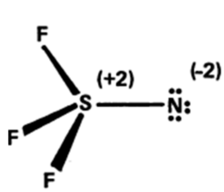
We may contrast the bonding for F_3NO with that for $(CH_3)_3NO$. The C-N and N-O lengths[10] of $(CH_3)_3NO$ are 1.495 Å and 1.404 Å, which are respectively only slightly longer and shorter than estimates of 1.47 Å and 1.44 Å for C-N and N-O single bonds. Therefore, with respect to these bond-lengths, the Lewis structure (**19**) gives a fairly satisfactory representation of the electronic structure of $(CH_3)_3NO$. A small amount of oxygen π and $\bar{\pi}$ electron delocalization, to give "increased-valence" structures of type (**20**), could be responsible for the small C-N lengthenings and N-O shortening.





(19) (20)

For F_3SN, the standard Lewis structures are of types (**21**)-(**23**). These structures satisfy the Lewis-Langmuir octet rule, but each carries a formal charge of +2 on the sulphur atom.



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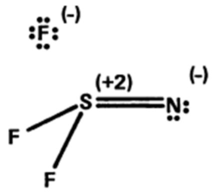
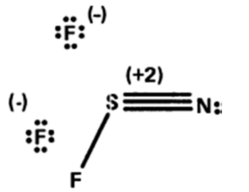


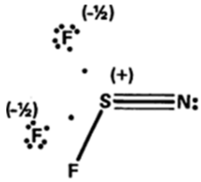
(22)



(23)

We may reduce the magnitudes of the formal charges by either

(a) delocalizing N^{2-} or F^{-} electrons into bonding or anti-bonding orbitals, to obtain “increased-valence” structures such as (**24**)-(**26**)



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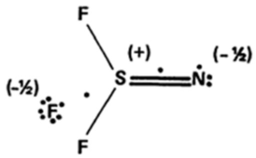

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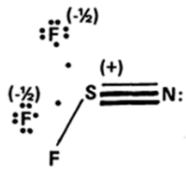
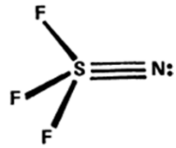


(26)

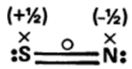


(27)

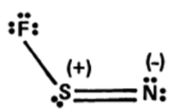
or

(b) delocalizing N^{2-}, N^{-} or F^{-} electrons into vacant d-orbitals on the sulphur atom, to afford the Lewis structure (**27**) with an expanded valence-shell for the sulphur atom.

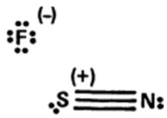
To help decide which set of delocalizations predominates, initially we shall give consideration to the bonding for FSN. For this molecule, the S-N and S-F bond-lengths[11] of 1.45 Å and 1.65 Å are respectively shorter than 1.50 Å for free SN (with the Pauling “3-electron bond” structure (**28**)),



(28)

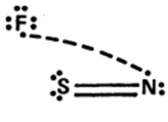


(29)

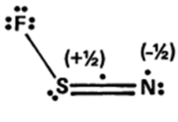


(30)

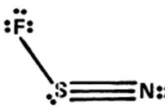
and longer than the S-F single-bond length of 1.54 Å. Resonance between the standard Lewis structures (**29**) and (**30**), do account for these observations. However, the “long-bond” structure (**31**),



(31)



(32)



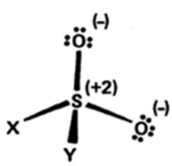
(33)

with zero formal charges on all atoms should also make an important contribution to the ground-state resonance. "Increased-valence" structure (**32**), which is obtained either by spin-pairing the odd-electron of SN with that of a fluorine atom, or by delocalizing a nitrogen $\overline{\pi}$-electron of structure (**29**) into a bonding S-N orbital, is equivalent to resonance between (**29**) and (**31**). Resonance between the increased-valence" structures (**30**), (**32**) and (**33**), with structure (**32**) predominating, accounts for the observed bond-lengths for FSN; it also must represent a rather lower energy arrangement for the electrons than does resonance between structures (**29**) and (**30**).

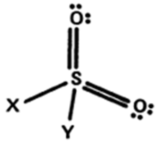
If we use the expanded valence-shell Lewis-structure (**33**) to represent the electronic structure of FSN, we cannot account for the observed lengthening of the S-F bond relative to that of a single bond. By contrast, the S-F bond-length of 1.55 Å for F_3SN is essentially that of a single bond, and the expanded valence-shell Lewis structure (**27**) is in accord with this observation. This structure for F_3SN is also able to account for the observed shortening of the S-N bond (1.42 Å) relative to those of free SN (1.50 Å) and FSN (1.45 Å), whose electronic structures are to be described by (**28**) and resonance between (**32**) and (**33**) respectively.

17-4 Sulphones $XYSO_2$

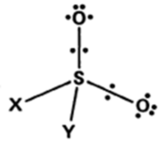
For SO_4^{2-}, which is isoelectronic with F_3SN, the Lewis octet, expanded valence-shell and "increased-valence" (with no valence-shell expansion) structures are of types (**4**)-(**6**). Similar valence-bond structures for the $XYSO_2$ type sulphones of Table 17-1, which also have 32 valence-shell electrons, are structures (**34**)-(**36**).



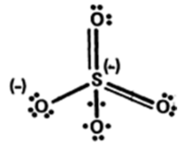
(34)



(35)



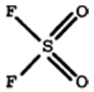
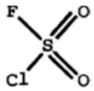
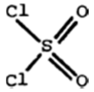
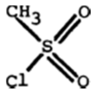
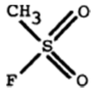
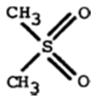
(36)



(37)

For the sulphones of Table 17-1, the S-X and S-Y bond-lengths are not longer than the estimates of 1.54, 2.01 and 1.82 Å (Sections 11-3, and 17-2) for standard

Table 17-1: Bond-lengths (Å) for some sulphones.

		r(SX)	*r*(SY)	*r*(SO)
	(a)	1.530	1.530	1.397
	(b)	1.530	1.530	1.405
	(c)	1.55	1.985	1.408 (ass.)
	(d)	2.011	2.011	1.404
	(e)	1.763	2.046	1.424
	(f)	1.759	1.561	1.410
	(g)	1.777	1.777	1.431

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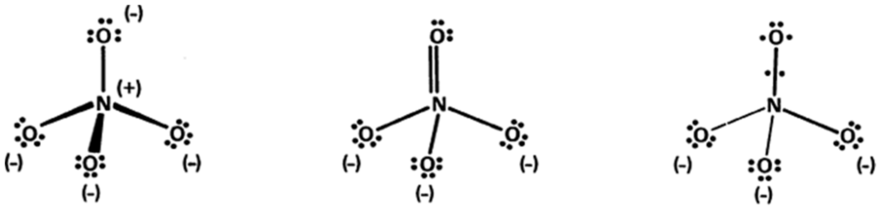
S-F, S-Cl and S-C single bonds, and the S-O bond-lengths are shorter than the 1.48 Å for the double bond of free SO. With respect to the S-O bond-lengths, each of the structures (**35**) and (**36**) alone predicts double-bond character. However, the bond-lengths reported in Table 17-1 suggest that the expanded valence-shell structures account better for the S-X and S-Y bond-lengths than do the "increased-valence" structures with no valence shell expansion. As is the case for F_3SN, the sulphur atom carries a formal charge of +2 in the Lewis octet structure (**34**). Presumably, expanded valence-shell structures of type (**5**) should be similarly preferred to structures of type (**6**) for SO_4^{2-}, whose S-O bond lengths of 1.48 Å [13] are much shorter than the single-bond length of 1.70 Å. It should be noted however, that for structure (**5**), some further "increased-valence" may be developed by delocalizing non-bonding π- or $\bar{\pi}$-electrons from the O^- into bonding S-O orbitals to afford the more-stable valence-bond structures of type (**37**). Because the sulphur atom of structure (**5**) is already neutral, these delocalizations are not expected to be appreciable but must occur to some extent (cf. $C_2O_4^{2-}$ of Section 13-2).

17-5 NO_4^{3-}, PO_4^{3-} and F_3PO

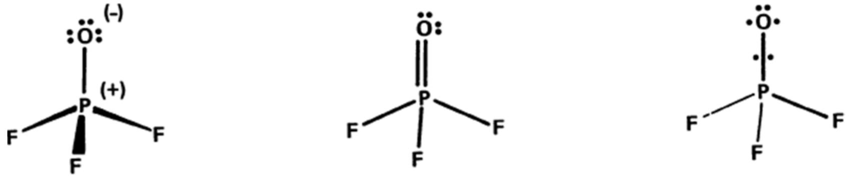
Because nitrogen 3d-orbitals do not participate in bonding as hybridization functions, "increased-valence" structure (**40**),



(38) (39) (40)

rather than the expanded valence-shell structure (**39**) is an appropriate type of valence-bond structure for the ground-state of NO_4^{3-}. The "increased-valence" structure (**40**) may be constructed either by delocalizing oxygen π- or $\bar{\pi}$-electrons of the standard Lewis structure (**38**) into bonding N-O orbitals, or by means of the reaction $NO^* + 3O^-$ with valence-bond structure (**63**) (Section 11-8) for NO*. Resonance between "increased-valence" structures of type (**40**) accounts for the observation that the N-O bond-lengths[14] of 1.39 Å for NO_4^{3-} are shorter than the estimate of 1.44 Å for an N-O single bond (cf. structure (**20**) for $(CH_3)_3NO$).

In the Lewis octet structures for PO_4^{3-} ((**38**) with P^+ replacing N^+), the phosphorus atom carries a formal charge of +1, and both expanded valence-shell and "increased-valence" structures that are similar to structures (**39**) and (**40**) may be constructed. F_3PO is isoelectronic with PO_4^{3-}, and the corresponding valence-bond structures are (**41**)-(**43**).

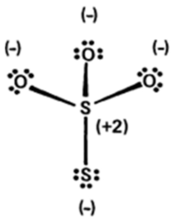


(41) (42) (43)

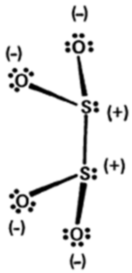
The P-F bond-lengths[15] of 1.523 Å for F_3PO are shorter than the 1.561 A[16] for PF_3 (with formal single-bonds), and this suggests that the expanded valence-shell structure is more appropriate than the "increased-valence" structure. Should this be the case, it is probable that the expanded valence-shell structure of type (**39**) (with P replacing N) is of greater significance than "increased-valence" structures of type (**40**) for PO_4^{3-}, whose P-O bond-lengths[17, 18] of 1.54 Å are longer than the 1.437 Å for F_3PO but much shorter than the estimate of 1.73 Å for a P-O single bond[18].

17-6 $S_2O_n^{2-}$ (n = 3, 4, 5, 6)

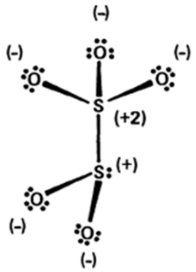
The thio anions $S_2O_n^{2-}$ (n = 3-6) provide a set of systems to contrast the alternative delocalization theories of Sections 17-1 to 17-5, namely those of delocalization of lone-pair electrons into either vacant sulphur 3d- orbitals or vacant bonding orbitals. (Such delocalizations generate electron-pair bonds and one-electron bonds, respectively.) For these anions, the standard Lewis octet structures are structures (**44**)-(**47**), each of which involves considerable formal charge separation.



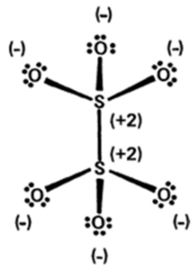
(44)



(45)

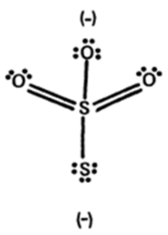


(46)



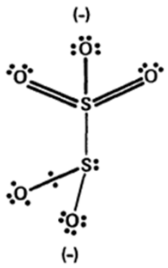
(47)

On the basis of the discussions in Sections 17-1 – 17-5, we suggest that the oxygen lone-pair delocalization into sulphur 3d-orbitals is appropriate when the sulphur atoms carry formal charges of +2 in the Lewis octet structure. But, when the sulphur atoms carry formal charges of +1, delocalization of oxygen lone-pair electrons into S-O bonding orbitals is of greater relevance. Using these delocalizations, we can generate valence-bond structures of types (**48**)-(**51**) from structures (**44**)-(**47**).

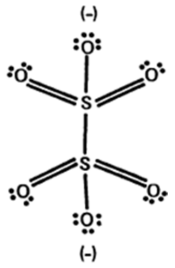


(48)

(49)



(50)



(51)

For each SO_3^- linkage of structures (**48**), (**50**) and (**51**), we have indicated delocalizations of two O^- electrons into sulphur 3d orbitals. A small amount of delocalization of O^- electrons into bonding S-O orbitals will also occur (cf. structure (**37**) for SO_4^{2-}).

The valence-bond structures (**48**)-(**51**) suggest that the S-S lengths should increase in the order $S_2O_3^{2-} < S_2O_6^{2-} < S_2O_5^{2-} < S_2O_4^{2-}$, and the measured lengths[19-22] of 1.97 Å, 2.08-2.16 Å, 2.17 Å and 2.39 Å show this to be the case. For $S_2O_3^{2-}$, the two $d_\pi - p_\pi$ bonds should be delocalized fairly evenly over the S-S and three S-O bonds, to give bond-numbers of 1.5 for each bond.

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Addendum Chapter 17

In Refs. 23 and 24, further consideration is given to valence-bond structures that involve expansion of the valence shell for second-row and higher-row elements - for example the use of sulphur 3d orbitals as valence orbitals in SF_6. See also Ref. 25 for another type of SF_6 increased-valence structures that does not involve expansion of the sulphur valence shell. In Ref. 26, increased-valence structures are presented for OSSSO (see also Ref. 27) and O_2SSSO_2 with two tetrahedral sulphur atoms.

For phosphorus, sulphur and chlorine (and other main-group element) atoms, “it has been shown by many researchers that d orbitals do not act primarily as valence-shell orbitals but instead as polarization functions or as acceptor orbitals for back-donation from the ligands, thus disproving the expanded octet model”[28], i.e. for these atoms, one should speak of “d functions, not d orbitals”[29].

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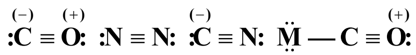
Chapter 18 Transition Metal Complexes with CO, N_2, NO and O_2 Ligands

The diatomic molecules and ions, CO, N_2, CN^-, NO and O_2, can bond to transition metals. Isoelectronic CO, N_2 and CN^-, with ten valence-shell electrons, have triple bonds and no unpaired electrons in their Lewis octet structures (**1**)-(**3**).



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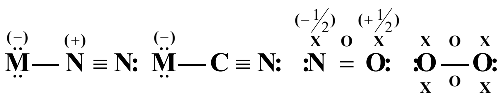

(5) (6) (7) (8)

Each of these structures can use a lone-pair of electrons to coordinate with a transition metal, as in structures (**4**)-(**6**), thereby functioning initially as Lewis bases. The ground-states of NO and O_2, with 11 and 12 valence-shell electrons respectively, have one and two unpaired electrons. Their valence-bond structures (**7**) and (**8**) involve one or two Pauling "3-electron bonds" as well as lone-pairs of electrons. The possibility exists that these molecules may react either as Lewis bases or as free radicals. For NO, examples of both Lewis base and free radical behaviour are known, but ground-state O_2 seems to behave exclusively as a free radical. We shall now describe valence-bond structures for a few transition metal complexes that involve some of these ligands.

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Lecture Notes in Chemistry 90, DOI 10.1007/978-3-319-16676-6_18

18-1 Carbonyl Complexes

In the standard Lewis structures (**4**), (**5**) and (**6**), we have used a lone-pair of carbon or nitrogen electrons to form a σ-single bond with the metal M.

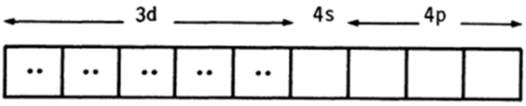
Carbonyl, dinitrogen and cyanide complexes of transition metals are generally not stable unless the metal has lone-pair electrons occupying atomic orbitals that overlap with ligand π orbitals. In structures (**4**)-(**6**), we have indicated two sets of lone-pair electrons. If we assume that these electrons occupy metal d_{xz} and d_{yz} atomic orbitals, then they can overlap with the atomic orbitals that form the π_x and π_y bonds of the ligands. For a M-CO linkage, we show the overlap of these orbitals in Fig. 2-4. These are the types of π-orbital overlaps that pertain for trigonal bipyramidal and octahedral carbonyl compounds, such as $Fe(CO)_5$ and $Cr(CO)_6$. For tetrahedral compounds such as $Ni(CO)_4$, the metal-carbon π overlaps are similar to those described in Section 5-5 with the d_{z^2} and $d_{x^2-y^2}$ metal orbitals forming strong σ-bonds, and the d_{xy}, d_{yz} and d_{xz} orbitals forming weak π-bonds.

Table 18-1: Data for some carbonyl compounds. [a]Experimental estimates.

	ν_{CO} /cm^{-1}	n_{CO}	n_{MC}
CO	2150	3.0	
$Ni(CO)_4$	2056	2.5 (2.64)[a]	1.5 (1.33)[a]
$Co(CO)_4^-$	1886	2.375 (2.14)[a]	1.625 (1.89)[a]
$Fe(CO)_4^{2-}$	1786	2.25 (1.85)[a]	1.75 (2.16)[a]

The tetracarbonyls $Ni(CO)_4$, $Co(CO)_4^-$ and $Fe(CO)_4^{2-}$ are isoelectronic and tetrahedral in shape. In Table 18-1, we have reported C-O stretching frequencies $\nu_{CO}(cm^{-1})$, and calculated and (in parentheses) experimental[1] C-O and M-C bond orders and bond-numbers n_{CO} and n_{MC}. The C-O stretching frequencies show that the strengths of the C-O bonds decrease in the order $CO > Ni(CO)_4 > Co(CO)_4^- > Fe(CO)_4^{2-}$.

The electronic configurations of isoelectronic Ni, Co^- and Fe^{2-} are $(3d)^8\,(4s)^2$, from which we can obtain the low-spin valence-state configuration of (**9**)



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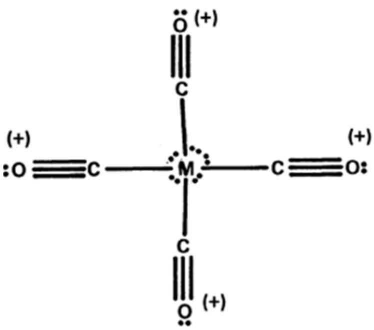

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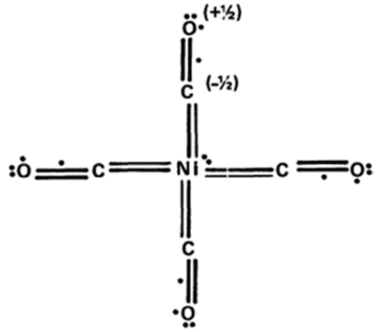
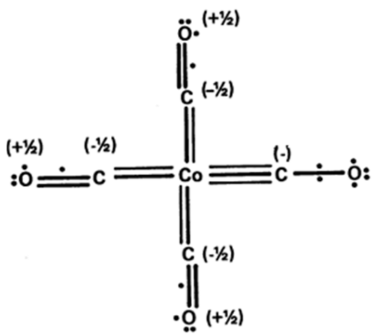


(11)

with four vacant orbitals. These orbitals may be sp^3 hybridized, and used by the four C-O ligands to form four coordinate bonds, as in structure (**10**). The metal then acquires formal negative charges of -4 for Ni, -5 for Co and -6 for Fe.

To remove formal charge from the metal and the oxygen atoms, we delocalize metal electrons into antibonding C-O orbitals. For Ni^{4-} and Co^{5-}, we can delocalize four and five 3d electrons, to generate "increased-valence" structures (**11**) and (**12**).



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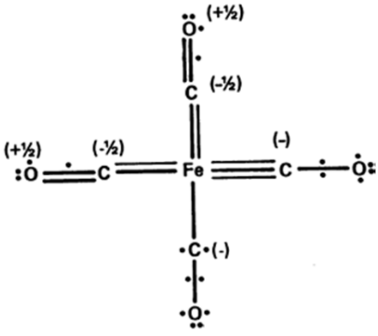
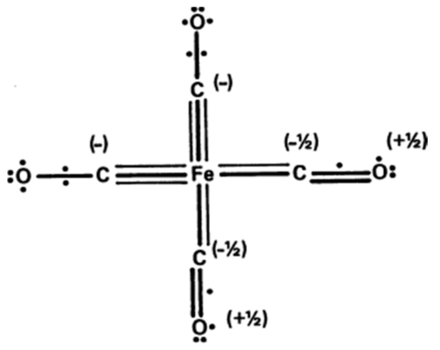


(13)

In each of these structures, we have obtained an uncharged metal atom, and some (fractional) double bonding for the Ni-C and Co-C bonds. To generate neutral iron in $Fe(CO)_4^{2-}$, we need to delocalize six electrons into antibonding C-O orbitals. Because Fe^{6-} in structure (**10**) has only five lone-pairs of valence electrons, we must generate "increased-valence" structure (**13**). The CO^- ligand of this structure possesses two Pauling "3-electron bonds" with uncompensated electron spins. Therefore because it can imply paramagnetism, structure (**13**) is unsatisfactory. To obtain a diamagnetic structure, and a neutral iron atom, we shall assume here that an iron 3p electron can participate in M-CO bonding. If we delocalize a 3p electron as well as five 3d electrons, we generate "increased-valence" structure (**14**). (To obtain a consistent valence-bond treatment of M-CO bonding for tetra, penta and hexacarbonyls, it seems necessary to include 3p electrons as bonding electrons. The hypothesis invoked here is that the transition metal carries zero formal charge in the valence-bond structures.)



(14)

Because each $\mathrm{M} — \mathbf{C} \cdot \dot{\mathrm{O}}$ "increased-valence" bonding unit is equivalent to the resonance of $\mathrm{M} — \mathrm{C} \quad \ddot{\mathrm{O}} \leftrightarrow \dot{\mathrm{M}} \quad \ddot{\mathrm{C}} \quad \dot{\mathrm{O}}$, the M-C and C-O bond indices will both equal $\frac{1}{2}$ if we assume here that the two structures contribute equally to the resonance. The calculated bond orders of Table 18-1 follow the experimental trends in bond properties. An empirical relationship that has been established[2] between ν_{CO} and n_{CO}, namely $\nu_{CO} = 413\, n_{CO} + 904$, gives CO bond-orders of 2.79, 2.38 and 2.14 for the three tetracarbonyls of Table 18-1.

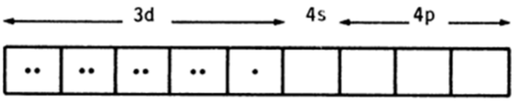
18-2 Dinitrogen Complexes

Numerous complexes of N_2 with transition metals have been prepared[3], and the geometries for many of them are known. Here, we shall describe the metal- N_2 bonding for $CoH(N_2)(PPh_3)_3$ and $[\{Ru(NH_3)_5\}_2N_2]^{4+}$.

18-2(a) $CoH(N_2)(PPh_3)_3$

For $CoH(N_2)(PPh_3)_3$, the $Co-N_2$ linkage has been found to be linear[4], with Co-N and N-N lengths of 1.802 Å and 1.126 Å. We may compare these lengths with the estimate of 1.96 Å for a Co-N single bond[4], and the 1.098 Å for the triple bond of free N_2.

From the $(3d)^7(4s)^2$ ground-state configuration of Co, we may obtain a $(3d)^9$ valence-electron configuration (**14**)



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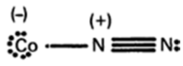
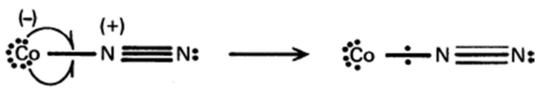


(15)

with one unpaired electron. This electron may be used for σ-bonding with a hydrogen atom. The four vacant orbitals of configuration (**14**) may be used for σ-bonding by N_2 and the three PPh_3 ligands. In structure (**15**), we show the Co-N σ-bonding for the $Co-N_2$ linkage.

To form five σ-bonds, the cobalt may use hybrid orbitals that are constructed from its $3d_{z^2}$, 4s and three 4p orbitals. The cobalt is then dsp^3 hybridized. If we assume that the cobalt and two nitrogen atoms lie along the z-axis, then the cobalt lone-pair electrons of structure (**15**) occupy $3d_{xy}$, $3d_{yz}$, $3d_{xz}$ and $3d_{x^2-y^2}$ orbitals. The $3d_{yz}$ and $3d_{xz}$ orbitals overlap with the π_y and π_z bonds of the N_2 ligand.

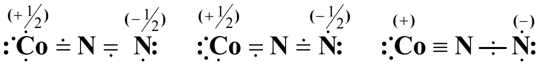
In structure (**15**), the formal charge for the cobalt atom and the adjacent nitrogen atom are negative and positive respectively, relative to their values prior to coordination. We may reduce their magnitudes by delocalizing one electron from each of the d_{yz} and d_{zx} orbitals into bonding Co-N π_y and π_z orbitals, to obtain "increased-valence" structure (**16**).



(15) (16)

In structure (**16**), the N-N π-bonds have bond-numbers less than unity and therefore the N-N bond should be longer than that of free N_2. The Co-N bond of this structure has double-bond character, and therefore this bond would be expected to be shorter than a single bond. The bond lengths reported above confirm these expectations.

We note that the $Co-N_2$ bonding is similar to that which we have described for N_2O in Section 13-1. Other "increased-valence" structures such as (**17**), (**18**) and (**19**) may also be constructed. Elsewhere[5], we have shown that structure (**16**) should be the most important of the four types of structures, but all will participate in resonance to some extent.



(**17**) (**18**) (**19**)

18-2(b) $[\{Ru(NH_3)_5\}_2N_2]^{4+}$

N_2 can bond simultaneously to two Ru(II) ions, and this occurs in the cation $[\{\mathbf{Ru(NH_3)_5}\}_2\mathbf{N_2}]^{4+}$. The Ru^{2+} configuration is $(4d)^6$, and the σ-bonding with the N_2 is shown in the Lewis structure (**20**).

(20) (21)

The formal charges displayed for the ruthenium ions in this structure are those that are relative to Ru^{2+}. By delocalizing $4d_{xz}$ and $4d_{yz}$ electrons of Ru^{2+} of structure (**20**) into vacant bonding Ru-N π-orbitals, we generate the "increased-valence" structure (**21**). For each set of π-electrons, there is a 6-electron 4-centre bonding unit.

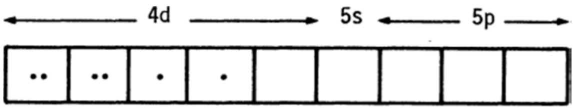
Reported Ru-N and N-N bond lengths[6] are 1.928 Å and 1.124 Å. An estimate of the length of an Ru-N single bond[7] is 2.125 Å, and structure (**21**) indicates clearly that the Ru-N bonds of $[\{Ru(NH_3)_5\}_2N_2]^{4+}$ are shorter than single bonds. The N-N length is longer than the triple bond of free N_2, and structure (**21**) with fractional N-N π-bonds shows why this should be so.

Numerous other binuclear dinitrogen complexes have been characterized[3], with N-N bond-lengths that are also longer than the 1.098 Å for N_2. "Increased-valence" structures that are similar to structure (**21**) are appropriate for each of these systems, and they account for the observation that the N-N and M-N bond lengths are respectively longer than triple bonds and shorter than single bonds.

18-3 Transition Metal Nitrosyl Compounds

In the introduction to this chapter we have indicated that NO may react with transition metals either as a free radical, by using its unpaired electron, or as a Lewis base by using the nitrogen lone-pair of electrons. To give consideration to these two types of behaviour, we shall examine the bonding for the Ru-NO linkages of the diamagnetic complex $[RuCl(PPh_3)_2(NO)_2]^+$, which we shall initially express in terms of its components as $Ru^{2+} + Cl^- + 2\,PPh_3 + 2NO$. The bond-angles for the two Ru-NO linkages are[8] 178° and 138°, and therefore essentially linear and angular linkages are present in this complex.

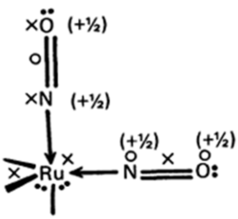
The valence-shell electronic configuration of Ru^{2+} is $(4d)^6$ of configuration (**22**).



(22)

To form a diamagnetic complex, it is necessary for this configuration to have two unpaired electrons available for spin-pairing with the unpaired electrons of the two NO ligands. Therefore, we have represented the $(4d)^6$ configuration of configuration (**22**) with two unpaired electrons, with a t_{2g} orbital and an e_g orbital singly-occupied. The t_{2g} orbital can overlap with an antibonding π^*_{NO} orbital of NO.

In configuration (**22**), there are five vacant orbitals that may be dsp^3 hybridized, and used for σ-coordination with five ligands. If this is done, we obtain the valence-bond structure (**23**)



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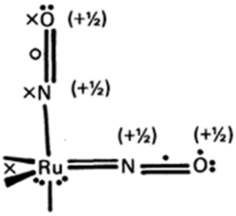

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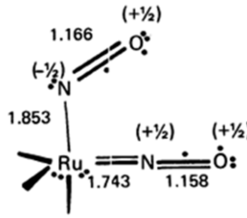
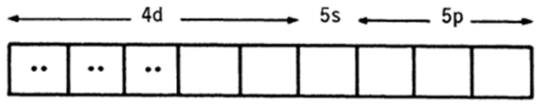


(25)

with four unpaired electrons. Because the singly-occupied t_{2g} orbital and a π^*_{NO} orbital can overlap, we may spin-pair two electrons to obtain the "increased-valence" structure (**24**). This structure has two unpaired electrons that occupy non-overlapping e_g and π^*_{NO} orbitals, and the lowest-energy arrangement for these electrons occurs when they have parallel spins. Thus, if both Ru-NO linkages are linear, the complex would have a paramagnetic ground state.

To obtain diamagnetism, it is necessary to assume that one of the NO ligands does not coordinate to the Ru^{2+} as a Lewis base, and that the π^*_{NO} unpaired electron of this ligand spin-pairs with the e_g unpaired electron of structure (**22**). This e_g orbital can hybridize with the 5s and 5p orbitals to form five dsp^3 hybrid orbitals. The spin-pairing can only provide a Ru-N bonding interaction if this linkage is angular. The resulting valence-bond structure, together with the experimental bond-lengths[8], for the complex is (**25**), with one linear and one angular Ru-NO linkage. This valence-bond structure makes immediately clear why the observed N-O lengths[8] for the complex are similar to those of free NO (1.15 Å) with valence-bond structure (**7**), and why the Ru-N bond of the linear Ru-NO linkage is shorter than is that for the angular linkage.

It is often considered[9] that NO^+ and NO^-, with Lewis-type valence-bond structures (**26**) and (**27**)



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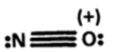

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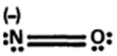

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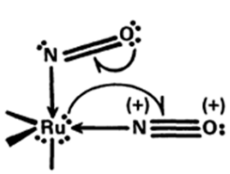

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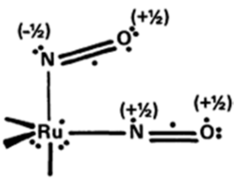


(30)

are the formal ligands for linear and angular M-NO linkages. If this point of view is adopted, then the valence-bond structure (**29**) is obtained for the $[RuCl(PPh_3)_2(NO)_2]^+$ complex, in which both NO^+ and NO^- have coordinated to the low-spin Ru^{2+} with the $(4d)^6$ configuration of (**28**). It is now possible to generate "increased-valence" structure (**25**) from the Lewis (**29**) by delocalizing (i) a non-bonding t_{2g} electron from the ruthenium into a vacant π^*_{NO} orbital of the NO^+, thereby reducing the magnitudes of the formal charges, and (ii) a non-bonding $\overline{\pi}_O$ electron of the coordinated NO^- into the adjacent NO bond-region. These delocalizations generate structure (**30**), from which increased-valence structure (**25**) is obtained when the remaining t_{2g} and π^*_{NO} odd-electrons are spin-paired. However, it seems easier to generate structure (**25**) by assuming that free NO radicals rather than NO^+ and NO^- are the valence-states for the ligands.

Further examples of "increased-valence" descriptions for transition-metal nitrosyls are provided in Ref. 10.

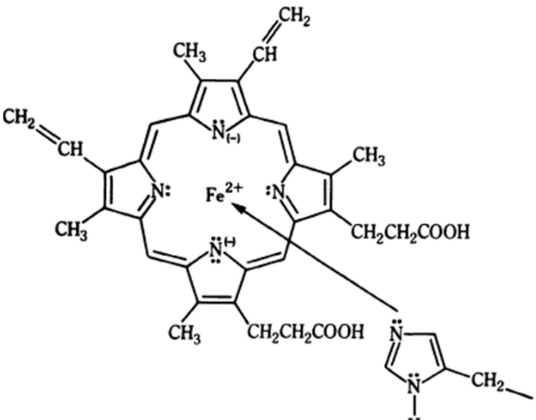
18-4 Dioxygenyl Adducts

Many transition metal complexes form adducts with molecular oxygen. Those that combine reversibly with O_2 are designated as oxygen carriers; adducts in which O_2 is absorbed irreversibly are also known. Here, we shall provide "increased-valence" descriptions for some reversible Fe(II) and Co(II) dioxygenyl adducts, thereby contrasting different formulations for the oxidation state of the metal ion that have been proposed for these types of complexes.

18-4(a) Oxyhemoglobin

Hemoglobin (Hb) transports O_2 from the lungs to the tissues of the body. At high pressures in the lungs, O_2 combines with the iron atoms of hemoglobin, and is released into the body tissues at low pressures.

Hemoglobin has a molecular weight of ~64500 and contains four (formally Fe(II)) iron atoms. Each of these atoms is coordinated to four nitrogen atoms of porphyrin, and to the nitrogen atom of a proximal histidine group. This bonding is shown in structure (**31**),



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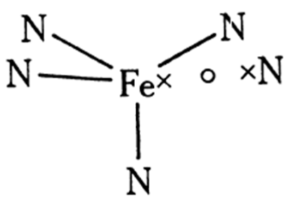

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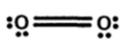
and the iron has been estimated[11] to lie 0.83 Å below the plane of the four porphyrin nitrogen atoms.

Each of the Fe(II) ions of hemoglobin has four unpaired electrons with parallel spins in the ground-state, and therefore the molecule is paramagnetic[12]. The six electrons of an Fe^{2+} ion have the orbital occupations displayed in Fig. 5-1 for high-spin S = 2 spin-states. Because five ligand nitrogen atoms of structure (**31**) can coordinate to the high-spin Fe^{2+}, and there are only four vacant orbitals (4s and 4p) for this ion, hemoglobin is an example of a *hypoligated* complex (Section 5-1). The bonding of the four nitrogen atoms of porphyrin to the iron may be described by utilizing three electron-pair bonds and a Pauling "3-electron bond". The remaining vacant orbital of Fe^{2+} may be used to form an Fe-N single bond between Fe^{2+} and the nitrogen atom of the proximal histidine of structure (**31**). Resonance between the four valence-bond structures of type (**32**) therefore provides a valence-bond description of the Fe-N bonding for each heme group of hemoglobin.

When four oxygen molecules bind to the four iron atoms of hemoglobin, oxyhemoglobin is formed. Magnetic susceptibility measurements[13, 14] indicate that each $Fe(II)O_2$ linkage of oxyhemoglobin is diamagnetic at room temperature, i.e. no unpaired electron spins are present. (It may be noted that magnetic susceptibility measurements[15] through the temperature range of 25-250 K indicate that although the ground-state is an S = 0 spin state, antiferromagnetic rather than diamagnetic behaviour occurs as the temperature is raised above 50 K. However, the experimental basis for this work was questioned[14].) Here we shall describe some bonding theories for the S = 0 spin ground-state of each $Fe(II)O_2$ linkage. Similar theories are also appropriate for oxymyoglobin with one $Fe(II)O_2$ linkage, and the "picket fence" Fe(II) oxygen carriers.

To account for the diamagnetism of oxyhemoglobin, in 1936 Pauling and Coryell[13] suggested that an S = 0 spin excited state with valence-bond structure (**33**)



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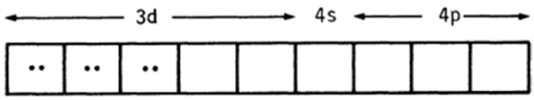

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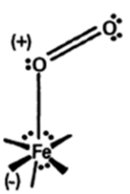

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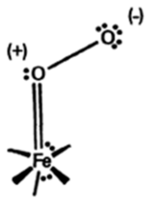

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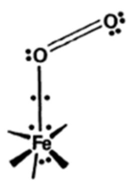

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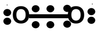
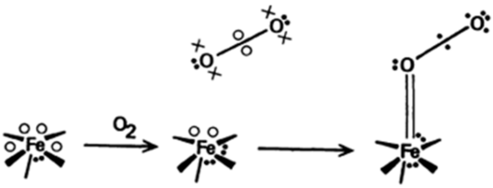
(38)

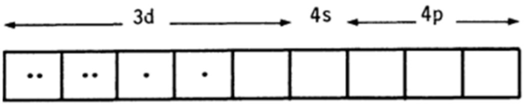
for O_2 could coordinate with the low-spin ($S = 0$) configuration (**34**) for Fe^{2+}. In (**34**), the six vacant orbitals may be d^2sp^3 hybridized. Five of these orbitals may be used for coordination with the five nitrogen atoms of structure (**31**), and the sixth orbital is available for coordination with the O_2. For oxyhemoglobin, the iron atoms lie in the plane of the nitrogen atoms of the porphyrin ligands[11]. By coordinating the O_2 of structure (**33**) to the Fe^{2+} of the configuration (**34**), Pauling and Coryell[13] obtained the standard Lewis structure (**35**) for each $Fe-O_2$ linkage of oxyhemoglobin. This valence-bond structure can then participate in resonance with the standard Lewis structure (**36**). By comparison of these structures with their Pauling "3-electron bond" ground-state structure for O_2 (cf. Fig. 2-1), Pauling and Coryell concluded that a "profound change in the electronic structure of O_2 occurs when it bonds to hemoglobin". However, if we use structures (**35**) and (**36**) to generate "increased-valence" structures (**37**) and (**38**), it is possible to show that this need not be the case.

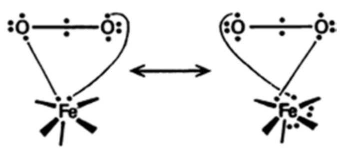
By delocalizing lone-pair electrons from the Fe^- and O^- of structures (**35**) and (**36**) into vacant bonding Fe-O or O-O orbitals, we reduce the magnitude of the atomic formal charges, and obtain "increased-valence" structures (**37**) and (**38**)[16-20].

In structures (**37**) and (**38**), the O_2 excited and ground-state structures (**33**) and (**8**) are respectively bonded to the iron. We might therefore expect structure (**38**) to be more stable than structure (**37**). If this is so, then we may give the following description of the reaction between O_2 and an iron atom of hemoglobin. As the ground-state of O_2 approaches the high-spin Fe(II), the latter is promoted to the valence-state configuration of (**39**), which is an intermediate-spin state (S = 1) with two unpaired electrons. These two electrons spin-pair with the two unpaired electrons of O_2 to generate an S = 0 spin Fe(II)O_2 linkage with the "increased-valence" structure (**38**). Thus, we can write.



(38)





(39) (40) (41)

In 1960, McClure[21] had suggested that this promotion of Fe^{2+} to the intermediate-spin state of configuration (**39**) occurs when it reacts with O_2, and we have given here the valence-bond structure that corresponds to this description. The results of some Mössbauer measurements[22] indicate that the promotion energy is small – ~ 250 cm^{-1}.

The $\mathrm{Fe(II)}\,(S=1)+\mathrm{O_2}\,(S=1)$ spin theory for the bonding of O_2 to hemoglobin has been discussed on a number of occasions[16-21,23-26]. Generalized valence-bond[27] and molecular orbital calculations[28] provide further support for this hypothesis, although it has been questioned[29].

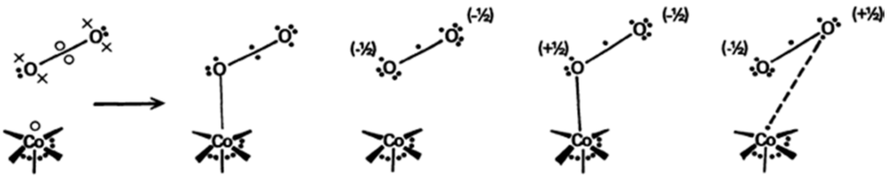
Although the possibility also exists that the O_2 may bond symmetrically to the Fe(II), as occurs in "increased-valence" structures (**40**) and (**41**), theoretical and experimental evidence[27,30] favours the non-symmetrical conformation displayed in valence-bond structures (**35**)-(**38**).

The O-O stretching frequency of 1107 cm^{-1} for oxyhemoglobin[31] was often cited[32-34] as evidence that the superoxide anion O_2^- is bonded to low-spin $(S=\frac{1}{2})\mathrm{Fe}^{3+}$, with spin-pairing of the unpaired-electrons of these two species to form S = 0 spin $\mathrm{Fe(III)\,O_2^-}$ linkages. For O_2^-, as in KO_2, the O-O stretching frequency is 1145 cm^{-1}, whereas that for free ground-state O_2 is 1556 cm^{-1} [32]. However, when the O_2 ground-state is bonded to Fe(II), as in structure (**38**), the electronegativity of one oxygen atom must be altered relative to that of the other, and an unequal sharing of the four O-O bonding electrons may therefore occur. The O-O bond-order for structure (**38**) can therefore be reduced below the value of 2 for free O_2, thereby leading to a reduction of the O-O stretching frequency for oxyhemoglobin[18]. Molecular orbital calculations[28] give an O-O bond-order of 1.6 when the O_2 ground-state is bonded to the Fe(II).

"Increased-valence" descriptions of the bonding for the Fe-CO and Fe-NO linkages for the CO and NO derivatives of hemoglobin are described in Ref. 17.

18-4(b) Cobalt-Molecular Oxygen Carriers

Molecular oxygen can form both 1:1 and 2:1 adducts ($\mathrm{Co-O_2}$ and $\mathrm{Co-O_2-Co}$) with different Co(II) complexes. For the 1:1 adducts, the O-O stretching frequencies are similar to those[32-34] of O_2^- and an unpaired electron is located mainly on the two oxygen atoms. On the basis of these observations, the adducts have been formulated[32-34] as $\mathrm{Co(III)O_2^-}$, with the O_2^- forming a coordinate bond to low-spin Co(III), which has a $(3d)^6$ configuration. Alternatively, we may formulate[16-20] the electronic structure as $\mathrm{Co(II)O_2}$, for which the O_2 valence-bond structure (**8**) has spin-paired one of its two unpaired electrons with the unpaired electron of low-spin Co(II) $(3d)^7$. Thus, we may generate the "increased-valence" structure (**42**) by means of this reaction.

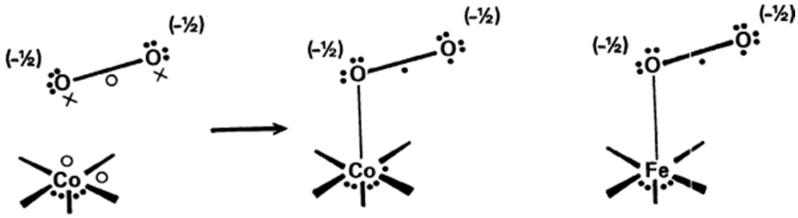


(42) (43) (44) (45)

The $Co(II)O_2$ structure (**42**) accounts simply[18] for the observations discussed above. The O_2 retains one unpaired-electron, and because the oxygen atom bonded to the cobalt must have a different electronegativity from that of the terminal oxygen atom, the four O_2 bonding electrons will not be shared equally by the two oxygen atoms. This reduction in the extent of covalent bonding for the O_2 of structure (**42**) should be chiefly responsible for the decrease in O-O stretching frequency that is observed when O_2 bonds to Co(II).

We shall now compare the $Co(II)O_2$ and the $Co(III)O_2^-$ structures. The valence-bond structures for low-spin Co(III) and O_2^- are shown in (**43**). On coordinating the O_2^- with Co(III), we obtain the $Co(III)O_2^-$ valence-bond structure (**44**). We may also form the "long-bond" $Co(III)O_2^-$ structure (**45**), which for non-symmetrical coordination, should be less stable than structure (**44**). We now note that the $\mathbf{Co — O \cdot \dot{O}}$ bonding unit summarizes resonance between $\mathbf{Co — O\ \ddot{O}}$ and $\mathrm{Co\ \ \ddot{O}\ \ \dot{O}}$. Therefore, the $Co(II)O_2$ structure (**42**) is equivalent to resonance between structures (**44**) and (**45**), and each of these $Co(III)O_2^-$ structures is now a special form of the $Co(II)O_2$ structure. The $Co(II)O_2$ structure must be more stable than either of the $Co(III)O_2^-$ structures.

We may construct another $Co(III)O_2^-$ structure, namely the "increased-valence" structure (**47**).



(46) (47) (48)

To do this, we spin-pair the unpaired electron of O_2^- with one of the two unpaired electrons of the Co(III) configuration of structure (**46**). Because structure (**47**) retains an unpaired electron on the cobalt, it cannot represent the ground-state for any of the adducts which have so far been studied. However, it must participate in resonance with the $Co(II)O_2$ structure (**42**), with the latter making the major contribution to the bonding. Similarly, for oxyhemoglobin (HbO_2), the $Fe(III)O_2^-$ structure (**48**) will participate in resonance with the $Fe(II)O_2$ structure (**38**), but, because the latter structure has three extra bonding electrons, it should be more stable than structure (**48**).

The $S = \frac{1}{2}$ and $S = 0$ spin wave-functions for the $Co(II)O_2$ and $Fe(II)O_2$ linkages of "increased-valence" structures (**42**) and (**38**), with three and four singly-occupied orbitals, are described in Section 15-2 and in Refs. 20 and 16.

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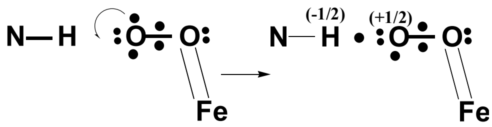
Addendum Chapter 18

See Ref. 35 for: (a) further consideration of the Pauling-Coryell, McClure and Weiss models of Fe-O_2 bonding in oxyhemoglobin, and (b) Refs. 19, 24 and 62 therein for reviews of computational studies of heme-O_2 and heme-NO bonding.

In the Supplementary Material for Ref. 35, the valence-bond formulation below is provided for the interaction of the terminal oxygen atom of a heme Fe-O_2 substituent with a hydrogen atom of the distal histidine.

When one of the p_y or p_z atomic orbitals on the terminal oxygen atom of the Fe^{II}-O_2 increased-valence structure (**38**) overlaps with the **N-H** hydrogen atomic orbital of the distal histidine, a (weak **H-O**) 6-electron 5-centre bonding unit is established, as in structure (**48**) → (**49**).



(**48**) (**49**)

The weak **NH • O** interaction can supplement the electrostatic interaction that arises in the absence of this type of bonding unit. The more negatively-charged is the terminal oxygen atom, the greater will be strength of the **NH • O** interaction. Distal histidine interactions on the O_2 binding to heme enlongate the Fe-O and O-O bonds by ~ 0.01-0.02 Å[36].

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Chapter 19 Some Electron-Excess σ Bonded Systems

Most of the "increased-valence" structures that we have discussed so far may be derived from Lewis structures by delocalizing lone-pair π and/or $\bar{\pi}$ electrons into vacant bonding or antibonding orbitals. The atomic orbital overlaps that are appropriate for some of these delocalizations are shown in Figs. 1-5 and 2-4. We shall now consider a few systems whose "increased-valence" structures can be constructed by delocalizing one or more lone-pair σ electrons of a Lewis structure into bonding or antibonding σ orbitals. Some other examples will also be discussed in Chapter 20, where the theory will be presented in a slightly different form. However, the principles for both chapters are the same.

19-1 Trihalide Anions and some Related Molecules

Each of the trihalide anions I_3^-, Br_3^-, Cl_3^- and ICl_3^-, and XeF_2, has 22 valence-shell electrons. XeF_2 is a symmetrical linear molecule[1], and a similar geometry has been reported for each of I_3^-, Br_3^- and ICl_2^- [2]. Non-symmetrical geometries for some of these trihalide ions are also known[2], but we shall not concern ourselves with them here. Excluding the possibility of d-orbital participation, we shall now describe standard Lewis, "increased-valence" and Linnett (Section 2-2) non-paired spatial orbital bonding schemes for these systems, using I_3^- and XeF_2 as representative examples. Such molecules are often designated as geometrical "hypervalent" molecules, for which the number of ligands bonded to a central atom exceeds the covalence of the central atom in the standard Lewis octet structures. Musher[3] has discussed various examples of hypervalent molecules. We point out here that geometric hypervalence for an atom **A** may arise whenever valence-bond resonance of the type

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Lecture Notes in Chemistry 90, DOI 10.1007/978-3-319-16676-6_19

$$\ddot{\mathbf{Y}}\ \mathbf{A}—\mathbf{B} \longleftrightarrow \mathbf{Y}—\mathbf{A}\ \ddot{\mathbf{B}}$$

can occur for four σ-electrons. Therefore, the bonding schemes for this chapter do not differ from those of the previous chapters, except in so far as we shall be dealing only with σ-bonding. It is well-known that geometrical hypervalence is an extremely widespread phenomenon.

The delocalized molecular orbital theory for hypervalent molecules involves 3-centre molecular orbitals, and we have given an account of it in Section 2-3(a), for the simplest hypervalent system H_3^-. This molecular orbital theory was first proposed in 1951 by Pimentel[4], and Hach and Rundle[5], and has been used subsequently by many workers[2, 6–9] to describe 4-electron 3-centre σ-bonding. Of course, it is also appropriate for π bonding, as we have indicated in earlier chapters.

For linear, symmetrical I_3^- the equivalent standard Lewis structures are structures (**1**) and (**2**),

$$\underset{(1)}{\overset{(-)}{:\ddot{\underset{..}{\mathbf{I}}}:}\ \ \mathbf{I}—\mathbf{I}} \leftrightarrow \underset{(2)}{\mathbf{I}—\mathbf{I}\ \ \overset{(-)}{:\ddot{\underset{..}{\mathbf{I}}}:}} \qquad \underset{(3)}{\overset{(-)}{:\ddot{\underset{..}{\mathbf{F}}}:}\ \ \overset{(+)}{\mathbf{Xe}}—\mathbf{F}} \leftrightarrow \underset{(4)}{\mathbf{F}—\overset{(+)}{\mathbf{Xe}}\ \ \overset{(-)}{:\ddot{\underset{..}{\mathbf{F}}}:}}$$

each of which has an I_2 and an I^- component. Similarly, for XeF_2, the corresponding $XeF^+ + F^-$ structures are the Lewis structures (**3**) and (**4**). For each of the structures (**1**)-(**4**), there is an octet of valence-shell electrons arranged around the atomic kernels. The standard Lewis descriptions of I_3^- and XeF_2 therefore consist of resonance between structures (**1**) and (**2**), and between structures (**3**) and (**4**). (To simplify the valence-bond structures in this chapter we shall often omit some of their non-bonding electrons.)

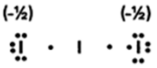
To form the I-I and Xe-F bonds in these structures, the simplest descriptions use the overlap of the 5pσ orbitals on the iodine atoms, and the overlap of the xenon 5pσ orbital with the 2pσ orbital of the fluorine. This type of σ-orbital overlap for 3-centre bonding is displayed in Fig. 2-4.

By delocalizing an electron from each of I^- and F^- either into vacant bonding I-I and Xe-F orbitals, or into vacant antibonding I-I and Xe-F orbitals, we may obtain the "increased-valence" structures (**5**) and (**6**).

$$\underset{(5)}{\overset{(-\frac{1}{2})}{:\ddot{\underset{..}{\mathbf{I}}}\cdot}\ \cdot\ \overset{(-\frac{1}{2})}{\mathbf{I}}—\mathbf{I} \leftrightarrow \mathbf{I}—\overset{(-\frac{1}{2})}{\mathbf{I}}\ \cdot\ \overset{(-\frac{1}{2})}{\cdot\ddot{\underset{..}{\mathbf{I}}}:}} \qquad \underset{(6)}{\overset{(-\frac{1}{2})}{:\ddot{\underset{..}{\mathbf{F}}}\cdot}\ \cdot\ \overset{(+\frac{1}{2})}{\mathbf{Xe}}—\mathbf{F} \leftrightarrow \mathbf{F}—\overset{(+\frac{1}{2})}{\mathbf{Xe}}\ \cdot\ \overset{(-\frac{1}{2})}{\cdot\ddot{\underset{..}{\mathbf{F}}}:}}$$

For XeF_2, Bilham and Linnett[10] have calculated that the resonance of (**3**) ↔ (**4**) has a higher energy than has the "long-bond" structure (**7**). Use of the "increased-valence" structures of (**6**) ensures that the three Lewis structures participate in resonance.


(7)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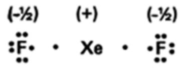
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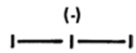

(10)

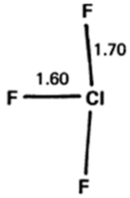
Possibly the most convenient valence-bond structures for I_3^- and XeF_2 are the Linnett non-paired spatial orbital structures (**8**) and (**9**), each of which two ("pseudo"[24]) one-electron σ bonds.

In Chapter 23, comparisons are made between the wave-functions for Lewis, "increased-valence" and non-paired spatial orbital structures, and the Rundle-Pimentel molecular orbital formulation.

For I_3^- and XeF_2, the bond lengths of 2.93 Å and 2.01 Å are longer than the single bond lengths[2, 1, 11] of 2.67 Å and 1.81 Å for I_2 and XeF_5^+. Each of the valence-bond representations above indicates the presence of long I-I or Xe-F bonds. If we include the $5d_{z^2}$ orbital on the central atom of either system as a hybridization function (cf. Sections 1-1 and 17-1), the valence-bond structures, such as two of type (**10**) for I_3^-, have single bonds between the central and both terminal atoms, and therefore alone they do not imply that the bonds should be long. Of course the two expanded valence-shell structures of type (**10**) participate in resonance with the increased-valence structures of (**5**), but they are not the primary valence-bond structures.

If only the 3s and 3p orbitals of the second-row atoms are assumed to participate in bonding, the axial σ-bonding for each of ClF_3, SF_4 and PF_5 is similar to that which we have described for XeF_2, i.e. 4-electron 3-centre bonding is involved. The geometries, standard Lewis and "increased-valence" and non-paired spatial orbital structures are displayed in (**11**)-(**21**), (with only one equivalent "increased-valence" structure displayed for SF_4 and PF_5). The bond-properties implied by each set of valence-bond structures are in accord with the observation[12–14] that the axial bonds are longer than the equatorial bond(s) for each molecule. However, because the "increased-valences" structures are equivalent to resonance between standard and "long-bond" Lewis structures (for example, for SF_4, (**19**) ≡ (**18**) ↔ (**22**)), resonance between the "increased-valence" structures must provide a more stable representation of the electronic structure than does the more-familiar resonance between the standard Lewis structures.

In Section 4-8, we have generated Pauling "3-electron bond" structures for ClF_2 and SF_3 from ClF + F and $SF_2 + F$. We may use a similar procedure to construct the "increased-valence" structures for ClF_3, SF_4 and PF_5. For example, by writing down SF_4 as $SF_2 + 2F$ as in (**23**), then (i) delocalizing a sulphur 3p electron into an axial S-F bonding σ-orbital, and (ii) spin-pairing the unpaired-electron of SF_3 with that of a second axial fluorine atom, we obtain "increased-valence" structure (**19**). Alternatively by delocalizing both of the sulphur 3p electrons of SF_2 into separate axial S-F bonding σ-orbitals, as in structure (**24**), we obtain the Linnett structure (**25**) for SF_4.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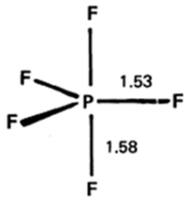
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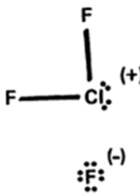
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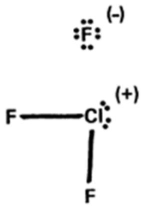
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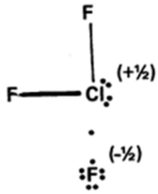
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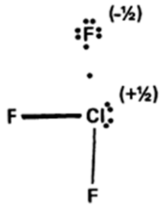
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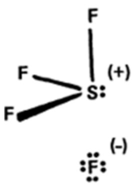
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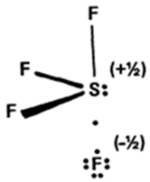
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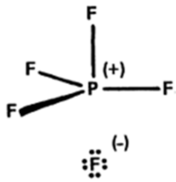
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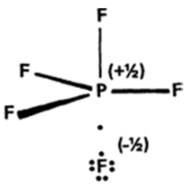
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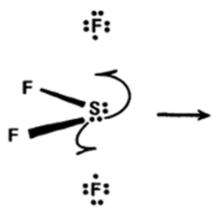
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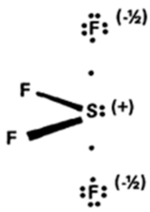
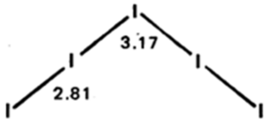

(25)

19-2 The Polyiodide Anions

Geometries[2] for the polyiodide anions I_5^-, I_7^- and I_8^{2-} are given in (**26**), (**27**) and (**28**).



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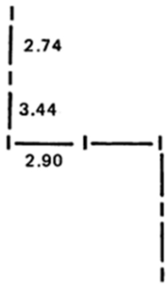
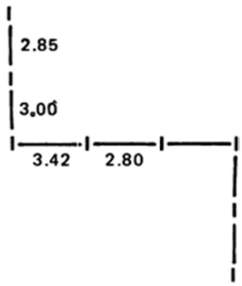


(27)



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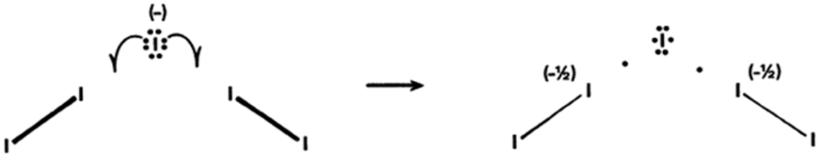
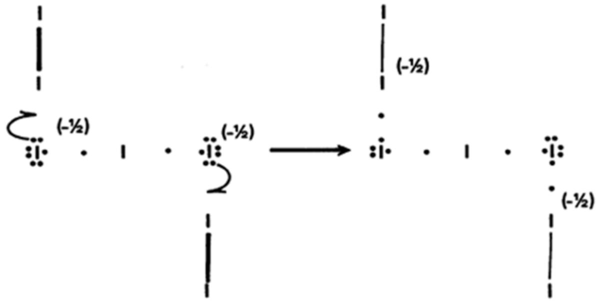
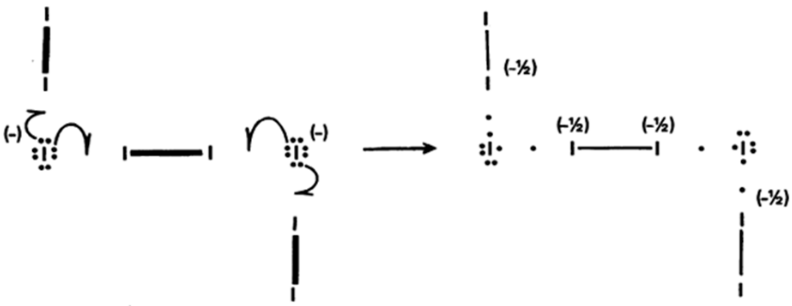


(29) (30)



(31) (32)

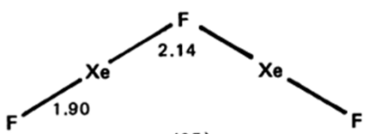


(33) (34)

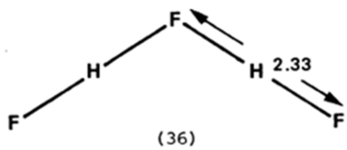
The lengths of their I-I bonds are longer than the I-I single bond length of 2.67 Å for free I_2. We can account for these observations by inspection of the "increased-valence" structures (**30**), (**32**) and (**34**), which we may derive from the Lewis or non-paired spatial orbital structures (**29**), (**31**) and (**33**). For the latter three structures, we have subdivided the ions into $I_2 + I^- + I_2$, $I_2 + I_3^- + I_2$, and $I_2 + I^- + I_2 + I^- + I_2$ components, and used the non-paired spatial orbital structure (**8**) for I_3^-. All of the bonds are σ-bonds.

19-3 $Xe_2F_3^+$ and $H_2F_3^-$

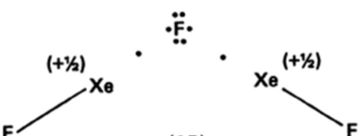
The penta-atomic ions $Xe_2F_3^+$ and $H_2F_3^-$ have the bond-lengths[15,16] shown in (**35**) and (**36**).



(35)



(36)



(37)

(38)

We may generate the "increased-valence" structures (**37**) and (**38**) from the Lewis structures for $XeF^+ + F^- + XeF^+$ and $HF + F^- + HF$. These "increased-valence" structures are similar to structure (**30**) for I_5^-, and imply that the two terminal bonds of each ion should be shorter than the two bridging bonds, and that all bonds should be longer than the single bond lengths of 1.81 and 0.92 Å for XeF_5^+ and HF.

The above description is strictly valid only for 90° bridging bond-angles. When this occurs, two of the bridging fluoride 2p atomic orbitals overlap with the xenon 5pσ or hydrogen 1s atomic orbitals, as is shown in Fig. 19-1 for $Xe_2F_3^+$. Two 4-electron 3-centre bonding units therefore pertain for the eight σ-electrons of these ions. However, both $Xe_2F_3^+$ and $H_2F_3^-$ have bridging bond-angles[15, 16] that are larger than 90°, namely 150° and 118°. If the bridging bond-angle were 180°, then only one 2p orbital of the bridging fluorine is available for σ-bonding with the

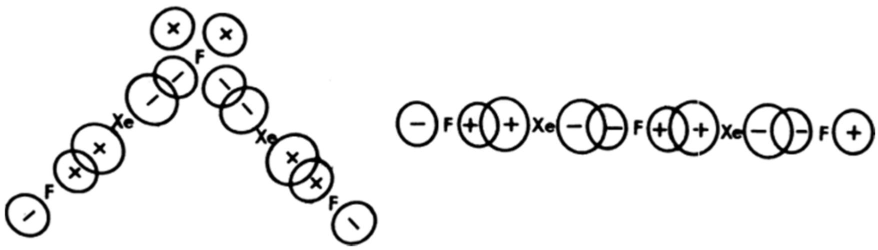
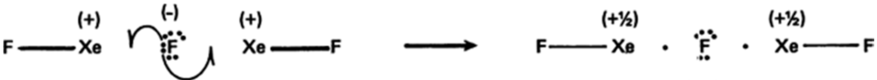


Figure 19-1: Atomic orbitals for 4-electron 3-centre and 6-electron 5-centre σ-bonding units for $Xe_2Fe_3^+$.

xenon or hydrogen atoms. For linear $Xe_2F_3^+$, the orbital overlaps are displayed in Fig. 19-1; a 5-centre overlapping scheme is involved, which accommodates six electrons (two for F^- and two from each XeF^+ fragment); cf. Section 13-6 for a discussion of 6-electron 5-centre bonding.

We can construct an $Xe_2F_3^+$ "increased-valence" structure with a 6-electron 5-centre bonding by commencing with the standard Lewis structure (**39**), and then delocalizing each of the non-bonding 2pσ-electrons on the bridging F^- into the two adjacent Xe-F bonding orbitals[17]. We thereby obtain "increased-valence" structure (**40**), for which all Xe-F bonds should be longer than single bonds. The terminal bonds are fractional electron-pair bonds, and each of the central bonds involves one bonding electron. The shorter lengths for the terminal bonds imply that their bond-numbers are larger than the bond-orders for the central bonds. It should be noted that because the bridging bond-angle is 150°, the electron distributions for both of the structures (**37**) and (**40**) (with the same geometry) are needed to describe the electronic structure of $Xe_2Fe_3^+$.



(39) (40)

Evidence has been provided[18] for the existence of a near-linear I_5^-; the appropriate "increased-valence" structure (**41**) for it is similar to structure (**40**) for $Xe_2Fe_3^+$.

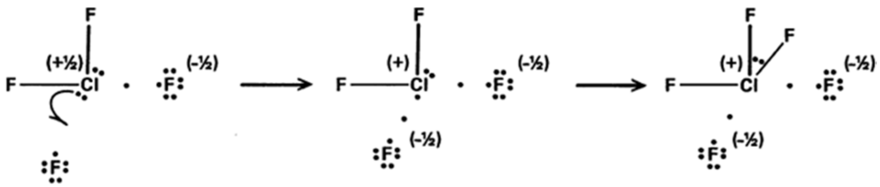
(41)

19-4 ClF_5 and SF_6

Table 19-1: Axial and equatorial bond-lengths (Å) for AF_5 molecules.

	$r(A-F_{ax})$	$r(A-F_{eq})$		$r(A-F_{ax})$	$r(A-F_{eq})$
ClF_5 [i]	1.571	1.669	SbF_5^{2-} [ii]	1.916	2.075
BrF_5 [iii]	1.699	1.768	TeF_5^- [iv]	1.862	1.952
IF_5 [v, vi]	1.834	1.868	XeF_5^+ [vii, viii]	1.813	1.843
	1.817	1.873		1.793	1.845 (av)

Without d-orbital participation in σ-bonding by the **A**-atom in AF_5 molecules, "increased-valence" structures that are similar to structure (**43**) for ClF_5 can account for the observed lengthenings of the equatorial bonds relative to the axial bonds for the AF_5 molecules listed in Table 19-1. If we use ClF_5 as the example, we may construct "increased-valence" structure (**43**) for it via structures (**16**) and (**42**) for ClF_3 and ClF_4. Starting with $ClF_3 + F$, a Pauling "3-electron bond" is developed in structure (**42**) for ClF_4 by delocalizing a non-bonding 3p electron into a Cl-F bonding orbital (cf. $ClF + F \rightarrow ClF_2$ in Section 4-8). The resulting anti-bonding Cl-F σ* electron is then spin-paired with the unpaired electron of a fifth fluorine atom to afford structure (**43**) for ClF_5.



(16) (42) (43)

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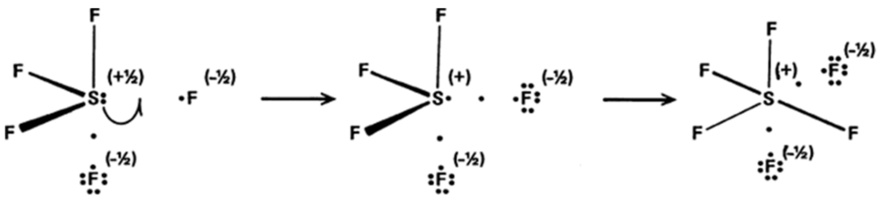
[viii] Bartlett, N., Gennis, M., Gibber, D.D., Morrell, B.K. and Zalkin, A., Inorg. Chem., 1973, **12,** 1717.

We may similarly proceed to SF_6 via SF_4 and SF_5. When a fifth fluorine atom bonds to SF_4, it is able to utilize the equatorial lone-pair on the sulphur atom of structure (**19**) for SF_4, as in structure (**44**),

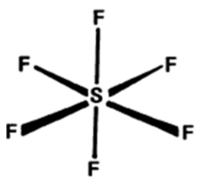


(44) (45) (46)

to form "increased-valence" structure (**45**) for SF_5. In this structure, the newly-formed equatorial S-F bond involves a Pauling "3-electron bond". If the $F_{ax} - S - F_{eq}$ bond angles are assumed here to be 90°, then the sulphur atom is sp^2 hybridized for the equatorial σ-bonds.

To use the unpaired electron of the equatorial bond for SF_5 to bind to a sixth fluorine atom, a hybridization change must occur in order that good overlap can exist between the two odd-electron orbitals. Best overlap is obtained when the $2p\sigma_F$, $3p\sigma_S$ and $2p\sigma_F$ orbitals are colinear. This is achieved when the equatorial bond-angles are 90°, to give the two equatorial electron-pair bonds sp hybridization for the sulphur atom. The valence-bond structure (**46**) for SF_6 has "increased-valence" representations for its two 4-electron 3-centre bonding units. In order that the six S-F bonds have equivalent lengths, (1.561 Å)[19], structure (**46**) must participate in resonance with other equivalent structures that differ in the locations of the 4-electron 3-centre bonding units and the electron-pair bonds, i.e. the sulphur 3s orbital can participate in the axial as well as the equatorial bonding.

The S-F bond-lengths of 1.561 Å for SF_6 are only slightly longer than the estimate of 1.54 Å for an S-F single bond (Section 11-5), and if this lengthening is significant, the development of two 4-electron 3-centre bonding units does not account well for this observation. If the difference is not significant, then it is necessary to assume that the sulphur atom expands its valence-shell to form six electron-pair σ-bonds, as in the Lewis structure (**47**).



(47)

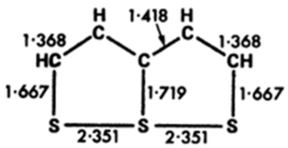
(48) (49)

Maclagan[20] has discussed the bonding for SF_6, and has concluded that ionic Lewis structures such as structure (**48**), which also involve an expansion of the sulphur valence shell, should have larger weights than has structure (**47**). Each of these ionic structures can be stabilized by delocalizing a non-bonding 2pσ-electron from each of the F^- into a bonding S-F σ-orbital to generate "increased-valence" structure (**49**), which is more stable than structure (**48**). "Increased-valence" structure (**49**) has an expanded valence shell, and a 4-electron 3-centre bonding unit with a Pauling "3-electron bond" as a component. The bond-lengths for SF_6 suggest that resonance between "increased-valence" structures of type (**49**), together with some contribution from structure (**47**), provides a more suitable representation of the electronic structure than does resonance between "increased-valence" structures of type (**46**). In structures (**47**) and (**49**), the sulphur hybridizations are sp^3d^2 and sp^3d, respectively, which involve with the sulphur e_g – type 3d orbitals.

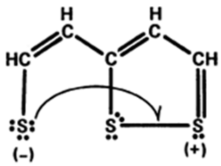
Studies[21] of the geometry for SF_5Cl give $S-F_{ax} = 1.571$ Å, $S-Cl_{ax} = 2.055$ Å and $S-F_{eq} = 1.570$ Å, which are similar to the earlier reported lengths of 1.588, 2.047 and 1.566 Å. Resonance between valence-bond structures similar to structures (**47**) and (**49**) accounts for the observed bond lengthenings relative to the estimates of 1.54 and 2.01 Å for S-F and S-Cl single bonds.

19-5 Thiothiophthenes

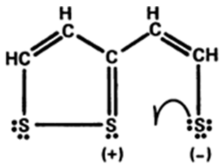
Bond lengths[22] for thiothiophthene are reported in (**50**).



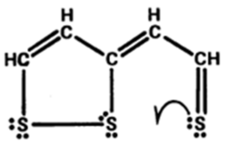
(50)



(51)



(52)



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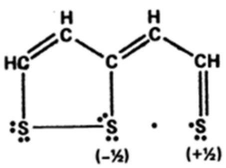

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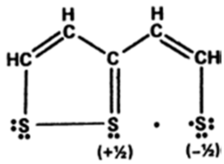

(55)

The S-S bonds for this molecule and many of its derivatives[22, 23] are appreciably longer than the standard single-bond length of 2.06 Å. (For the derivatives, the two S-S bond-lengths are usually unequal, due presumably to the nature of the substituent[23].)

For thiothiophthene, we can use the numerous standard Lewis structures such as (**51**), (**52**) and (**53**) + mirror images to construct the (more-stable) "increased-valence" structures (**54**) and (**55**) by means of the delocalizations indicated. Resonance between either set of structures accounts for the lengthening of the S-S bonds, but additional considerations are required to rationalize the observed variations in the C-S and C-C bond lengths.

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Chapter 20 Intermolecular Donor-Acceptor Complexes

20-1 Quantum Mechanical Description of Donor-Acceptor Complexes

Mulliken[1–3] has provided a quantum mechanical description of molecular complexes that are formed by reaction between an electron-donor (**D**) and an electron acceptor (**A**). The wave-function for the normal or ground-state of the complex may be expressed approximately according to Eqn. (1).

$$\Psi_N \cong a\,\Psi_0(\mathbf{D},\mathbf{A}) + b\,\Psi_1\left(\mathbf{D}^+ —— \mathbf{A}^-\right) \tag{1}$$

Here we have retained only the first two terms of a more general expression for Ψ_N which has been described by Mulliken. The (**D**,**A**) and ($\mathbf{D}^+$ — $\mathbf{A}^-$) are called "*no-bond*", and "*dative*" or "*charge-transfer*" structures, respectively. The designation of "no-bond" structure for (**D**, **A**) refers to the absence of covalent bonding between the donor and the acceptor.

In this Chapter, aspects of the electronic structures of complexes formed from n-type electron donors and sacrificial electron acceptors will be examined. An *n-type donor* donates an electron from essentially a lone-pair atomic orbital on a key atom, and a *sacrificial acceptor* accepts an electron into an antibonding molecular orbital[1]. (Mulliken[3] has also designated n-type donors as *increvalent donors*). Therefore, for this type of complex, **D** has a lone-pair of electrons and **A** has a vacant antibonding orbital in Eqn. (1). We shall assume here that the antibonding orbital of **A** extends over two adjacent atomic centres, and that the corresponding bonding molecular orbital of **A** is doubly occupied.

Using our discussion above, and that of Chapter 14, we may deduce that the dative structure $\mathbf{D}^+$ — $\mathbf{A}^-$ of Eqn. (1) (which arises from the transfer of an electron from a lone-pair atomic orbital on **D** into a vacant antibonding of **A**) corresponds

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Lecture Notes in Chemistry 90, DOI 10.1007/978-3-319-16676-6_20

to an "increased-valence" structure. We shall now describe two examples which illustrate this type of bonding scheme. In Section 20-4, we shall examine an alternative procedure that may be used to describe such complexes.

20-2 Complexing of Trimethylamine with Molecular Iodine

Trimethylamine (Me_3N) can form a crystalline complex with I_2. The N-I and I-I bond-lengths have been measured[4], and they are shown in (1). The I-I length of 2.83 Å is longer than the 2.67 Å for free I_2, and the N-I length of 2.27 Å is longer than the single bond length of 2.03 Å. Measurements[5] for a number of other amine-I_2 complexes show that as the N-I bond-length decreases, the I-I bond-length increases.

$$\mathbf{(CH_3)_3N \cdots\cdots\cdots\cdots I — I}$$
$$2.27 \quad 2.83$$

(1)

In Eqn. (1), Mulliken[3] has assumed that **D** = Me_3N, **A** = I_2, $\mathbf{D}^+$ = Me_3N^+ and $\mathbf{A}^-$ = I_2^- and has written the wave-function for the complex as Eqn. (2).

$$\Psi_N \cong a\,\Psi_0\left(Me_3N, I_2\right) + b\,\Psi_1\left(Me_3N^+ \text{——} I_2^-\right) \tag{2}$$

Because I_2 has a single bond, the extra electron of I_2^- must occupy an anti-bonding molecular orbital. Therefore, the valence-bond structure for I_2^- must be the Pauling "3-electron bond" structure $(\mathbf{{}^{\bullet}I \cdot I^{\bullet}})^-$. By spin-pairing the unpaired electrons of I_2^- and Me_3N^+, we may represent $Me_3N^+ — I_2^-$ by the "increased-valence" structure (**3**), and describe (approximately) the electronic structure of the complex in terms of resonance between structures (**2**) and (**3**).

$$\mathbf{(CH_3)_3N{:}\;\; I — I \leftrightarrow (CH_3)_3 \overset{(+)}{N} — \overset{(-\frac{1}{2})}{I} \cdot \overset{(-\frac{1}{2})}{\ddot{\underset{\cdot\cdot}{I}}}{:}}$$

(2) (3)

20-3 Hydrogen Bonding Between two H_2O Molecules

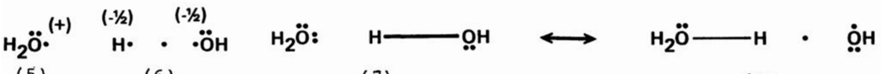
In the vapour, free H_2O molecules have O-H bond-lengths of 0.976 Å. When H_2O molecules associate to form clusters in the gaseous, liquid or solid states, these O-H bonds lengthen and weaken a little, and the intermolecular O-H hydrogen bonds are long and weak. Some bond-lengths are reported in (**4**) for $(D_2O)_2$ and (D_2O). The D-O stretching frequency is reduced from 2727 cm^{-1} in HDO vapour[7] to 2454 cm^{-1} in ice IX.

(4)

We shall assume here that the two H_2O molecules of the water dimer form a charge-transfer complex, and describe the intermolecular bonding by means of Eqn. (1). To do this, we require one molecule to be the electron donor, and the other to be the electron acceptor. Thus, we have **D** = H_2O, **A** = H_2O, $\mathbf{D}^+ = H_2O^{\bullet+}$ and $\mathbf{A}^- = H_2O^{\bullet-}$, and write the wave function for the complex as Eqn. (3).

$$\Psi_N \cong a\,\Psi_0(H_2O, H_2O) + b\,\Psi_1\left(H_2O^+ \text{——} H_2O^-\right) \tag{3}$$

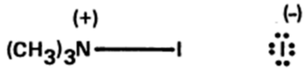
To form H_2O^-, we have transferred a non-bonding electron from the donor H_2O into a vacant antibonding O-H orbital of the acceptor H_2O, to generate the Pauling "3-electron bond" structure (**6**). By spin-pairing its unpaired electron with the unpaired electron of (**5**) for H_2O^+, we obtain the "increased-valence" structure (**8**) for the dative structure H_2O^+—H_2O^-. The $(H_2O)_2$ complex may then be described by means of the (**7**) ←→ (**8**) resonance. It may be noted that the dipole-dipole theory of hydrogen bonding is based on dipolar attractions that may exist between the two H_2O molecules of the "no-bond" structure (**7**).



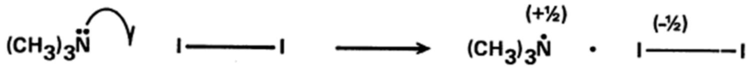
(5) (6) (7) (8)

20-4 Reformulation of Charge-Transfer Theory[8]

Mulliken[3] has shown that the dative structure $\left(\mathbf{D}^{+}\text{——}\mathbf{A}^{-}\right) = \mathrm{Me_3N^{+}}\text{——}\mathrm{I_2^{-}}$ for the $Me_3N...I_2$ complex summarizes resonance between the standard and "long-bond" Lewis structures (**9**) and (**10**), i.e. "increased-valence" structure (**3**) summarizes resonance between these two Lewis structures, each of which has a Heitler-London type wave-function for the electron-pair bond. Resonance between the standard Lewis structure (**2**) (with a Heitler-London type wave-function for the I-I bond) and the "long-bond" structure (**10**) is equivalent to using "increased-valence" structure (**12**).

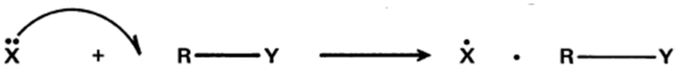

(9)


(10)


(11) (12)

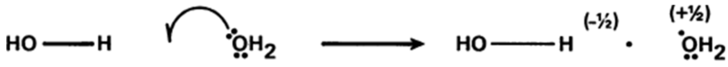
We can construct this "increased-valence" structure by delocalizing a nitrogen non-bonding electron of (**2**) into a bonding N-I orbital, as is shown in (**11**). Of the two "increased-valence" structures (**3**) and (**12**), the formal charges suggest that (**12**) should be the more important for the ground-state of the complex. If this is assumed, we are able to deduce the properties of the complex by examination of (**12**) alone. This "increased-valence" structure indicates immediately that both the N-I and I-I bonds are longer than single bonds. To deduce this result from the theory of Section 20-2, it was necessary to invoke resonance between the "no-bond" and dative valence-bond structures (**2**) and (**3**). A more economical representation of the electronic structure is therefore obtained by delocalizing a non-bonding electron of the donor into a bonding orbital between the donor and the acceptor, rather than into an anti-bonding orbital of the acceptor. By using "increased-valence" structure (**12**) to represent (approximately) the electronic structure of the complex, we may describe the intermolecular bond as primarily a 1-electron bond.

If $\ddot{\mathbf{X}}$ and **R—Y** are the generalized electron donor and electron acceptor, then we may represent the formation of the complex **X...RY** as follows. As **X** approaches **RY** so that the **X** and **R** atomic orbitals (x and r) overlap, one of the non-bonding electrons of **X** delocalizes into the two-centre bond-orbital $\psi_{xr} = x + \ell_r$ (with $\ell > 0$) which is constructed from these atomic orbitals. The "increased-valence" structure (**13**) is thereby generated. Thus, we may write



(13)

For the hydrogen bonding interaction between two water molecules we may write



(14)

to obtain a 1-electron bond as the intermolecular hydrogen bond, and reducing the bond-number for the adjacent H—O bond below the value that pertains for a free H_2O molecule.

In the theory of Sections 20-1 to 20-3, the electron donor ($\ddot{\mathrm{X}}$) and the electron acceptor ($\mathbf{R—Y}$) were designated as *increvalent* and *sacrificial* donors and acceptors respectively. Here, in structures (**12**), (**13**) and (**14**), donors and acceptors are both increvalent species.

For structures (**12**) and (**14**), we show the relevant atomic orbital overlaps in Figure 20-1.

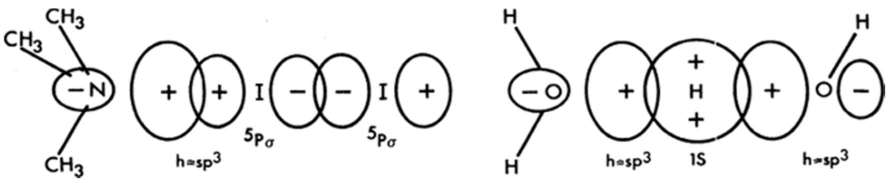


Figure 20-1: Atomic orbital overlaps of $Me_3N + I_2$ and $H_2O + H_2O$.

20-5 "Increased-Valence" Structures with three 2-Centre Bond Orbitals

An interesting result is obtained if 2-centre bond-orbitals are used to accommodate all of the bonding electrons in the "increased-valence" structure (**13**) and the standard Lewis structure (**15**). We shall designate these bond orbitals as $\psi_{xr} = x + \ell r$ and $\psi_{ry} = r + ky$, with the bond parameters ℓ and k both > 0. The $S = 0$ spin wave-functions for structures (**13**) and (**15**) are then given by Eqs. (4) and (5) (cf. Eqn. (7) of Chapter 15).

$$\Psi(\dot{\mathrm{X}} \cdot \mathbf{R—Y}) = |\mathbf{x}^{\alpha}\psi^{\beta}_{\mathbf{xr}}\psi^{\alpha}_{\mathbf{ry}}\psi^{\beta}_{\mathbf{ry}}| + |\psi^{\alpha}_{\mathbf{xr}}\mathbf{x}^{\beta}\psi^{\alpha}_{\mathbf{ry}}\psi^{\beta}_{\mathbf{ry}}| \quad (4)$$

$$\Psi(\ddot{\mathrm{X}}\ \ \mathbf{R—Y}) = |\mathbf{x}^{\alpha}\mathbf{x}^{\beta}\psi^{\alpha}_{\mathbf{ry}}\psi^{\beta}_{\mathbf{ry}}| \tag{5}$$

The wave-function for the dative structure $\mathbf{X}^{+}—\mathbf{RY}^{-}$, for which one non-bonding electron of structure (**15**) has been transferred into the antibonding **RY** orbital $\psi^{*}_{\mathrm{ry}} = k^{*}\mathrm{r} - \mathrm{y}$, is given by Eqn. (6).

$$\Psi(\mathrm{X}—\mathbf{R}\cdot\dot{\mathrm{Y}}) = |\mathbf{x}^{\alpha}\psi^{*\beta}_{\mathbf{ry}}\psi^{\alpha}_{\mathbf{ry}}\psi^{\beta}_{\mathbf{ry}}| + |\psi^{*\alpha}_{\mathbf{ry}}\mathbf{x}^{\beta}\psi^{\alpha}_{\mathbf{ry}}\psi^{\beta}_{\mathbf{ry}}| \tag{6}$$

It has been deduced[8c] that the Mulliken wave-function for the complex, namely Eqn. (1), is equivalent to the wave-function of Eqn. (4) for the "increased-valence" structure (**13**). Therefore, the Mulliken wave-function of Eqn. (1) implies, but conceals an (approximate) description of the intermolecular bond as a 1-electron bond.

$$\begin{array}{ccc} \dot{\mathbf{X}} & \cdot & \mathbf{R—Y} \\ (\mathbf{x})^{1} & (\psi_{\mathbf{xr}})^{1} & (\psi_{\mathbf{ry}})^{2} \end{array} \qquad\qquad \begin{array}{cc} \ddot{\mathbf{X}} & \mathbf{R—Y} \\ (\mathbf{x})^{2} & (\psi_{\mathbf{ry}})^{2} \end{array}$$

(13) (15)

20-6 $H_5O_2^+$ and HF_2^-

The isoelectronic ions $H_5O_2^+$ and HF_2^- with 16 valence-shell electrons, are examples of systems that have strong hydrogen bonds[9]. In Fig. 2-4, we have displayed the set of hydrogen 1s and fluorine 2pσ-atomic orbitals of HF_2^- that may be utilized for 4-electron 3-centre bonding. For $H_5O_2^+$, oxygen hybrid orbitals replace the fluorine 2pσ-orbitals, and the standard Lewis structures are those of (**16**) and (**17**).

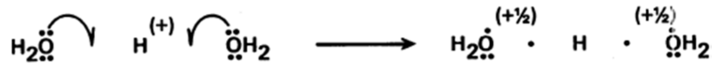
$$\mathbf{H_2\overset{(+)}{\underset{..}{O}}—H\ \ \underset{..}{\ddot{O}}H_2 \leftrightarrow H_2\underset{..}{\ddot{O}}\ \ H—\overset{(+)}{\underset{..}{O}}H_2}$$

(16) (17)

$$\mathbf{H_2\overset{(+)}{\underset{..}{O}}—\overset{(-\frac{1}{2})}{H}\ \cdot\overset{(+\frac{1}{2})}{\underset{..}{\dot{O}}}H_2 \leftrightarrow H_2\overset{(+\frac{1}{2})}{\underset{..}{\dot{O}}}\cdot\ \overset{(-\frac{1}{2})}{H}—\overset{(+)}{\underset{..}{O}}H_2}$$

(18) (19)

As well as using the above structures, we may also use[8b] the Linnett non-paired spatial orbital structure (**21**)

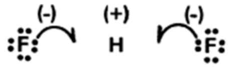


(20) (21)

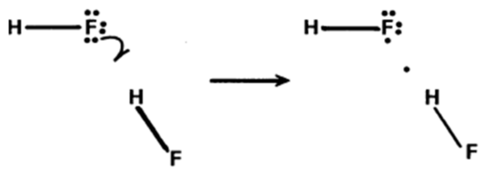
to represent the electronic structure of $H_5O_2^+$. By hydrogen-bonding the oxygen atoms of two H_2O molecules to a proton, we may generate structure (**21**) from the Lewis structure (**20**). As each H_2O molecule approaches the proton, one oxygen lone-pair electron delocalizes into an intermolecular O-H bonding orbital. In structure (**21**), the two H_2O molecules are hydrogen bonded to the proton by means of 1-electron bonds.

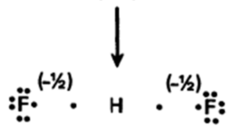
We may provide a simple explanation as to why the bridging O-H bond-lengths of 1.23 Å for $H_5O_2^+$ are appreciably shorter[9] than the 1.808 Å for the hydrogen-bond of $(D_2O)_2$. Relative to an oxygen atom, the H^+ of structure (**20**) is more electronegative than is a hydrogen atom in structure (**7**). The greater electronegativity of H^+ should induce more delocalization of an oxygen lone-pair electron in structure (**21**), to generate an increase in the bond-order for each one-electron bond of $H_5O_2^+$.

For $(HF)_2$ and HF_2^-, the 1-electron hydrogen bonds of structures (**23**) and (**25**) are formed by the one-electron delocalizations shown in structures (**22**) and (**24**). Using electronegativity considerations, as we have done for $H_5O_2^+$, we can explain why the H-F bond-lengths of 1.13 Å for HF_2^- are shorter[9] than the length of 1.55 Å for the hydrogen-bond of $(HF)_2$.



(24)





(22) (23) (25)

For HF_2^-, the "increased-valence" structures are (**26**) and (**27**)

(26) (27) (28) (29)

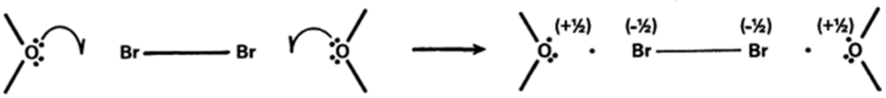
(cf. structures (**18**) and (**19**) for $H_5O_2^+$), with both structures having equal weights and equal H-F bond-lengths when the HF_2^- is located in a symmetrical environment. Williams and Schneemeyer[10] have reported the geometries of (**28**) and (**29**) for HF_2^- and HCl_2^- in non-symmetrical environments. Each of the bond-lengths is longer than the single-bond lengths of 0.92 and 1.27 Å for gaseous HF and HCl. "Increased-valence" structures of type (**26**) alone (with unequal bond-lengths) are compatible with the observed bond-lengths for both anions, although of course (**26**) will be stabilized by resonance with (**27**). The latter structure will have the smaller weight.

The anion $HOHOH^-$ is isoelectronic with $H_5O_2^+$ and HF_2^-, and a suitable valence-bond structure for it is similar to structure (**25**), with OH replacing F, i.e. $\mathbf{H\overset{(-\frac{1}{2})}{\underset{\cdot\cdot}{O}}\cdot H \cdot \overset{(-\frac{1}{2})}{\underset{\cdot\cdot}{\dot{O}}}H}$. The bridging O-H bonds of $H_5O_2^+$ and $HOHOH^-$ have been estimated to have similar lengths and strengths[11].

Firestone[12] has also used Linnett structures to describe the electronic structures of symmetrical hydrogen-bonded molecules.

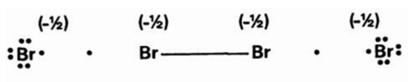
20-7 2:1 Donor-Acceptor Complexes

Two molecules of acetone or dioxan can interact with one molecule of Br_2 to form the intermolecular complexes $Me_2CO....Br_2....OCMe_2$ and $C_5H_{10}O....Br_2....OC_5H_{10}$. The reported Br-Br lengths[4] of 2.28 Å and 2.31 Å are not sufficiently different from the length of 2.28 Å for free Br_2 to indicate much interaction of Br_2 with these solvents. The "increased-valence" structure (**31**), which we may generate from the Lewis structure (**30**)



(30) (31)

by delocalizing oxygen non-bonding electrons into bonding O-Br orbitals, will account for any lengthening of the Br-Br bond. A similar "increased-valence" structure, namely (**32**),



(32)

is certainly compatible with the measured bond-lengths of Br_4^{2-}. The terminal and central bond-lengths of 2.98 Å and 2.43 Å are appreciably longer than the 2.28 Å for free Br_2 [13].

For each of the structures (**31**) and (**32**), there is an "increased-valence" representation for the 6-electron 4-centre bonding unit, and we remind the reader that its wave-function corresponds to the covalent component of the delocalized molecular orbital configuration for the six electrons (Section 10-2). The relevant atomic orbitals for Br_4^{2-} are displayed in Fig. 2-6.

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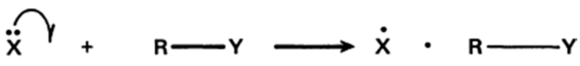
Chapter 21 Base-Displacement Reactions and Electron Conduction in Alkali Metals

21-1 Introduction

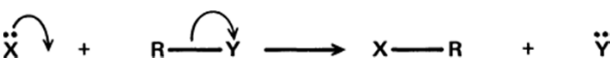
The donor-acceptor complexes of Chapter 20 were usually formed by reacting a neutral electron donor $\ddot{\mathbf{X}}$ with a neutral electron acceptor $\mathbf{R}$—$\mathbf{Y}$. When the **X** and **R** atomic orbitals overlap, delocalization of an $\ddot{\mathbf{X}}$ electron of valence-bond structure (**1**) into a vacant **X-R** bonding orbital generates the one-electron **X-R** bond of increased-valence structure (**2**).



(1) (2)

We shall now provide an "increased-valence" formulation for the general base-displacement reaction $\ddot{\mathbf{X}} + \mathbf{R}—\mathbf{Y} \rightarrow \mathbf{X}—\mathbf{R} + \ddot{\mathbf{Y}}$, which involves the displacement of the base $\ddot{\mathbf{Y}}$ from a substrate **RY** by the base $\ddot{\mathbf{X}}$. This reaction may occur when $\ddot{\mathbf{X}}$ is an anion and $\mathbf{R}$—$\mathbf{Y}$ is a cation, but it can also pertain when $\ddot{\mathbf{X}}$ is either an anion or neutral and, correspondingly, $\mathbf{R}$—$\mathbf{Y}$ is either neutral or a cation. We shall discuss some examples of each of these three types of reactants.

The electronic reorganization that occurs in a base displacement reaction is usually formulated according to Eqn. (1) (with atomic formal charges omitted here):

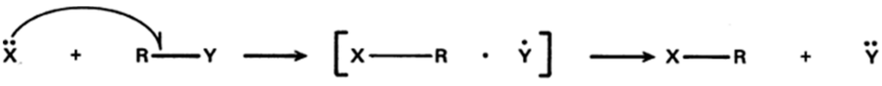
 (1)

A pair of electrons is delocalized from an atomic orbital on $\ddot{\mathbf{X}}$ into the **X-R** bond region, and simultaneously the two electrons that form the $\mathbf{R}$—$\mathbf{Y}$ bond are

R.D. Harcourt, *Bonding in Electron-Rich Molecules*,
Lecture Notes in Chemistry 90, DOI 10.1007/978-3-319-16676-6_21

transferred into an atomic orbital on **Y**. (This atomic orbital is the same orbital that is used by **Y** to form the bond of **R—Y**). The transition state is usually represented as **X—R—Y**, which shows the simultaneous making of the **X-R** bond and breaking of the **R-Y** bond. Since **X**, **R** and **Y** each contribute one atomic orbital for the bonding, the **X-R** and **R-Y** bond orbitals of this transition state cannot be orthogonal, and therefore the divalence of **R** is *apparent*, not real (cf. Chapter 16). Firestone[1] has also used the Linnett theory to formulate the transition state as $\dot{\mathbf{X}} \cdot \mathbf{R} \cdot \dot{\mathbf{Y}}$.

One type of "increased-valence" formulation[2,3] of the generalized base displacement reaction, involves the delocalization of one electron from $\ddot{\mathbf{X}}$ into the antibonding orbital of **R—Y** .



(1) (3)

In the "increased-valence" structure (**3**), we have formed a fractional two-electron **X-R** bond and a one-electron **R-Y** bond. This structure is identical with the structure for Eqn. 20-6, and both have been formed in the same manner. In Chapter 20, we have indicated that for a given (finite) **X-R** distance, structures (**1)** and (**3**) can participate in resonance[2]. Therefore, for a base displacement reaction, structure (**3**) alone is not the transition state. However, structure (**3**) does show clearly how one bond is made and how the other is broken simultaneously.

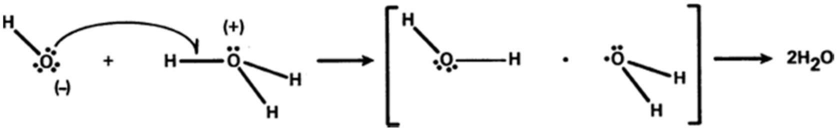
We may therefore distinguish two types of reactions between the electron donor and acceptor $\ddot{\mathbf{X}}$ and **R—Y** . Delocalization of an $\ddot{\mathbf{X}}$ electron into an **X-R** bonding orbital generates the reactant-like complex (**2**), whereas delocalization of the electron into the antibonding **R-Y** orbital generates the product-like complex (**3**) which is involved in the base displacement reaction. For nucleophilic addition of $\ddot{\mathbf{X}}$ to **R—Y** , the electronic structure of the product resembles[2] that of structure (**3**).

Shaik[4] has provided valence-bond descriptions for a variety of organic reactions. Shaik's approach (without "increased-valence") to nucleophilic additions and substitutions in particular is essentially identical with that presented in this chapter, being based primarily on the Mulliken formulation of Eqn. (20-1) for donor-acceptor complexes. The acceptor orbital is an antibonding orbital in both treatments.

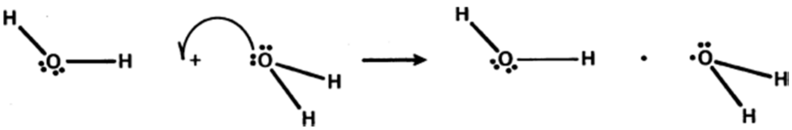
21-2 Lowry-Brønsted Acid-Base Reactions

In Lowry-Brønsted acid-base theory, an acid is a proton donor and a base is a proton acceptor. Since proton acceptors contribute a pair of electrons for bonding with the proton, a Lowry-Brønsted base is also a Lewis base, and therefore a Lowry-Brønsted acid is a special form of Lewis acid.

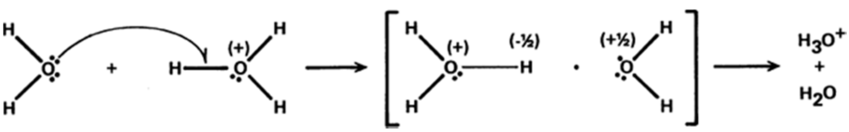
We can formulate the reaction between the Lowry-Brønsted acid and base H_3O^+ and OH^- according to Eqn. (2)[2], in which a non-bonding electron of OH^- is transferred into an antibonding H-O orbital of H_3O^+.



In Section 20-4, we have shown that the entity in parenthesis can represent the hydrogen-bonded complex $(H_2O)_2$. There, we demonstrated that this complex may also be formed from two H_2O molecules by means of the reaction of Eqn. (3),

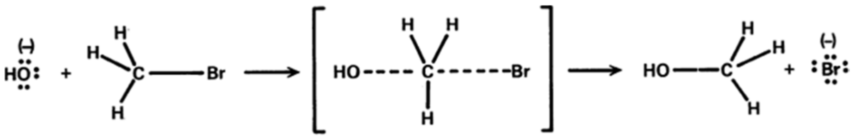


which involves the delocalization of an oxygen lone-pair electron of one molecule into an O-H bonding orbital between the two molecules. The ionization potential of H_2O is 12.6 eV, and this is sufficiently large to make an antibonding O-H orbital of a second H_2O inaccessible at intermolecular distances that are either equal to or greater than the equilibrium value of 1.8 Å, i.e. the energy for $\Psi(H_2O,H_2O)$ is less than the energy for $\Psi(H_2O^+,H_2O^-)$ for this distance. On the other hand, an antibonding **O-H** orbital of H_3O^+ should be of lower energy, and the reaction $H_2O + H_3O^+ \rightarrow H_3O + H_2O$ may proceed by transferring an electron from H_2O into an antibonding **O-H** orbital of H_3O^+. We have thereby formulated the Grotthus mechanism for proton transfer using "increased-valence" structures according to Eq.(4).



21-3 Walden Inversion Mechanism

In aqueous alkali, methyl bromide may be hydrolysed to form methanol, with the OH^- displacing Br^- from its attachment to the carbon atom. The kinetics indicate that a bimolecular transition state is formed[5], and that the methyl group undergoes inversion of configuration as the reaction proceeds. The electronic reorganization that is associated with this S_N2 reaction is usually represented according to Eqn. (5)[5]:



(5)

(4)

In the transition state (**4**), the carbon atom is bonded simultaneously to five atoms. To account for this (apparent) quinquevalence, some workers have assumed that a carbon 3d orbital as well as the 2s and 2p orbitals can participate as a hybridization function in the bonding[6, 7]. But it is more probable that the carbon uses primarily only its 2s and 2p orbitals, and forms two bonds which are not orthogonal, as we have described for the general transition state of Section 21-1. For this latter bonding scheme, the atomic orbital overlaps are shown in Figure 21-1.

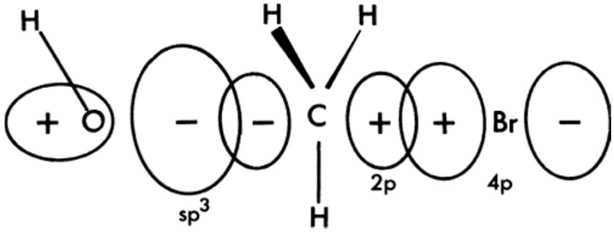
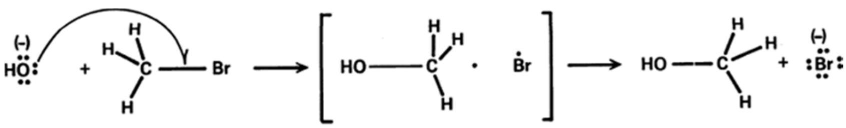


Figure 21-1: Atomic orbital overlaps for the transition state (**4**), omitting carbon 3d orbitals.

An "increased-valence" formulation[2] of Eqn.(6) for the reaction



(6)

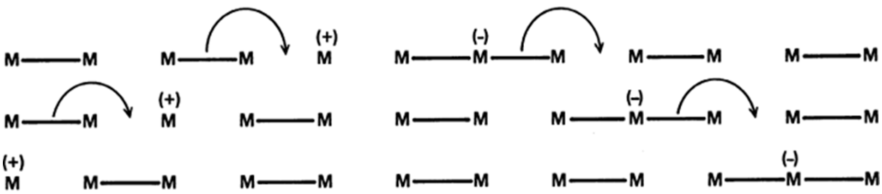
(5)

indicates simply and clearly how the bonds are made and broken, and also provides an explanation for the inversion of configuration. The reaction can proceed by the transfer of an electron from OH^- into an antibonding **O-Br** orbital of CH_3Br ; this creates a fractional **O-C** electron-pair bond and a one-electron **C-Br** bond in the increased-valence structure (**5**) for the complex. As the reaction proceeds, the fractional **O-C** bond of structure (**5**) must become stronger than the one-electron **C-Br** bond. When this occurs, the O-C bond repels the three **C-H** bonds more strongly than does the **C-Br** bond, thereby leading to inversion of configuration. For some early molecular orbital studies of S_N2 reactions, see for example Ref. 8.

21-4 Electron Conduction in Alkali Metal Solids

In the resonating valence-bond theory of metallic solids, Pauling[9, 10] has suggested that alkali metals use their p as well as their s atomic orbitals for bonding. Pauling designated the p orbitals as "metallic orbitals". When both s and p orbitals are used for bonding in the solid alkali metal lithium, the electronic structure of the metal involves resonance between the diatomic Li_2 structures of structure (**6**) (with **M** = Li) and the "bicovalent" Li_3^- structures of type (**7**). On application of an electric field, electron conduction proceeds by means of the "pivotal" resonance which is shown in structure (**8**).

(6) (7)



(8)

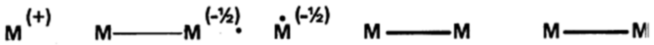
Instead of using the p atomic orbitals as the metallic orbitals of the valence-bond structures, we may use the antibonding σ*2s molecular orbital[11], which is vacant in the diatomic structures of the type Li—Li . (We assume here that each Li atom uses only its 2s atomic orbitals for bonding in the simplest description of this diatomic structure. Of course, the 2p orbitals can hybridize with the 2s orbitals in a more elaborate bonding scheme, but we do not need to consider this hybridization here.) We may write down the diatomic structures of structure (**9**), and on application of an electric potential, obtain structure (**10**).

(9)

(10)

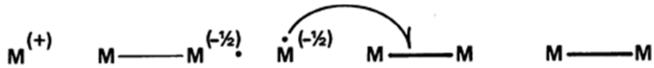
One electron of Li^{-} may now be delocalized into an antibonding orbital of an adjacent Li—Li structure, to generate the "increased-valence" structure for the Li_3^- component of structure (**12**).

(11)

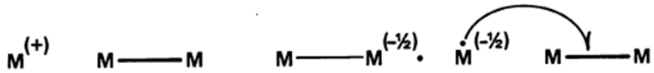


(12)

We can now delocalize the electron that occupies the atomic orbital of the $\mathbf{Li}^{(-½)}$ of structure (**12**) into another antibonding Li_2 orbital, as shown in structure (**13**), to obtain structure (**14**). Electron conduction can proceed further in a similar manner, i.e. by delocalizing an electron from an $\mathbf{Li}^{(-½)}$ atomic orbital into an antibonding **Li-Li** orbital.



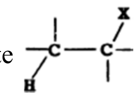
(13)

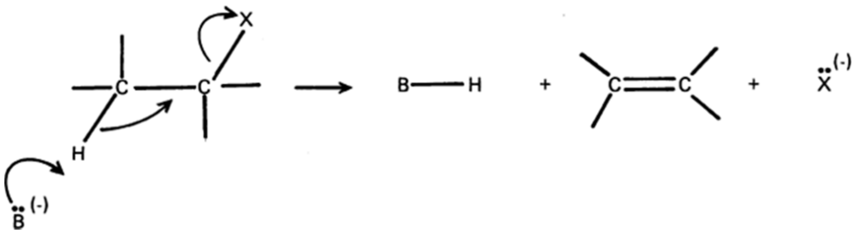


(14)

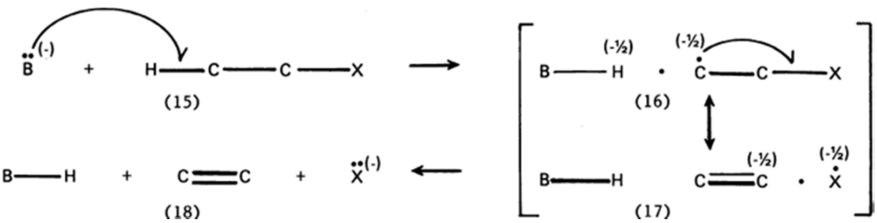
This "increased-valence" description of electron conduction combines features of both the delocalized molecular orbital and the Pauling valence-bond and theories. The simplest "increased-valence" theory need use only the 2s orbitals for bonding (cf. the simplest form of delocalized molecular orbital theory), and it uses localized bonds as does the valence-bond theory.

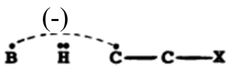
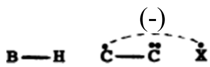
21-5 E2 Elimination Reactions

E2 elimination reactions – for example $EtO^{-} + CH_3CH(CH_3)Br \rightarrow EtOH + CH_2 = CHCH_3 + Br^{-}$ – involve the simultaneous rupture of a **C-H** bond and a **C-X** bond of the substrate  by reaction with the nucleophile $\ddot{\mathbf{B}}^{(-)}$. The usual representation for this type of reaction is the following[12]:



An "increased-valence" formulation of the electronic reorganization[2] involves the transfer of an electron from $\ddot{\mathbf{B}}^{(-)}$ into the antibonding **C-H** σ* orbital, i.e. (**15**) → (**16**), and the transfer of an electron from a carbon atomic orbital of structure (**16**) into the antibonding **C-X** σ* orbital, i.e. (**16**) → (**17**. (For convenience of representation only, we have displayed the relevant atoms in a linear manner.) The wave-function $\Psi = C_{15}\Psi_{15} + C_{16}\Psi_{16} + C_{17}\Psi_{17}$ may be used to describe the course of the reaction, with $C_{16} = C_{17} = 0$ initially and $C_{15} = C_{16} = 0$ at its conclusion when the structure (**17**) goes over to form the products in structure (**18**). The electron of the $\mathbf{C} \cdot \dot{\mathbf{X}}$ bond occupies the bonding molecular orbital $\psi_{CX} = sp_C^n + kp\sigma_X$, with both n and $k \to \infty$ as $C_{17} \to 1$ near the conclusion of the reaction. The six mobile or active space electrons of structures **16** and **17** form a 5-centre bonding unit (cf. Section 13-6).



The "long bond" structures  and  contribute to structures (**16**) and (**17**). For overlap reasons (see Appendix), we would consider them to be more important than is normally supposed.

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2. R.D. Harcourt, J. Chem. Educ., **45,** 779 (1968); **46,** 856 (1969).
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7. C.A. Coulson, Nature, **221,** 1106 (1969).
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10. L. Pauling, Nature of the Chemical Bond, 3rd. Ed., 1960, p. 400.
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12. J. March, ref. 5, p. 896.

Addendum Chapter 21

1. Electron Conduction with Positive Hole + Electron Transfer

In Ref. 13, the electron conduction mechanisms of Section 21-4 are modified to allow for positive hole transfer as well as electron transfer. The modified antibonding molecular orbital mechanism is displayed in Figure 21-2.

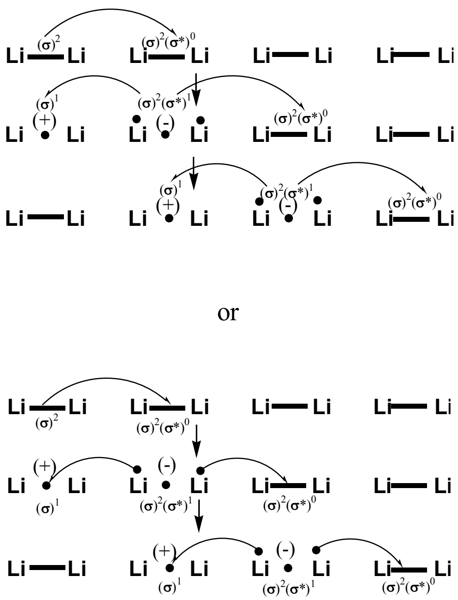
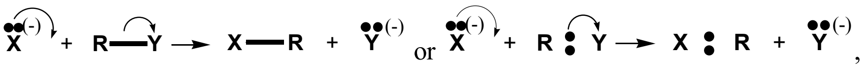


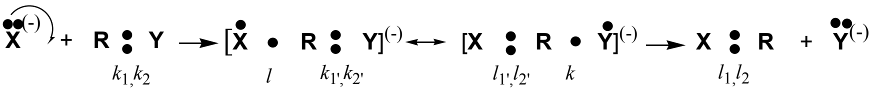
Figure 21-2: Electron conduction with positive hole + electron transfer.

2. More on Base Displacement Reactions[14,15]

The variationally-best formulation for the generalised base displacement reaction,

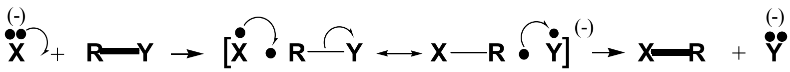


with overlapping AOs x, r and y that form a 4-electron 3-centre bonding unit, has also been formulated as



Reactants **Reactant-like Complex** **Product-like Complex** **Products**

or



in which parameters of the types k_1, k_2, and l pertain to Coulson-Fischer orbitals r + k_1y and y + k_2r, and the molecular orbital x + lr, respectively. (This formulation has also been used by Sun[16].)

For the reactant-like complex, the **X-R** and **R-Y** bonding electrons occupy the ψ_{xr} = x + lr and Coulson-Fischer molecular orbitals ψ'_{ry} = r + $k_{1'}$y and ψ''_{yr} = y + $k_{2'}$r, in which the l, $k_{1'}$ and $k_{2'}$ are polarity parameters. The corresponding **X-R** and **R-Y** bonding MOs for the product-like complex are ψ''_{rx} = x + $l_{2'}$r and ψ'_{xr} = r + $l_{1'}$x, and ψ_{ry} = r + ky. State correlation diagrams, such as that of Figure 21-3 for the identity gas-phase S_N2 reaction, can then be constructed[14(c,d,e,f,g),15].

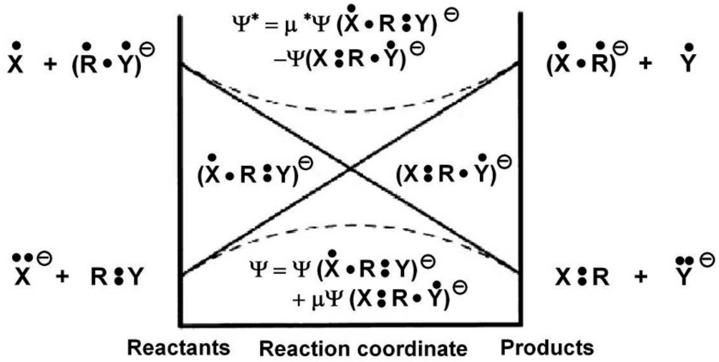


Figure 21-3: Schematic state correlation diagram for the identity gas-phase reaction, $\mathbf{X^- + RY \rightarrow XR + Y^-}$. (The formation of reactant-like and product-like complexes as possible intermediates is not indicated. Calculations are needed to determine whether Ψ and Ψ^* have a maximum and a minimum, respectively (or vice versa) at the crossing point.)

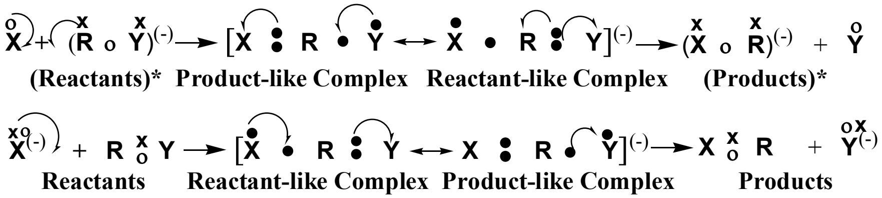
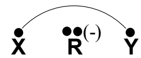
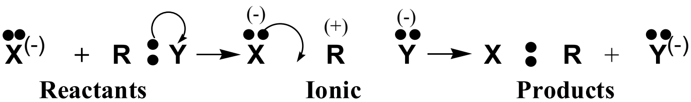


Figure 21-4: (Reactants) → (Products) and (Reactants)* → (Products)* for X^{-} + RY → XR + Y^{-}.

The (S = 0 spin) excited states for the reactants and products are (Reactants)* = $\mathbf{X}^{\bullet}$ + $(\mathbf{RY})^{\bullet-}$ and (Products)* = $(\mathbf{XR})^{\bullet-}$ + $\mathbf{Y}^{\bullet}$, respectively. The valence-bond formulation for conversion of the (Reactants)* into (Products)* is essentially the reverse of the ground-state formulation. Both formulations are shown in Figure 21-4.

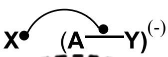
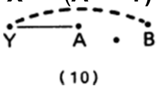
The singlet diradical Lewis structure  does not contribute to the canonical Lewis structure resonance scheme for the ground-state reactants and products, whether or not the closed-shell ionic structures $\mathbf{X:}^{(-)}$ $\mathbf{R:}^{(-)}$ $\mathbf{Y}^{(+)}$, $\mathbf{X:}^{(-)}$ $\mathbf{R}^{(+)}$ $\mathbf{Y:}^{(-)}$ and $\mathbf{X}^{(+)}$ $\mathbf{R:}^{(-)}$ $\mathbf{Y:}^{(-)}$ are included in the valence-bond descriptions of the reactants and products. It is needed to help form the reactant-like and product-like complexes. Therefore unless the singlet diradical structure is included in the valence-bond formulation for the $\mathbf{X:}^{(-)}$ + **R-Y** → **X-R** + $\mathbf{Y:}^{(-)}$ reaction, reactant-like and product-like complexes with intermolecular one-electron bonds will not be formed. A non-concerted S_N1 reaction mechanism, formulated[14(l)] as



rather than the concerted S_N2 mechanism of Figure 21-3, is then obtained.

It is also deduced[14(d,f,j)] that the mechanisms for ground-state and excited state base displacement reactions cannot proceed via movements of pairs of electrons in concert, i.e. the fishhook arrow for a one-electron transfer replaces the curly arrow for concerted electron-pair transfer (see Chapter 21, Addendum 3).

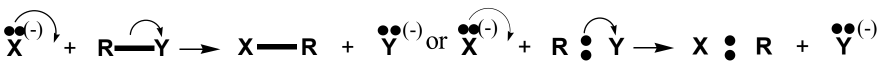
In Chapter 25, section 2, the analogous increased-valence formulation for the radical-transfer reaction $\mathbf{X}^{\bullet}$ + **R-Y** → **X-R** + $\mathbf{Y}^{\bullet}$ is presented.

Non-increased-valence formulations for this type of reaction and for $\mathbf{X:}^{(-)}$ + **R-Y** → **X-R** + $\mathbf{Y:}^{(-)}$ are developed in Ref. 17. However it is noted that the  of Ref. 17 is equivalent to the increased-valence structure  of Chapter 3. See for example Refs. 14e,18, for a comparison of these types of valence-bond symbolisms.

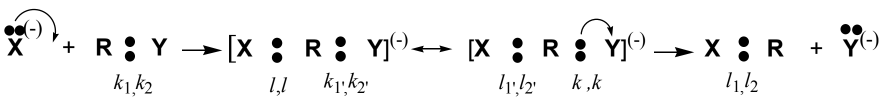
3. Robinson's Curly Arrow and the Fishhook Arrow

Robinson's "curly arrow"[19] is used to show the movements of pairs of electrons in a reaction mechanism. "The tail of a curly arrow 'starts' at a mobile electron pair and its head points to the 'destination' of the electron pair. Fishhook arrows indicate cleavage or movement of a single electron shown as a single-headed curved arrow. They are widely used in radical chemistry to represent the homolytic cleavage and reactions of radicals."[20]

Using Robinson's curly arrow, as discussed in Section 21-1, the reaction of a nucleophile **X:**$^{(-)}$ with a substrate **R:Y** to form the ground-state **X:R** + **Y:**$^{(-)}$ products is usually formulated as

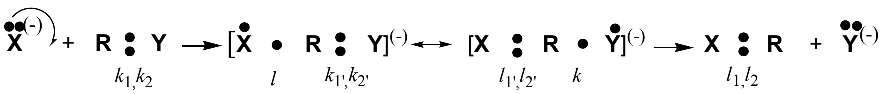


In more detail:



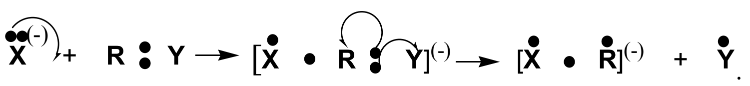
in which, for example, parameters of the types $k_{1'}$, $k_{2'}$, and l pertain to the **R:Y** molecular orbitals r + $k_{1'}$y and y + $k_{2'}$r, and the **X:R** molecular orbital configuration $(x + lr)^2$, respectively.

As is shown in the Chapter 21 Addendum 2, the fishhook arrow formulation of this reaction is:

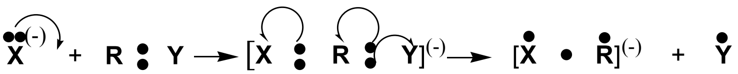


for which at intermediate stages along the reaction coordinate, the variationally-best values of the orbital parameters differ from those of curly arrow formulation.

In Refs. 14(d,f),21, comparisons are made between the above curly arrow and fishhook arrow formulations of base displacement reactions. One of them involves the formation of the $[\dot{X} \bullet \dot{R}]^{(-)} + \dot{Y}$ excited state of the products via the dissociation of the reactant-like complex using one-electron transfers, as in



To form the excited state of the products, the concerted 2-electron transfer formulation



requires three one-electron transfers to occur in $[\mathbf{X} : \mathbf{R} : \mathbf{Y}]^{(-)}$. Because only two one-electron transfers are needed for $[\dot{\mathbf{X}} \bullet \mathbf{R} : \mathbf{Y}]^{(-)}$, it was concluded[14(d,f)] that fishhook arrow formulations are to be preferred to curly arrow formulations. It is of course recognized that the curly arrow formulation $\mathbf{X}:^{(-)} + \mathbf{R}\text{—}\mathbf{Y} \rightarrow \mathbf{X}\text{—}\mathbf{R} + \mathbf{Y}:^{(-)}$ provides a compact procedure to show how reactants are converted into products.

4. Spin-coupled valence-bond formulations for $\mathbf{X}:^{(-)} + \mathbf{R}\text{-}\mathbf{Y} \rightarrow \mathbf{X}\text{-}\mathbf{R} + \mathbf{Y}:^{(-)}$

As discussed in Ref. 14(l), and restated here, spin-coupled valence-bond formulations[22] for $\mathbf{X}:^{(-)} + \mathbf{R}\text{-}\mathbf{Y} \rightarrow \mathbf{X}\text{-}\mathbf{R} + \mathbf{Y}:^{(-)}$ reactions have used one configuration with four 3-centre non-orthogonal orbitals to accommodate the four active-space electrons, and two $S = 0$ spin configurations. Therefore, the most-general type of valence-bond structure that can be obtained from such a treatment corresponds approximately to $(\mathbf{X} : \mathbf{R} : \mathbf{Y})^{(-)}$. Depending on the nature of the orbitals, this structure can approximate to any of $(^{\bullet}\mathbf{X} \bullet \mathbf{R} : \mathbf{Y})^{(-)}$, $(\mathbf{X} : \mathbf{R} \bullet \mathbf{Y}^{\bullet})^{(-)}$, $^{\bullet}\mathbf{X} \bullet \mathbf{R} \bullet \mathbf{Y}^{\bullet})^{(-)}$, $\mathbf{X}^{\bullet}\ \mathbf{R}:^{(-)}\ \mathbf{Y}^{\bullet}$ (i.e. $\dot{\mathbf{X}}\ \ \mathbf{R}:^{(-)}\ \ \dot{\mathbf{Y}}$) and the reactant or product valence-bond structures.

With extended basis sets, eight spin-coupled delocalized orbitals (four for each of the reactant-like and product-like complexes) could be constructed, and used to help accommodate at least the ground-state valence-bond mechanism of Figure 21-4. (For a symmetrical 4-electron 3-centre bonding unit with a minimal basis set, use of delocalized orbitals introduces redundancies.)

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22. D.L. Cooper and P.B. Karadakov, Int. Rev. Phys. Chem. **28**, 169 (2009).

Chapter 22 Free-Radical and Spin-Paired Diradical Reactions

22-1 Types of Free Radical Reactions

Free radicals, with odd numbers of electrons, must have at least one orbital (atomic or molecular) singly occupied. In the previous chapters, we have met with the following types of reactions between univalent free radicals:

(a) $\dot{\mathbf{A}} + \dot{\mathbf{B}} \rightarrow \mathbf{A}\!-\!\!-\!\mathbf{B}$

(b) $\dot{\mathbf{Y}} + \dot{\mathbf{A}} \cdot \dot{\mathbf{B}} \rightarrow \mathbf{Y}\!-\!\!-\!\mathbf{A} \cdot \dot{\mathbf{B}}$

(c) $\dot{\mathbf{A}} \cdot \dot{\mathbf{B}} + \dot{\mathbf{C}} \cdot \dot{\mathbf{D}} \rightarrow \dot{\mathbf{A}} \cdot \mathbf{B}\!-\!\!-\!\mathbf{C} \cdot \dot{\mathbf{D}}$

For (a), the **A** and **B** are two species (atomic or molecular), each of which has an unpaired electron localized essentially in an atomic orbital. If the atomic orbitals overlap, then the unpaired electrons may be spin-paired (or antiferromagnetically coupled) to form a covalent bond if the electronegativities of A and B are not too dissimilar. Examples of this type of reaction are $\mathbf{H}+\mathbf{H} \rightarrow \mathbf{H}_2$, and $\mathbf{CH}_3+\mathbf{CH}_3 \rightarrow \mathbf{C}_2\mathbf{H}_6$.

Each of the $\dot{\mathbf{Y}}$ and $\dot{\mathbf{A}} \cdot \dot{\mathbf{B}}$ reactants of (b) has one unpaired electron; **Y** is an atomic or molecular species with its unpaired electron occupying an atomic orbital. The molecular species $\dot{\mathbf{A}} \cdot \dot{\mathbf{B}}$ has a Pauling "3-electron bond". In Section 3-6, we have found that the Pauling "3-electron bond" may be described *either* as two bonding electrons + one antibonding electron, *or* as two "non-bonding" electrons with parallel spins + one bonding electron with opposed spin. The bonding and antibonding electrons occupy molecular orbitals, and the non-bonding electrons occupy atomic orbitals. In the reactions of (b), the unpaired

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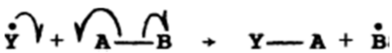
Lecture Notes in Chemistry 90, DOI 10.1007/978-3-319-16676-6_22

electron of atom **Y** spin-pairs with the unpaired antibonding electron of **AB** to generate the "increased-valence" structure $\mathbf{Y}—\mathbf{A}\cdot\dot{\mathbf{B}}$. We indicate again that because the **Y-B** bonding (———) in this structure is weak when **Y** and **B** are non-adjacent atoms, we have for convenience of representation omitted it. Some examples of this type of free radical reaction, which we have discussed in Chapter 11, are F + NO → FNO and $F + O_2 \rightarrow FO_2$.

We have also discussed numerous examples of reactions of type (c), namely reactions in which both reactants have a Pauling "3-electron bond". Representative examples are $2NO \rightarrow N_2O_2$, $NO + NO_2 \rightarrow N_2O_3$, $2NO_2 \rightarrow N_2O_4$ and $2ClO \rightarrow Cl_2O_2$.

A fourth type of free radical reaction, in which one reactant molecule has an unpaired electron that occupies an atomic orbital, and the other species has an electron-pair bond, is customarily represented as (d).

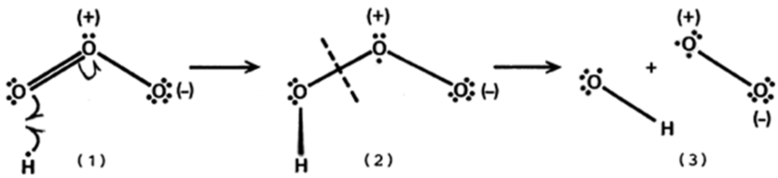
(d) 

We shall now examine other aspects of the reactions (b)-(d). In particular, we shall show how the products of these reactions may themselves sometimes involve electronic rearrangements and decompositions.

22-2 R + O₃ → RO + O₂, with R = H, Cl, and NO

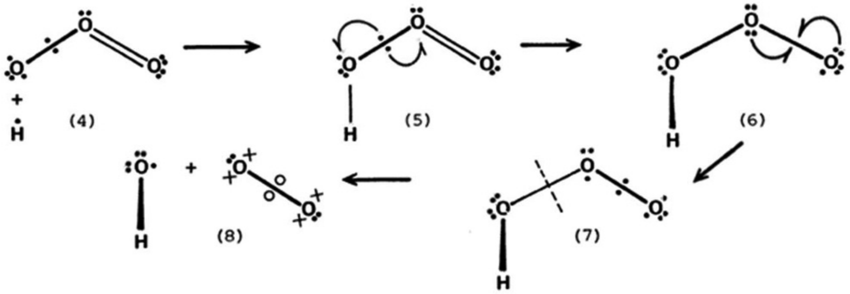
Reactions between O_3 and univalent radicals – in particular, chlorine atoms and NO – are of ecological concern, because it has been suggested that they might lead to some destruction of the protective ozone layer in the stratosphere[1,2]. These reactions generate univalent free radicals, for example ClO and NO_2 [1,2]. To examine how electronic reorganization might proceed for these types of reactions, we shall initially examine mechanisms for the reaction of ozone with hydrogen atoms, using both standard Lewis and "increased-valence" structures.

For O_3 the standard Lewis structures are of type (**1**), with no unpaired-electrons. If we use it to represent the electronic structure, it is necessary to formulate the reaction of O_3 with a hydrogen atom according to mechanism (d) of Section 22-1, as follows:



The electronic reorganization displayed in structures (**1**)-(**3**) does not make clear why the HO-O bond of structure (**2**) should break homolytically, and retains formal charge separation on the two oxygen atoms in structure (**3**).

An "increased-valence" mechanism for the reaction does not have these disadvantages[3]. The "increased-valence" structure for O_3, namely (**4**) (Section 11-6)



may be generated (Fig. 12-1) from the standard Lewis structure (**1**) by delocalizing two lone-pair π- and $\bar{\pi}$-electrons from the terminal O^- into two bonding $O^- - O^+$ orbitals. In the reaction steps of structures (**4**)-(**8**), the atomic formal charges for all of the valence-bond structures can remain unaltered at each stage. The mechanism involves the following electronic reorganization:

(a) A hydrogen atom forms a weak O-H bond with O_3 by spin-pairing some of its electron charge with the equivalent fractional unpaired-electron charge[i] that is present on a terminal oxygen atom of "increased-valence" structure (**4**). "Increased-valence" structure (**5**) is thereby generated for HO_3.

(b) The two electrons that form the 1-electron π-bonds of structure (**5**) may be transferred from the O-O bond region into the partially occupied oxygen atomic orbitals of structure (**5**). The 1-electron transfers that are indicated in (**5**) generate the valence-bond structure (**6**) with a strengthened O-H single bond and the odd-electron located on the terminal oxygen atom. In structure (**6**), we have obtained a hydrogen-peroxide type structure for the H-O-O linkage.

---

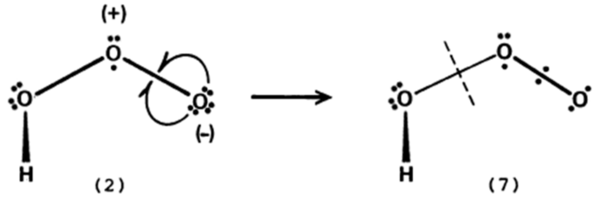
[i] In structure (**5**), an "increased-valence" 5-electron 4-centre bonding unit is present, namely **H—O · O—O**. This structure summarizes resonance between the Lewis structures H—O $\ddot{O}$ $\dot{O}$, $\dot{H}$ $\ddot{O}$ O—O , H O O O, H O O O, H O O O and H O O O if a valid $S = 1/2$ spin wave-function is constructed according to Eqn. (15-9). These structures show that much of the remainder of the hydrogen odd-electron charge is used to form "long" H-O bonds between non-adjacent atoms.

(c) "Increased-valence" may be restored by delocalizing oxygen lone-pair electrons into the vacant O-O bonding π-orbitals, as is done in structure (**6**). The resulting "increased-valence" structure (**7**) has a weakened O-O bond between the H-O and O-O linkages.

(d) The weak O-O bond of structure (**7**) can now break to release the HO and O_2 products.

Although the reaction proceeds by means of a concerted mechanism, it is convenient to display a series of steps in the valence-bond representation of the electronic reorganization.

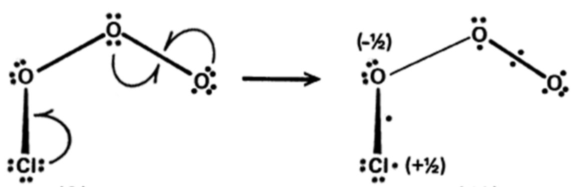
The HO_3 structure (**2**) can also be used to generate "increased-valence" structure (**7**), i.e. we may write



(2) (7)

For structure (**8**), its O_2 component corresponds to that which is appropriate for the S = 1 spin ground-state. It may be deduced[3] that the O_2 ground-state must be generated whenever the decomposition reaction $RO_2 \rightarrow R + O_2$ can occur. No evidence has been obtained[4] for the formation of an O_2 excited state for the reaction $X + O_3 \rightarrow XO + O_2$ when X = H or NO. It has therefore been concluded that the ${}^3\Sigma_g^-$ ground-state is generated[4], in accordance with the earlier deduction[3].

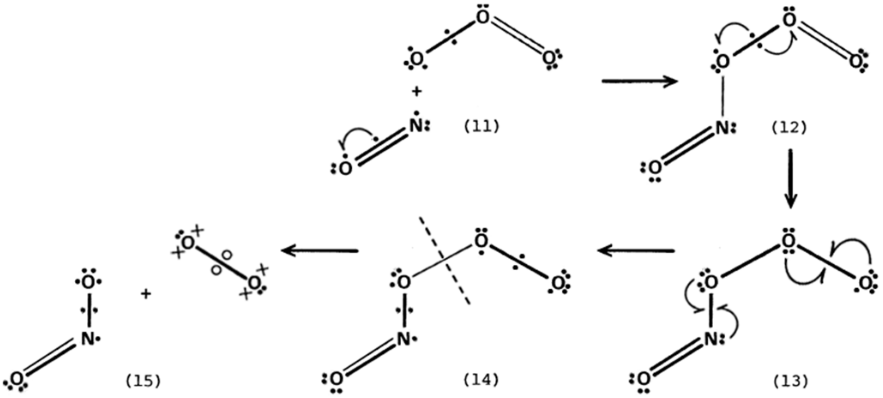
The reaction $Cl + O_3 \rightarrow ClO + O_2$ involves a similar type of electronic reorganization, but with the possibility for an additional electron delocalization step to occur at stage (**6**), namely that of structure (**9**).



(9) (10)

When the O-O bond of "increased-valence" structure (**10**) breaks, the ClO is generated with a Pauling "3-electron bond" (cf. Section 4-7).

The "increased-valence" formulation of the reaction steps for $NO + O_3 \rightarrow NO_2 + O_2$ involves the structures (**11**)-(**15**),



(11) (12) (13) (14) (15)

The delocalization of a nitrogen lone-pair electron of structure (**13**) into an N-O bonding orbital has two effects. It assists with the weakening of the adjacent $\mathbf{O}—\mathbf{O}$ bond, and generates a fractional unpaired-electron charge on the nitrogen atom. The results of electron spin resonance measurements[5] show that such a charge is present in the free NO_2 molecule. The "increased-valence" structure of (**15**) for NO_2 has been described previously in section 11-8.

22-3 Reactions of O_2 with Fe(II) Porphyrin Complexes

In Section 18-4, we have provided an "increased-valence" description of the bonding of O_2 to the Fe(II) porphyrin complex, hemoglobin. For each $Fe(II)O_2$ linkage of the ground-state of oxyhemoglobin, the O_2 ground-state is bonded to the intermediate-spin Fe(II) in the "increased-valence" structure. A number of other Fe(II) porphyrin complexes are irreversibly oxidized by O_2 to form oxo-bridged dimers[6]. One reaction scheme that has been proposed[6] is that of (e).

$$\begin{aligned}
&Fe(II) + O_2 \rightarrow Fe(II)O_2 && (Fe(III)O_2^-) \\
&Fe(II)O_2 + Fe(II) \rightarrow Fe(II)O_2Fe(II) && (Fe(III)O_2^{2-}Fe(III)) \\
&Fe(II)O_2Fe(II) \rightarrow 2Fe(II)O && (Fe(III)O^-) \qquad \text{(e)} \\
&Fe(II)O + Fe(II) \rightarrow Fe(II)OFe(II) && (Fe(III)O^{2-}Fe(III))
\end{aligned}$$

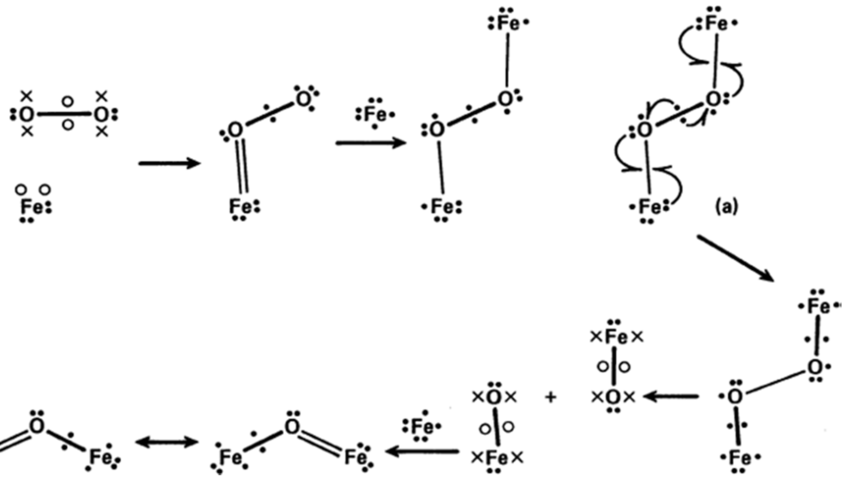


Figure 22-1: "Increased-valence" mechanism for oxidation of Fe(II) porphyrin complexes by O_2 to form μ-oxo bridged dimers.

(Alternative formulations for the oxidation states of the products of each reaction step are given in parentheses.) An electronic mechanism[7] for these reaction steps[i] is displayed in Fig. 22-1.

Ground-state O_2 and intermediate-spin Fe(II) are involved as reactants at the appropriate stages of the reaction scheme. In "increased-valence" structure (**a**), electrons are transferred either from O-O bonding molecular orbitals into oxygen atomic orbitals, or from Fe(II) and oxygen atomic orbitals into Fe(II)-O bonding molecular orbitals. (Overlap considerations require that hybridization changes must occur at the oxygen atoms in order that the delocalization of the oxygen non-bonding electrons into the Fe(II)-O molecular orbitals may proceed.) Because the intermediate-spin Fe(II) and $Fe(II)O_2$ reactants of the second step have $S = 1$ and $S = 0$ spin quantum numbers respectively, the $Fe(II)O_2Fe(II)$ species that is formed must have an $S = 1$ spin-state in order that spin be conserved. On decomposition of the $Fe(II)O_2Fe(II)$ complex, the Fe(II)O radicals are predicted to be generated with $S = 1$ spin-states[7]. However, an $S = 0$ spin-state is appropriate for the Fed(II)OFe(II) oxo-bridged dimer, as it is for the isoelectronic $Fe(II)O_2$ and this state may be generated through the reaction of an Fe(II)O ($S = 1$) radical with an intermediate-spin Fe(II) ($S = 1$).

[i] The mechanism of Ref. 8 involves additional steps that include $Fe(II)O + Fe(II)O_2Fe(II) \rightarrow Fe(II)OFe(II) + Fe(II)O_2$, $Fe(II)O_2 \rightarrow Fe(II) + O_2$, and $Fe(II)O + Fe(II)O_2 \rightarrow Fe(II)OFe(II) + O_2$.

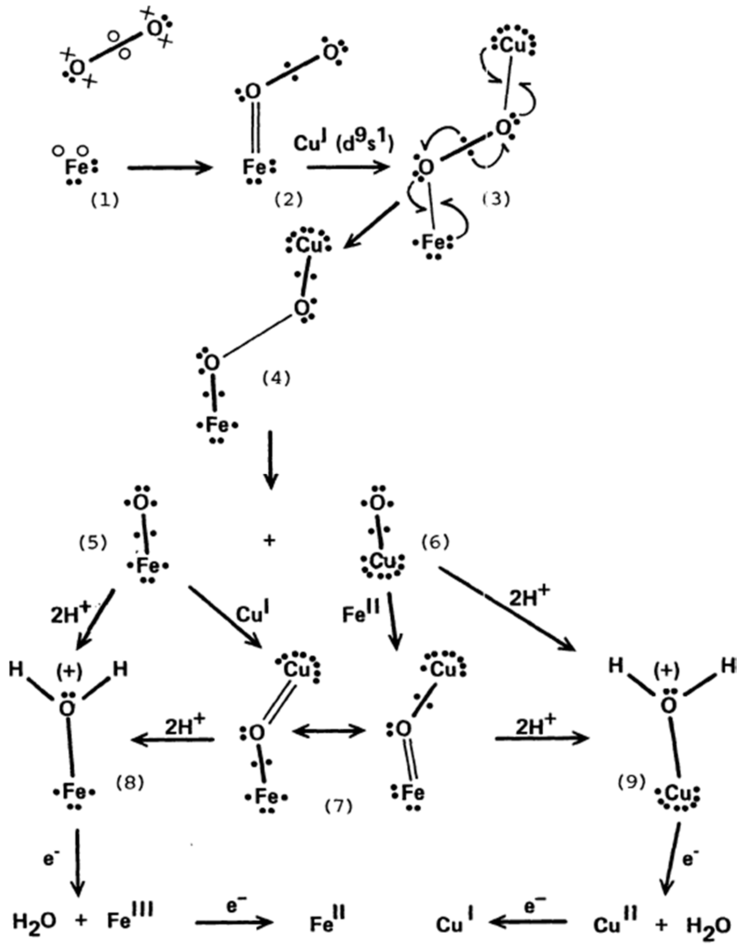


Figure 22-2: Cytochrome c oxidase catalysis of $4H^+ + 4e + O_2 \rightarrow 2H_2O$.

A similar type of electronic mechanism can also be formulated for the cytochrome c oxidase catalysis of the reaction $4H^+ + 4e + O_2 \rightarrow 2H_2O$. With some modifications, we shall follow the mechanism proposed by Reed and Landrum[9].

On reduction of Fe(III) and Cu(II) to Fe(II) and Cu(I), the Fe(II) can bind ground-state O_2 to form an Fe(II)O_2 complex with "increased-valence" structure (**2**) of Fig. 22-2. Cu(I) with a $3d^9 4s^1$ configuration can then bind to the Fe(II)O_2 complex to form the proposed "μ-peroxo dimer"[9], with "increased-valence" structure (**3**) (cf. structure (a) of Fig. 22-1 for the Fe(II)O_2Fe(II) complex). In structure (**3**), the antibonding π* electrons of O_2 are spin-paired with an unpaired electron for each of the S = 1 spin-states for Fe(II) and Cu(I). Electronic reorganization can then proceed as is shown in structure (**3**) to increase the number of bonding electrons, and simultaneously to generate an O-O bond-number which is less than unity in the resulting "increased-valence" structure (**4**). On breaking of the weakened O-O bond, the Fe(II)O and Cu(I)O radicals of structures (**5**) and (**6**) can then react with either Cu(I) or Fe(II) to form the μ-oxo Fe(II)OCu(I) complex (**7**), or $2H^+$ to form the $\mathrm{Fe(III)-OH_2^+}$ and $\mathrm{Cu(II)-OH_2^+}$ of structures (**8**) and (**9**). One-electron reduction of each of the latter species generates Fe(III), Cu(II) and H_2O. The Fe(II)OCu(I) complex corresponds to the $\mathrm{Fe(III)} \leftarrow \mathrm{O^{2-}} \rightarrow \mathrm{Cu(II)}$ resting state of the enzyme proposed by Reed and Landrum.

The $\mathrm{Fe(III)} \leftarrow \mathrm{O^{2-}} \rightarrow \mathrm{Cu(II)}$ may also react with H^+ to produce the $\mathrm{Fe(III)-OH_2^+}$ and $\mathrm{Cu(II)-OH_2^+}$ of structures (**8**) and (**9**). Whether or not structure (**7**) is formed directly or bypassed via structures (**5**) and (**6**) → (**8**) and (**9**) has yet to be ascertained. The essential point is that in the valence-bond representation for the mechanism, easily-visualized electronic reorganizations lead to the conversion of reactants into products, and these are achieved by utilizing the Pauling "3-electron bond" structure of (**1**) for the O_2 ground state.

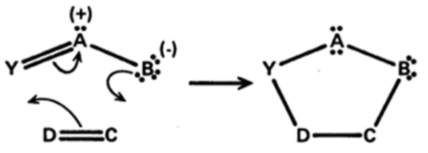
Consideration of the reactions of Sections 22-2 and 22-3, show that many diamagnetic molecules that do not have a net number of unpaired electrons may react as though they were free radicals. This is theoretically possible whenever we may construct an "increased-valence" structure for a molecule, with one or more "increased-valence" bonding units of the types (**16**) and (**17**).

(16) (17)

In these structures, fractional unpaired electron charges on the **B** atom of (**16**) and the **A** and **D** atoms of (**17**) can be made available for weak covalent bonding with the fractional unpaired-electron charge of another entity. In the following section, we shall discuss some radical-type reactions between a pair of molecules, neither of which is a free radical with an odd number of electrons.

22-4 "1,3 Dipolar" (or "Zwitterionic Diradical Hybrid") Cycloaddition Reactions

A large class of organic reactions that lead to the formation of five-membered heterocyclic molecules, have been designated as "1,3 dipolar" cycloaddition reactions[10]. Huisgen[10] has defined the "1,3 dipole" to be 'a species which is represented by zwitterionic resonance structures (i.e. the standard Lewis octet structures) and which undergoes 1,3 cycloadditions to a multiple bond system, the "dipolarophile"', as in structures (**18**) and (**19**).



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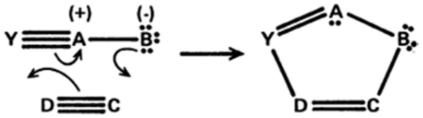
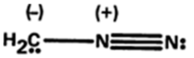


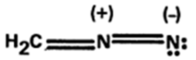
(19)

In Ref. 10c, “1,3 dipoles” with C, N and O centres are classified, with their zwitterionic structures displayed. “Increased-valence” structures for many of them are displayed in Ref. 11.

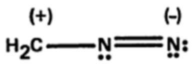
The addition of diazomethane to methyl acrylate to form 1-pyrazoline is an example of a “1,3 dipolar” cycloaddition reaction[10]. For CH_2N_2, the zwitterionic octet structures are (**20**) and (**21**).



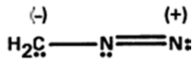
(20)



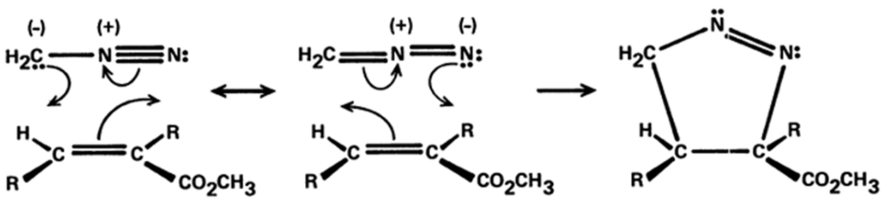
(21)



(22)



(23)



(24) (25)

These structures, together with the sextet structures (**22**) and (**23**) are usually assumed to be the important valence-bond structures for the construction of the electronic mechanism for cycloaddition[10]. For the latter two structures, the terminal atoms are both nucleophilic (–) and electrophilic (+), and it is these properties of the “1,3 dipole” that are often assumed to be implicated for the electronic mechanism of the cycloaddition. As CH_2N_2 approaches the methyl acrylate, one set of π-electron atomic orbitals of CH_2N_2 overlaps with the π-orbitals of methyl acrylate (see Fig. 22-3).

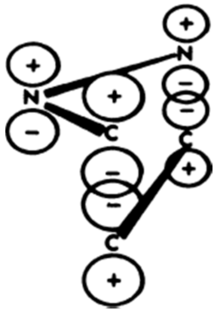
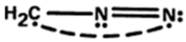
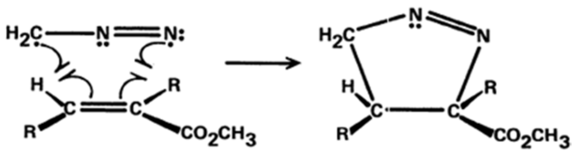


Figure 22-3: Overlapping π-electron atomic orbitals for "1,3 dipolar" cycloaddition reaction.and the electronic reorganization is assumed to proceed according to structures (**24**) → (**25**). A concerted mechanism is concomitant with this valence-bond description, with the new C-C and C-N bonds being formed synchronously.

Although zwitterionic octet structures have been used[10b,c] to represent the reaction mechanism, the assumption that the electrophilic nature of either terminal atom of the 1,3-dipole is also utilized implies that the sextet valence-bond structures must become important as the reaction proceeds. However, for the ground-state of free CH_2N_2, the electroneutrality principle suggests that these structures should not have large weights. Each of them has one fewer covalent bonds than has either of the zwitterionic structures, and a greater spatial separation of the + and – formal charges. The absence of formal charges in the "long-bond" structure (**26**)



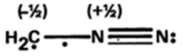
(26)



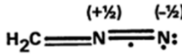
(27) (28)

would suggest that it should have a rather larger weight than has either of the structures (**22**) and (**23**). Bond-eigenfunction coefficients of 0.31, 0.23, 0.05, 0.10 and 0.38 for the valence-bond structures (**20**)-(**23**) and (**26**) have been calculated by Roso[12]. Hiberty and Le-Forestier[13] have calculated weights of 0.16, 0.41, 0.01, 0.04 and 0.28 for these structures. Both sets of calculations support the expectation that structure (**26**) should be a more important Lewis valence-bond structure for the ground-state than are the sextet structures. If it is assumed that this is also the case as the reaction with methyl acrylate proceeds, then we may formulate the cycloaddition mechanism according to[12,14] (**27**) → (**28**).

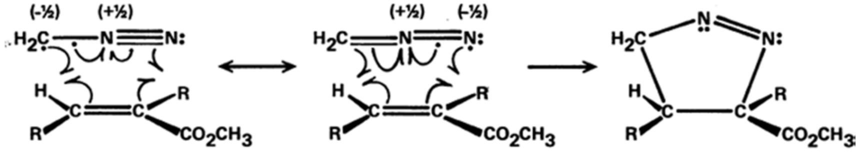
Of course, structure (**26**) is only one of the important valence-bond structures, and a better description of the electronic structure of CH_2N_2 is obtained by using[11,12] the "increased-valence" structures (**29**) and (**30**), which summarize resonance between the zwitterionic structures (**20**) and (**21**), and the "long-bond" structure (**26**) if a Heitler-London type formulation of wave-functions for electron-pair bonds is used. Thus, by using structures (**29**) and (**30**), we may construct the concerted mechanism of cycloaddition according to structure (**31**), and redesignate "1,3 dipolar" molecules as "zwitterionic diradical hybrids"[11,12,14].



(29)



(30)



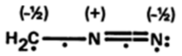
(31) (28)

The electron-spin theory which is appropriate for the "increased-valence" mechanism of "1,3 dipolar" cycloaddition is described in some detail in Ref. 11, where the importance of the "long-bond" structures (such as (**26**)) for the electronic structure and reactivity of any "1,3 dipolar" molecule has also been stressed. The latter conclusion has received support from a number of valence-bond calculations[12,13,15], and Goddard and Walch[16] have used structure (**26**) alone to represent the electronic structure of CH_2N_2.

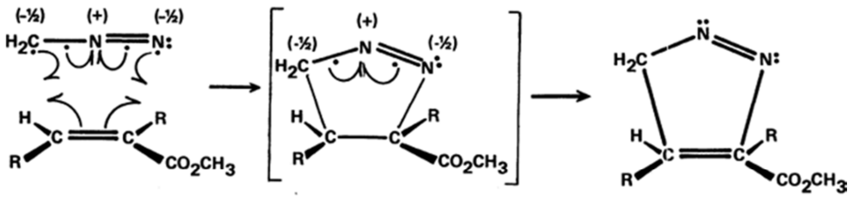
For the transition state of the "1,3 dipolar" cycloaddition, there are six electrons distributed amongst the five overlapping atomic orbitals of Fig. 22-3, for example. In Section 13-6, we have used "increased-valence" structure (**32**)

Y——A • B • C——D

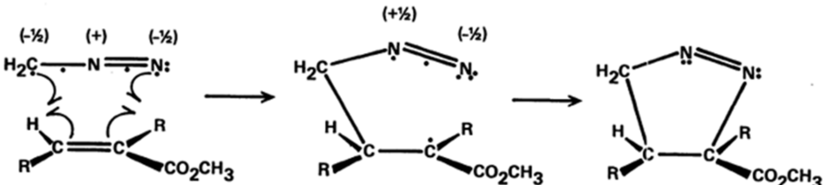
(32)



(33)



(34) (35) (36)



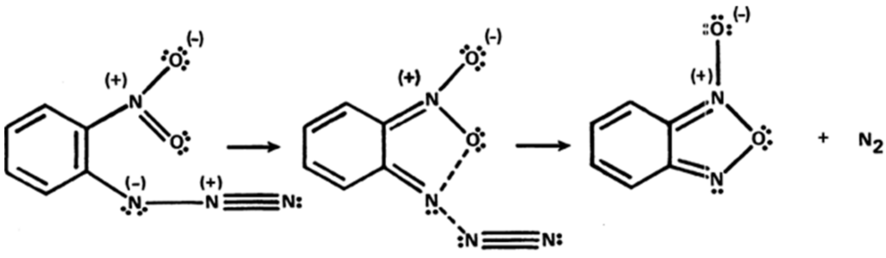
(37) (38) (39)

here to represent the electron distribution for a 6-electron 5-centre bonding unit. One way to obtain this type of "increased-valence" structure in the transition state for the "1,3 dipolar cycloaddition" involves the utilization of a Linnett non-paired spatial orbital structure to represent the electronic structure of the "1,3 dipole". Thus for CH_2N_2, the Linnett structure is (**33**)[17], and the concerted mechanism for the cycloaddition can be formulated[11,12,14] via structures (**34**), (**35**) and (**36**). In structure (**35**), there is an "increased-valence" bonding unit of type (**32**). Firestone used structure (**33**) to formulate the two-step mechanism of (**37**) → (**38**) →(**39**), with only one O-C bond formed initially between the two reactants[17].

Molecular orbital studies of 1,3-dipolar cycloaddition reactions are discussed in Ref. 18.

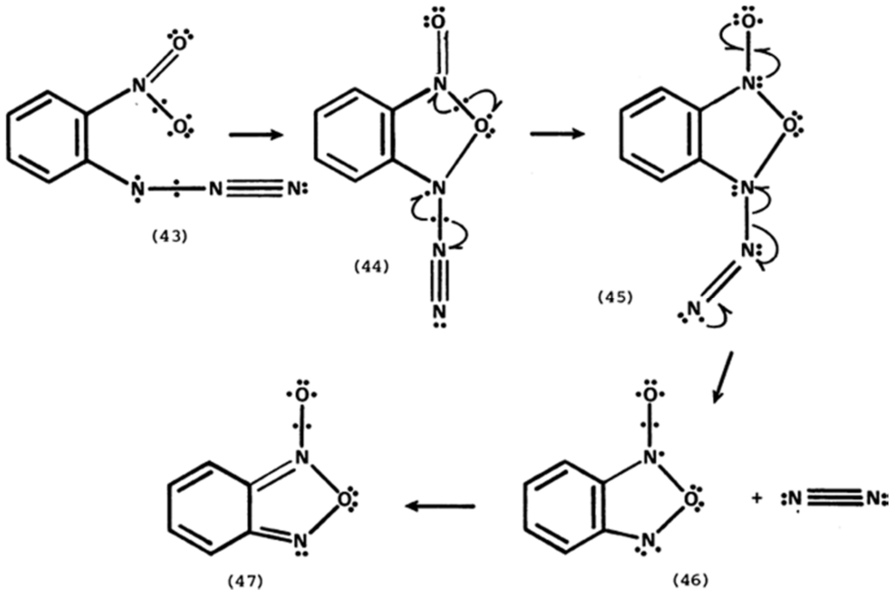
22-5 Thermal Decomposition of o-Nitrophenylazide

o-Nitrophenylazide decomposes thermally to give benzofurazan[19,20]. Using Lewis structures, the mechanism has been formulated as follows:



(40) (41) (42)

From structure (**40**), we may generate the increased-valence structure (**43**), which must be more stable than structure (**40**). Using structure (**43**), we may formulate the reaction steps of (**43**) → (**44**) → (**45**) → (**46**) → (**47**). In structure (**46**) we have unpaired π-electron charges on each nitrogen atom, and these may spin-pair with the two electrons of the adjacent C-C π-bond to generate structure (**47**). A justification for this is the assumption that structure (**47**) with two C-C and two (fractional) C-N π-bonds between adjacent atoms should be more stable than structure (**46**) with three C-C π-bonds between adjacent atoms.



By using “increased-valence” structures where appropriate for the reactants of this chapter, it has not been necessary to reorganize the electronic structures of the reactants in order to get the reactions started. For most of the reactions, the atomic formal charges have been able to remain constant throughout the course of the valence-bond formulations of the reactions. When bond-breaking has occurred, this has often been a consequence of the development of an “increased-valence” bonding unit by delocalizing a lone-pair electron into a two-centre bonding molecular orbital.

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Addendum Chapter 22

1.

In Refs. 21-24, increased-valence formulations are presented for:

a) metal-ion catalysed dehydrogenation reactions with O_2 and azide compounds as oxidants.

b) the four electron reduction of O_2 to H_2O in acid and alkaline solutions;

c) the reaction of HbO_2 with NO to form metHb + NO_3^-;

d) the formation and decomposition of N_2O_5.

2.

Further consideration for the singlet-diradical mechanism for 1,3-dipolar cycloadditions is provided in Refs. 25a-c. It is to be noted that, as discussed for S_N2 reactions in the Chapter 21 Addendum, a constribution from the singlet-diradical structure to the valence-bond resonance scheme is needed in order that the cycloaddition reaction be concerted. This occurs in the valence-bond formulations of both (**31**) → (**28)** and (**34**) →(**36**), but not for (**24**) → (**25**).

Spin coupled valence-bond formulations of the cycloaddition involve one four-orbital configuration for the active space electrons[26], and use $HC{\equiv}N{=}O$ and $H_2C{=}N{\equiv}N$ as the valence –bond structures for HCNO and CH_2NN.

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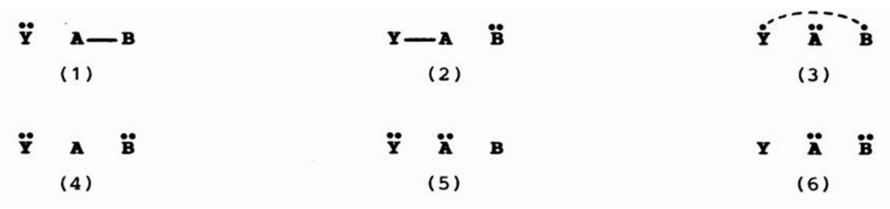
Chapter 23 Some Comparisons of Types of Wave-Funcions for 4-Electron 3-Centre Bonding Units

With the simplest form of "increased-valence" theory, we have been concerned with the "increased-valence" structure $\mathbf{Y}—\mathbf{A}\cdot\dot{\mathbf{B}}$, which summarizes resonance between the Lewis structures $\mathbf{Y}—\mathbf{A}\ \ddot{\mathbf{B}}$ and $\dot{\mathbf{Y}}\ \ \ddot{\mathbf{A}}\ \ \dot{\mathbf{B}}$, the latter structures having electron-pair bonds between adjacent and non-adjacent atoms respectively.

We shall now examine in more detail some wave-functions for "increased-valence" structures, and compare them with wave-functions that may be constructed for standard Lewis and Linnett non-paired spatial orbital structures, as well as with the delocalized molecular orbital wave-functions.

23-1 Complete Valence-Bond Resonance

For a triatomic electron-excess system, with four electrons and three over-lapping atomic orbitals, there are six Lewis structures in which all electrons are singlet ($S = 0$) spin-paired, either through double occupation of an atomic orbital, or by electron-pair bond formation between two electrons that singly-occupy different atomic orbitals with opposite spins. These valence-bond (or canonical) structures are (**1**)-(**6**).



R.D. Harcourt, *Bonding in Electron-Rich Molecules*,
Lecture Notes in Chemistry 90, DOI 10.1007/978-3-319-16676-6_23

We note that for paramagnetic (S = 1 spin) excited states, we would need to study the structures (**7**), (**8**) and (**9**), in which the unpaired electrons have parallel spins (with $S = S_z = 1$).

(7) (8) (9)

Because each of the structures (**1**)-(**6**) represents an S = 0 spin-paired electron distribution, we can form linear combinations of their wave-functions, and write

$$\Psi = C_1\Psi_1 + C_2\Psi_2 + C_3\Psi_3 + C_4\Psi_4 + C_5\Psi_5 + C_6\Psi_6 \tag{1}$$

If we choose the coefficients C_1 to C_6 so that the energy of Ψ is minimized, we shall obtain six linear combinations, one of which we shall designate as Ψ(best). Its energy is such that no other linear combination of Ψ_1 to Ψ_6 can generate a lower energy. Alternatively, we may say that this energy is the lowest that can arise from resonance between the valence-bond structures (**1**)-(**6**). Each of these six structures is stabilized to a maximum extent by resonance with the other five structures.

In Slater determinantal form, the wave-functions Ψ_1 to Ψ_6 are those of Eqn.(2).

$$\begin{aligned}
&\Psi_1 = |y^\alpha y^\beta a^\alpha b^\beta| + |y^\alpha y^\beta b^\alpha a^\beta| \;, \;\Psi_2 = |b^\alpha b^\beta y^\alpha a^\beta| + |b^\alpha b^\beta a^\alpha y^\beta|, \\
&\Psi_3 = |a^\alpha a^\beta y^\alpha b^\beta| + |a^\alpha a^\beta b^\alpha y^\beta|, \;\Psi_4 = |y^\alpha y^\beta b^\alpha b^\beta|, \\
&\Psi_5 = |y^\alpha y^\beta a^\alpha a^\beta|, \;\Psi_6 = |a^\alpha a^\beta b^\alpha b^\beta|
\end{aligned} \tag{2}$$

The wave-functions for the **A — B, Y — A** and $\overset{\frown}{\mathbf{Y}\quad\mathbf{B}}$ bonds of Ψ_1, Ψ_2 and Ψ_3 are of the Heitler-London type, i.e. they involve two singly-occupied atomic orbitals in which the electrons have opposite spins. In Section 3-7 we have shown that the Heitler-London wave-functions for the electron-pair bond of H_2 may be expressed as $|s_A^\alpha s_B^\beta| + |s_B^\alpha s_A^\beta|$, in which s_A and s_B are the two hydrogen atom 1s atomic orbitals, and α and β are the spin wave-functions. This type of bond wave-function occurs in Ψ_1, Ψ_2 and Ψ_3.

For systems such as H_3^-, O_3, NO_2^-, and HCO_2^-, the **Y** and **B** are symmetrically equivalent hydrogen and oxygen atoms. Consequently, Ψ_1 and Ψ_2 are degenerate, as are Ψ_5 and Ψ_6. Because of this degeneracy, we may form the linear combinations $\Psi_1+\Psi_2$, $\Psi_1-\Psi_2$, $\Psi_5+\Psi_6$ and $\Psi_5-\Psi_6$. Of these, only the symmetric functions $\Psi_1+\Psi_2$ and $\Psi_5+\Psi_6$ can interact with Ψ_3 and Ψ_4. We may therefore construct the linear combination

$$\Psi(\text{best}) = C_{\mathbf{I}}\Psi_{\mathbf{I}} + C_{\mathbf{II}}\Psi_{\mathbf{II}} + C_{\mathbf{III}}\Psi_{\mathbf{III}} + C_{\mathbf{IV}}\Psi_{\mathbf{IV}} \tag{3}$$

in which $\Psi_{\mathbf{I}} = \Psi_1+\Psi_2$, $\Psi_{\mathbf{II}} = \Psi_3$, $\Psi_{\mathbf{III}} = \Psi_4$, $\Psi_{\mathbf{IV}} = \Psi_5+\Psi_6$.

Linnett and his co-workers[1-6] have calculated the Ψ(best) for the four π-electrons of HCO_2^-, NO_2^-, O_3 and $C_3H_5^-$, and four σ-electrons of H_3^-. The coefficients of $\Psi_{\mathbf{I}}$ to $\Psi_{\mathbf{IV}}$ for each of these functions are reported in Table 23-1. To help compare the relative magnitudes of the coefficients, we have recalculated them *approximately* so that they pertain for normalized $\Psi_{\mathbf{I}}$ to $\Psi_{\mathbf{IV}}$. To do this, we have multiplied[i] $C_{\mathbf{I}}$ by 2, $C_{\mathbf{II}}$ and $C_{\mathbf{IV}}$ by $\sqrt{2}$, and $C_{\mathbf{III}}$ by unity. For H_3^-, the reported coefficients refer to approximately normalized basis functions[5]. The (approximately) normalized coefficients are shown in parentheses.

In Table 23-2, the energies of $\Psi_{\mathbf{I}}$ to $\Psi_{\mathbf{IV}}$, calculated relative to that of Ψ(best), are reported.

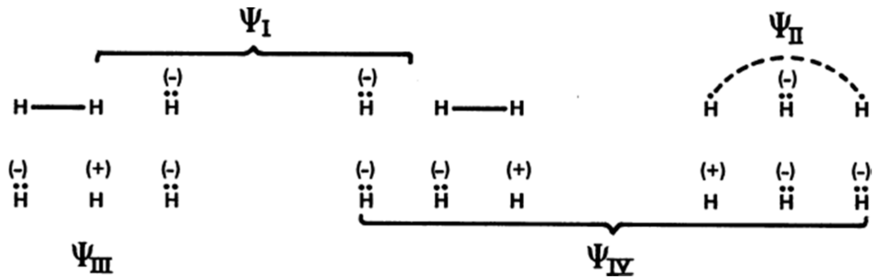


Figure 23-1: Canonical structures for H_3^-.

In Fig. 23.1, we show the canonical structures and formal charges that correspond to $\Psi_{\mathbf{I}}$ to $\Psi_{\mathbf{IV}}$ for H_3^-. The formal charges are also those for the corresponding valence-bond structures for NO_2^-, HCO_2^- and $C_3H_5^-$. The corresponding canonical structures for O_3 are displayed in Table 2-1.

The coefficients of Table 23-1 indicate that $\Psi_{\mathbf{I}}$ and $\Psi_{\mathbf{II}}$ are the most important functions for each system. Their energies in Table 23-2 are substantially lower than are those for $\Psi_{\mathbf{III}}$ and $\Psi_{\mathbf{IV}}$. Functions $\Psi_{\mathbf{I}}$ and $\Psi_{\mathbf{II}}$ represent the valence-bond structures that have an extra covalent bond (normal or long), smallest formal

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[i] We have omitted π-electron overlap integrals from the normalizing constants.

charge separations, and best electron charge correlation (i.e. best spatial separation

Table 23-1: Coefficients of C_I, C_{II}, C_{III} and C_{IV} for "best" valence-bond wave function. The values in parentheses are those for (approximately) normalized Ψ_I to Ψ_{IV}.

	C_I	C_{II}	C_{III}	C_{IV}
O_3 (4π)	0.351 (0.70)	0.390 (0.55)	0.124 (0.12)	0.028 (0.04)
H_3^- (4σ)	0.812 (0.81)	0.483 (0.48)	0.314 (0.31)	0.092 (0.09)
NO_2^- (4π)	0.306 (0.61)	0.391 (0.56)	0.185 (0.19)	0.070 (0.10)
HCO_2^- (4π)	0.273 (0.55)	0.415 (0.59)	0.168 (0.17)	0.078 (0.11)
$C_3H_5^-$ (4π)	0.318 (0.64)	0.304 (0.43)	0.195 (0.20)	0.045 (0.06)

of electrons and consequent reduction in interelectronic repulsion). Other studies for the numerous four π- or σ-electron systems[7-9], the eight π electrons of N_2O, CO_2, N_3^- and NO_2^+[10], and for ten σ-electrons of N_2O_4[11] also show that their low-energy canonical Lewis structures satisfy these requirements.

Table 23-2: Energies (in eV) of Ψ_I to Ψ_{IV} relative to Ψ(best).

	$C_3H_5^-$	NO_2^-	HCO_2^-
Ψ_I	1.94	4.93	5.6
Ψ_{II}	4.75	5.61	5.2
Ψ_{III}	8.90	16.72	16.77
Ψ_{IV}	16.04	23.21	22.56

23-2 Simple Molecular Orbital

For a symmetrical electron-excess system, the 3-centre molecular orbitals are $\psi_1 = \mathrm{y} + k_1\mathrm{a} + \mathrm{b}$, $\psi_2 = \mathrm{y} - \mathrm{b}$ and $\psi_3 = \mathrm{y} - k_3\mathrm{a} + \mathrm{b}$ (Section 2-3). We have assumed that the y, a and b atomic orbitals are oriented so that the overlap integrals S_{ya} and S_{ab} are both > 0. With respect to the **Y-A** and **A-B** bonds, ψ_1, ψ_2, and ψ_3 are respectively bonding, non-bonding and antibonding.

The molecular orbital configuration with lowest energy is $\Psi_1(\mathrm{MO}) = |\psi_1^\alpha\psi_1^\beta\psi_2^\alpha\psi_2^\beta|$. On substituting the LCAO forms of ψ_1 and ψ_2, we may expand $\Psi_1(\mathrm{MO})$ and express it as a linear combination[1-6,12] of the functions Ψ_I to Ψ_{IV}. Thus, we obtain

$$\Psi_1(\mathrm{MO}) = 2k_1\Psi_I - k_1^2\Psi_{II} + 4\Psi_{III} + k_1^2\Psi_{IV} \qquad (4)$$

with one variational parameter, k_1. Since Ψ(best) has three independent variation parameters, namely C_{I}, C_{II}, and C_{III}, with C_{IV} related to them through normalization, Ψ_1(MO) is a more-restricted function than is Ψ(best). Ψ_1(MO) also gives considerable weight to either or both Ψ_{III} and Ψ_{IV}, neither of which is important for the systems of Table 21-1.

In Table 23-3, some calculated energies for Ψ_1(MO) are reported; they are higher than the energies for Ψ(best).

Table 23-3: Energies (in eV) of VB, MO, IV and NPSO wave-functions relative to Ψ(best).

	$C_3H_5^-$	NO_2^-	HCO_2^-
VBHL(Ψ_1)	1.94	4.93	5.16
VBBO	3.01	5.92	5.82
MO	1.07	2.04	1.91
IVBO	0.99	1.91	1.82
IVHL	0.47	0.88	0.81
NPSO	0.41	0.59	0.80

23-3 Standard Valence-Bond Resonance

The standard valence-bond resonance formulation for an electron-excess system involves resonance between the standard Lewis structures (**1**) and (**2**), which have covalent bonds only between adjacent atoms, i.e. it is usual to write

$$\ddot{\mathbf{Y}}\quad \mathbf{A}\text{—}\mathbf{B} \;\leftrightarrow\; \mathbf{Y}\text{—}\mathbf{A}\quad \ddot{\mathbf{B}}$$

as in the Ψ_{I} of Fig. 23-1 for H_3^-.

For the **Y-A** and **A-B** bonds, we may use two types of wave-functions, namely (i) Heitler-London (HL) functions, and (ii) two-centre bond-orbitals (BO) of the type $\phi_L = y + ka$, $\phi_R = b + ka$ with $k > 0$.

Therefore, as wave-functions for the standard valence-bond resonance, we may write[1–5,10,12–14]

$$\text{(i)}\ \Psi(\mathrm{VBHL}) = |y^{\alpha}y^{\beta}a^{\alpha}b^{\beta}| + |y^{\alpha}y^{\beta}b^{\alpha}a^{\beta}| + |y^{\alpha}a^{\beta}b^{\alpha}b^{\beta}| + |a^{\alpha}y^{\beta}b^{\alpha}b^{\beta}| \equiv \Psi_{\mathrm{I}} \tag{5}$$

$$\text{(ii)}\ \Psi(\mathrm{VBBO}) = |y^{\alpha}y^{\beta}\phi_R^{\alpha}\phi_R^{\beta}| + |\phi_L^{\alpha}\phi_L^{\beta}b^{\alpha}b^{\beta}| = k\Psi_{\mathrm{I}} + 2\Psi_{\mathrm{III}} + k^2\Psi_{\mathrm{IV}} \tag{6}$$

We note that neither of these wave-function includes the "long-bond" function Ψ_{II}, and that Ψ(VBBO) overloads itself with the high-energy functions Ψ_{III} and

$\Psi_{\mathbf{IV}}$. In Table 23-3, neither Ψ(VBHL) nor Ψ(VBBO) has a low energy, and we may conclude that the standard valence-bond resonance does not give a suitable representation for the electronic structures of these systems.

23-4 Linnett Non-Paired Spatial Orbital

Valence-bond structure (**10**)

$$\dot{\mathbf{Y}} \cdot \mathbf{A} \cdot \dot{\mathbf{B}}$$

(10)

is the general non-paired spatial orbital (NPSO) structure for 4-electron 3-centre bonding[1-6,12,13] as occurs in the valence-bond structures  and $\overset{(-\frac{1}{2})}{\underset{\bullet}{\mathbf{H}}} \cdot \mathbf{H} \cdot \overset{(-\frac{1}{2})}{\underset{\bullet}{\mathbf{H}}}$ for O_3 and H_3^-. In structure (**10**), two electrons occupy y and b atomic orbitals, and two electrons occupy the two-centre bond orbitals $\phi_L = y + ka$ and $\phi_R = b + ka$ with $k > 0$.

Because the four electrons occupy different spatial orbitals, we may construct two singlet wave-functions, both with spin quantum numbers $S = S_Z = 0$. The details are described in Section 15-2 and it is possible to form linear combinations of these wave-functions[1-6,12]. For illustrative purposes here, the special linear combination that generates Eqn. (7),

$$\Psi(\text{NPSO}) = \left| y^{\alpha}\phi_L^{\beta}\phi_R^{\alpha}b^{\beta} \right| + \left| y^{\beta}\phi_L^{\alpha}\phi_R^{\beta}b^{\alpha} \right| \tag{7}$$

in which electrons that occupy spatially adjacent orbitals have opposite spins, is a satisfactory wave-function and this is the NPSO wave-function that we shall examine. In terms of the functions $\Psi_{\mathbf{I}}$ to $\Psi_{\mathbf{IV}}$, we may express it[1-6] as

$$\Psi(\text{NPSO}) = k\Psi_{\mathbf{I}} - k^2\Psi_{\mathbf{II}} + 2\Psi_{\mathbf{III}} \tag{8}$$

thereby showing that it includes the "long-bond" function $\Psi_{\mathbf{II}}$, and excludes the unimportant function $\Psi_{\mathbf{IV}}$. The opposite pertains for the Ψ(VBBO) of Section 23-3, and therefore we can understand why the Ψ(NPSO) of Table 23-3 generate much lower energies than do the Ψ(VBBO).

23-5 “Increased-Valence”

The general “increased-valence” structures are (**11**) and (**12**). As we have done so many times in this book, we may derive them from the standard Lewis structures (**2**) and (**1**) by delocalizing a **B** electron of structure (**2**) into a vacant **A-B** bonding orbital, and a **Y** electron of (**1**) into a vacant **Y-A** bonding orbital. Thus, we may write

(2) (11) (1) (12)

Above the arrowheads, we have indicated the orbitals that are involved in the delocalizations.

For the standard valence-bond resonance of Section 23-3, we have used two types of wave-functions for the electron-pair bonds, namely the Heitler-London and the bond-orbital functions. We may do the same for the “increased-valence” functions of this section[7,12-14]. If we assume that electrons which occupy spatially adjacent orbitals have opposite spins, we may write down the following Heitler-London and bond-orbital wave-functions for the resonance between the “increased-valence” structures of (**11**) and (**12**).

$$\Psi(\mathrm{IVHL}) = \left|y^{\alpha}a^{\beta}\phi_{R}^{\alpha}b^{\beta}\right| + \left|y^{\beta}a^{\alpha}\phi_{R}^{\beta}b^{\alpha}\right| + \left|b^{\alpha}a^{\beta}\phi_{R}^{\alpha}y^{\beta}\right| + \left|b^{\beta}a^{\alpha}\phi_{R}^{\beta}y^{\alpha}\right| = \Psi_{\mathrm{I}} - 2k\Psi_{\mathrm{II}} \tag{9}$$

$$\begin{aligned}\Psi(\mathrm{IVBO}) &= \left|\phi_{L}^{\alpha}\phi_{L}^{\beta}\phi_{R}^{\alpha}b^{\beta}\right| + \left|\phi_{L}^{\alpha}\phi_{L}^{\beta}b^{\alpha}\phi_{R}^{\beta}\right| + \left|\phi_{R}^{\alpha}\phi_{R}^{\beta}\phi_{L}^{\alpha}y^{\beta}\right| + \left|\phi_{R}^{\alpha}\phi_{R}^{\beta}y^{\alpha}\phi_{L}^{\beta}\right| \\ &= 3k\Psi_{\mathrm{I}} - 2k^{2}\Psi_{\mathrm{II}} + 4\Psi_{\mathrm{III}} + 2k^{2}\Psi_{\mathrm{IV}}\end{aligned} \tag{10}$$

Both Ψ(IVHL) and Ψ(IVBO) include the standard and “long-bond” structure wavefunctions Ψ_{I} and Ψ_{II}. In Table 23-3, the Ψ(IVHL) and the Ψ(NPSO) are the low-energy functions in each case, with Ψ(NPSO) being the slightly better function.

We may note that Ψ(MO) and Ψ(IVBO) of Eqs. (4) and (10) are similar wave-functions, and that their energies in Table 23-3 are very similar. This point has been discussed in more detail elsewhere[12].

23-6 “Improved” Ψ(IVBO) and Ψ(best)

In Sections 23-2–23-5, each of the Ψ(MO), Ψ(VBBO), Ψ(NPSO) and Ψ(IVBO) has one variational parameter (k_1 or k), i.e. one parameter that may be chosen so that the energy for each of these functions is minimized. Therefore, none of them can have energies as low as the Ψ(best) with three independent variational parameters. However, it is possible to improve these wave-functions by introducing additional variational parameters. We shall now discuss how this can be done.

For the molecular orbital description of H_2, we have shown in Section 3-3 that the bonding molecular orbital configuration $(\sigma 1s)^2$ could be improved through configuration interaction by linearly combining it with the antibonding configure-tion $(\sigma^* 1s)^2$. Through configuration interaction, we may also improve the $\Psi_1(\mathrm{MO})$ of Section 23-2. By constructing the configuration interaction (CI) wave-function of Eqn.(11)

$$\Psi(\mathrm{CI}) = C_1\Psi_1(\mathrm{MO}) + C_2\Psi_2(\mathrm{MO}) + C_3\Psi_3(\mathrm{MO}) + C_4\Psi_4(\mathrm{MO}) \tag{11}$$

in which

$$\begin{aligned} &\Psi_2(\mathrm{MO}) = \left|\psi_2^\alpha\psi_2^\beta\psi_3^\alpha\psi_3^\beta\right|, \quad \Psi_3(\mathrm{MO}) = \left|\psi_1^\alpha\psi_1^\beta\psi_3^\alpha\psi_3^\beta\right|, \\ &\Psi_4(\mathrm{MO}) = \left(\left|\psi_1^\alpha\psi_3^\beta\psi_2^\alpha\psi_2^\beta\right| + \left|\psi_3^\alpha\psi_1^\beta\psi_2^\alpha\psi_2^\beta\right|\right)/2^{\frac{1}{2}} \end{aligned} \tag{12}$$

and the coefficients C_1 to C_4 are chosen so that the energy of Ψ(CI) is a minimum, we obtain an (over-parametrized) wave-function which is equivalent to the Ψ(best). Without some transformation, this Ψ(CI) has the disadvantage that it does not correspond to one or two simple valence-bond structures.

For Ψ(VBBO) and Ψ(NPSO), we may use a different bond-parameter for each bond orbital[6b,13]. Thus, instead of using $\phi_L = y + ka$ for both **Y-A** bonding electrons of the valence-bond structure (**2**), we may use $\phi_L = y + ka$ for one electron and $\phi_L' = y + k'a$ for the other electron. Similarly, for the two **A-B** bonding electrons of structure (**1**), we may use the orbitals $\phi_R = b + ka$ and $\phi_R' = b + k'a$ instead of $\phi_R = b + ka$ for both electrons. The Ψ(VBBO) wave-function may now be expressed as

$$\Psi(\mathrm{VBBO}) = (k + k')\Psi_{\mathrm{I}} + 4\Psi_{\mathrm{III}} + 2kk'\Psi_{\mathrm{IV}} \tag{13}$$

which still omits the "long-bond" wavefunction Ψ_{II}.

In Table 23-4, we report the energies for some two-parameter wave functions[13]. They show that Ψ(VBBO) remains a high-energy function.

Table 23-4: Energies (in eV) of two-parameter VBBO, NPSO and IVBO wave-functions relative to Ψ(best).

	XeF_2	$C_3H_3^-$	NO_2^-	HCO_2^-
VBBO	8.08	1.20	2.98	3.37
NPSO	0.060	0.058	0.225	0.266
IVBO	0.190	0.003	0.00001	0.005

The Ψ(NPSO) may be improved by using the bond-orbitals $\phi_L = y + ka$, $\phi''_R = b + k''a$, $\phi''_L = y + k''a$, and $\phi_R = b + ka$ instead of $\phi_L = y + ka$ and $\phi_R = b + ka$. If this is done, Ψ(NPSO) is given by Eqn.(14),

$$\Psi(\text{NPSO}) = (k + k'')\Psi_{\text{I}} - 2kk''\Psi_{\text{II}} + 4\Psi_{\text{III}} \tag{14}$$

which generates low energies in Table 23-4. However, because it omits Ψ_{IV}, Ψ(NPSO) can never become equivalent to Ψ(best), With Ψ(IVBO), we may construct either two-parameter or three-parameter variational wavefunctions. For example, we may use $\phi_L = y + ka$ and $\phi'_L = y + k'a$ for both electrons of the (fractional) two-electron **Y-A** bond of structure (**11**), and $\phi''_R = b + k''a$ for the one-electron **A-B** bond of this structure, together with the $\phi_R = b + ka$, $\phi'_R = b + k'a$ and $\phi''_L = y + k''a$ for structure (**12**). By introducing these orbitals into Ψ(IVBO), we may express this wave function according to Eqn.(15)

$$\Psi(\text{IVBO}) = (k + k' + k'')\Psi_{\text{I}} - 2kk''\Psi_{\text{II}} + 4\Psi_{\text{III}} + 2kk'\Psi_{\text{IV}} \tag{15}$$

which may be shown[13] to be equivalent to $(4/C_3)\Psi$ (best). Therefore, for symmetrical systems, resonance between the two "increased-valence" structures (**11**) and (**12**) is equivalent to unrestricted resonance between the the canonical Lewis structures (**1**)-(**6**). Therefore, if we use non-orthogonal bond orbitals as wavefunctions for (fractional) electron-pair bonds and one-electron bonds, we may use "increased-valence" structures and know that these can correspond to the best description of symmetrical 4-electron 3-centre bonding units.

In Table 23-4, we have reported some two-parameter Ψ(IVBO), for which we have assumed that $k = k'$ in the bond orbitals for the two-electron bond. As is the case for the two-parameter Ψ(NPSO), the energies of these Ψ(IVBO) are very low.

If **Y** and **B** are non-equivalent atoms, the "increased-valence" structures (**11**) and (**12**) are non-equivalent structures, and they will have different energies. For neutral systems, we would expect that (**11**) will be the lower-energy structure if the formal charges of the standard Lewis structures (**1**) and (**2**) are those of (**13**) and (**14**).

(13) (14) (15)

If we use the non-orthogonal bond-orbitals ϕ_L, ϕ'_L and ϕ''_R for the **Y-A** and **A-B** bonding electrons of increased-valence structure (**11**), we obtain the three-parameter wavefunction of Eqn. (16),

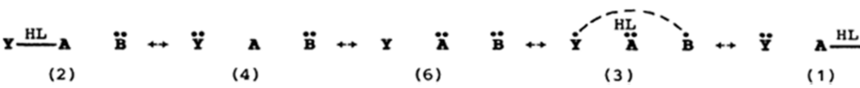
$$\Psi(\mathbf{Y}—\mathbf{A}\cdot\dot{\mathbf{B}},\ \text{IVBO}) = k''\Psi_1 + 2\,(k+k')\Psi_2 + k'k\Psi_3 + 2\Psi_4 + 2kk'\Psi_6 \tag{16}$$

for resonance between the five canonical Lewis structures (**1**)-(**4**) and (**6**). The formal charges for the omitted canonical structure (**15**) suggest that this structure should have a small weight, and therefore this three-parameter function should approximate closely to the Ψ(best) for $\Psi(\mathbf{Y}—\mathbf{A}\cdot\dot{\mathbf{B}}$,IVBO) .

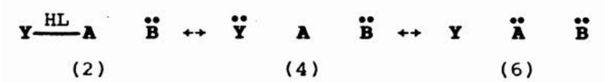
To obtain the variationally-best energy for $\Psi(\mathbf{Y}—\mathbf{A}\cdot\dot{\mathbf{B}}$,IVBO), a fourth variational parameter is needed. One (but not the only) way to introduce the additional parameter involves replacing $\phi_R'' = \mathrm{b} + k''\mathrm{a}$ with $\phi_R'' = \mathrm{b} + k''\mathrm{a} + l\mathrm{y}$.

23-7 Conclusions

Throughout this book, it will be noticed how usually we have used a Heitler-London type wave-function for the (fractional) two-electron **Y-A** bond of the "increased-valence" structure (**11**). Invoking such a wave-function is the simplest way to ensure that the "increased-valence" structure summarizes resonance between the standard and "long-bond" Lewis structures (**2**) and (**3**), each of which has a Heitler-London electron-pair bond. But, as we have done in Sections 23-3, 23-5, the Chapter 21 Addendum and Chapter 25, we may also use two-centre bond orbitals as wave functions for the two-electron **Y-A** bonds of structures (**2**) and (**11**) as well as for the one-electron **A-B** bond of structure (**11**). In Section 23-6, we have shown that $\mathbf{Y}\overset{\text{bo}}{—}\mathbf{A}\cdot\dot{\mathbf{B}}$ is equivalent to the resonance of



in which we have written bo (bond-orbital) and HL (Heitler-London) above or below the bonds to indicate the type of bond wave-function. Since the valence-bond structure $\mathbf{Y}\overset{\text{bo}}{—}\mathbf{A}\ \ddot{\mathbf{B}}$ with bond-orbitals for the **Y-A** bond is equivalent to the resonance



it follows that $\mathbf{Y}—\mathbf{A}\cdot\dot{\mathbf{B}}$ summarizes the resonance of

Such an "increased-valence" description is therefore more elaborate than that which uses the Heitler-London formulation for all two-electron bonds, namely

$$\mathbf{Y}\overset{\mathrm{HL}}{\text{—}}\mathbf{A}\cdot\dot{\mathbf{B}} \equiv \mathbf{Y}\overset{\mathrm{HL}}{\text{—}}\mathbf{A}\quad\ddot{\mathbf{B}} \leftrightarrow \dot{\mathbf{Y}}\quad\overset{\mathrm{HL}}{\ddot{\mathbf{A}}}\quad\dot{\mathbf{B}}$$

but both do include (in different ways) the standard and "long-bond" Lewis structures $\mathbf{Y}\text{—}\mathbf{A}\;\ddot{\mathbf{B}}$ and $\dot{\mathbf{Y}}\;\overset{\mathrm{HL}}{\ddot{\mathbf{A}}}\;\dot{\mathbf{B}}$. Our essential point is that by using $\mathbf{Y}\text{—}\mathbf{A}\cdot\dot{\mathbf{B}}$, we do stabilize $\mathbf{Y}\text{—}\mathbf{A}\;\ddot{\mathbf{B}}$ through interaction with $\dot{\mathbf{Y}}\;\overset{\mathrm{HL}}{\ddot{\mathbf{A}}}\;\dot{\mathbf{B}}$, no matter what type of wave function is used for the two-electron **Y-A** bonds. The fundamental process of (fractional or non-fractional) electron-pair bond formation involves spin-pairing two unpaired electrons with opposite spins that occupy overlapping orbitals, and the nature of the bond wave-functions need not be prescribed uniquely. Therefore, when we write

$$\dot{\mathbf{Y}} + \dot{\mathbf{A}}\cdot\dot{\mathbf{B}} \rightarrow \mathbf{Y}\text{——}\mathbf{A}\cdot\dot{\mathbf{B}}$$

we *must* obtain a lower energy than when we use $\mathbf{Y}\text{—}\mathbf{A}\;\ddot{\mathbf{B}}$ alone.

If we want to use one valence-bond structure to summarize resonance between the "long-bond" structure (**2**) and other canonical structures, in Section 23-4 we have found that we may also use the NPSO structure (**10**). Because this structure summarizes resonance between the canonical structures (**1**), (**2**), (**3**) and (**4**), Ψ(NPSO) must generate a lower energy than do the wave-functions for either $\mathbf{Y}\overset{\mathrm{HL}}{\text{—}}\mathbf{A}\cdot\dot{\mathrm{B}}$ or $\mathbf{Y}\overset{\mathrm{HL}}{\text{—}}\mathbf{A}\cdot\dot{\mathbf{B}} \leftrightarrow \dot{\mathbf{Y}}\cdot\mathbf{A}\overset{\mathrm{HL}}{\text{—}}\mathbf{B}$. (These "increased-valence" structures are equivalent to the (**2**) ↔ (**3**), and (**1**) ↔ (**2**) ↔ (**3**) resonances, respectively.) However, one advantage that is obtained by using either (**11**), or (**11**) ↔ (**12**), is that the "increased-valence" structures are very easily generated from the standard Lewis structure (**1**) and (**2**). And if we use bond-orbitals for all three bonding electrons of $\mathbf{Y}\overset{\mathrm{bo}}{\text{—}}\mathbf{A}\cdot\dot{\mathbf{B}}$, then this structure must be more stable than (**10**), since it is easy to show that $\mathbf{Y}\overset{\mathrm{bo}}{\text{—}}\mathbf{A}\cdot\dot{\mathbf{B}}$ summarizes resonance between structures (**10**) and (**6**), i.e

$$\mathbf{Y}\overset{\mathrm{bo}}{\text{——}}\mathbf{A}\cdot\dot{\mathbf{B}} \equiv \underset{(10)}{\dot{\mathbf{Y}}\cdot\mathbf{A}\cdot\dot{\mathbf{B}}} \leftrightarrow \underset{(6)}{\mathbf{Y}\quad\ddot{\mathbf{A}}\quad\ddot{\mathbf{B}}}$$

Usually, however, the contribution of structure (**6**) should be small. Therefore, when this is the case, the NPSO structure (**10**) is a good alternative to the "increased-valence" structure $\mathbf{Y}\overset{\mathrm{bo}}{\text{—}}\mathbf{A}\cdot\dot{\mathbf{B}}$.

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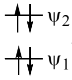
Addendum Chapter 23

1. Although the structural coefficients in Table 23-1 are now more than 40 years old, it should be satisfactory to use them in order to illustrate aspects of theory.
2. In Refs. 13 and 15, it has been shown that the Ψ_1(MO) of Eqn.(4) and the Ψ(IVBO) of Eqn. (15), namely Eqs. (16) and (17) here

$$\Psi_1(\mathrm{MO}) = 2k_1\Psi_{\mathbf{I}} - k_1{}^2\Psi_{\mathbf{II}} + 4\Psi_{\mathbf{III}} + k_1{}^2\Psi_{\mathbf{IV}} \tag{16}$$

$$\Psi(\mathrm{IVBO}) = (k + k' + k'')\Psi_{\mathrm{I}} - 2kk''\Psi_{\mathbf{II}} + 4\Psi_{\mathbf{III}} + 2kk'\Psi_{\mathbf{IV}} \tag{17}$$

are equivalent when $k = k_1$ and $k' = k'' = ½k_1$, i.e. $\Psi(\mathrm{IVBO},k_1,½k_1,½k_1) = \Psi_1(\mathrm{MO})$.

Also[16], $\Psi_1(\mathrm{MO}) = |\psi_1^\alpha\psi_1^\beta\psi_2^\alpha\psi_2^\beta|$ for 

with $\psi_1 = \mathrm{y} + k_1\mathrm{a} + \mathrm{b}$ and $\psi_2 = \mathrm{y} - \mathrm{b}$, is equivalent to $|\psi_L{}^\alpha\psi_L{}^\beta\psi_R{}^\alpha\psi_R{}^\beta|$, with $\psi_L = \mathrm{a} + 2k_1\mathrm{y}$ and $\psi_L = \mathrm{a} + 2k_1\mathrm{b}$. Therefore for these sets of k_1-dependent orbital parameters,

$\dot{\mathbf{Y}} \bullet \mathbf{A}\text{—}\mathbf{B} \leftrightarrow \mathbf{Y}\text{—}\mathbf{A} \bullet \dot{\mathbf{B}}$ and $\mathbf{Y}\text{—}\mathbf{A}\text{—}\mathbf{B}$ provide two types of compact valence-bond structures for the Ψ_1(MO) Hach-Rundle-Pimentel model[17,18] of symmetrical 4-electron 3-centre bonding.

3. In Ref. 13, it is also deduced that $\Psi(\mathrm{IVBO},k_1,\frac{1}{2}k_1,\frac{1}{2}k_1) = \frac{1}{2}\{\Psi(\mathrm{VBBO},k_1,k_1) + \Psi(\mathrm{NPSO},k_1,k_1)\}$ with $\Psi(\mathrm{VBBO},k_1,k_1) = 2k_1\Psi_{\mathbf{I}} + 4\Psi_{\mathbf{III}} + 2k_1{}^2\Psi_{\mathbf{IV}}$ and $\Psi(\mathrm{NPSO},k_1,k_1) = 2k_1\Psi_{\mathbf{I}} - 2k_1{}^2\Psi_{\mathbf{II}} + 4\Psi_{\mathbf{III}}$.

4. Other identities for both symmetrical and non-symmetrical 4-electron 3-centre bonding units are provided in the Addendum for Chapter 21.

5. A review of some of the wavefunctions considered in this Chapter is provided in Ref. 19. In Ref. 20, an *ab-initio* valence-bond study of XeF_2 is provided. Lewis structures (**1**)-(**4**), (with **Y** = F_Y, **A** = Xe and **B** = F_B) are included, together with four Lewis structures that involve the xenon $5d_{z^2}$ orbital in Xe-F bonding. The latter structures make only a small contribution to the valence-bond resonance scheme.

   In Ref. 21, it is shown how the $5p_z$ and the $5d_z{}^2$ Xe orbitals can both be included in the wavefunctions for increased-valence structures.

   As discussed in Section 23-4, resonance between the Lewis structures (**1**)-(**4**), with the same atomic orbitals used in each Lewis structure, is equivalent to using the non-paired spatial orbital structure (**10**). The procedure described in Ref. 22 can be used to construct "increased-valence" or non-paired spatial orbital wavefunctions when different atomic orbitals are used in different Lewis structures.

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Chapter 24 A Note on Pauling "3-Electron Bonds" and Covalent-Ionic Resonance

If a pair of electrons occupy two overlapping atomic orbitals centred on two atoms **X** and **Y**, then the **X-Y** bond may be described in terms of resonance between a covalent structure and two ionic structures, viz

$$\mathrm{X{-}Y} \leftrightarrow \overset{(-)}{\mathrm{X}\!:}\quad \overset{(+)}{\mathrm{Y}} \leftrightarrow \overset{(+)}{\mathrm{X}}\quad \overset{(-)}{:\!\mathrm{Y}}$$

This type of covalent-ionic resonance, which involves an electron-pair bond in the covalent structure, is widely known. The discussions of Section 7-3 and 8-1(c) show that for 6-electron 4-centre bonding units, another type of covalent-ionic resonance is also possible, namely that which generates a Pauling "3-electron bond" between the diatomic moieties. If we generalize the discussion of Section 7-3, for example, we may represent this type of resonance as (**1**) ↔ (**2**) and (**1**) ↔ (**3**). (Equivalent types of resonance exist for (**4**) with (**3**) and (**2**).)

(1) (2) (3) (4)

With respect to the **A-B** and **C-D** moieties, structures (**1**) and (**4**) are covalent, whereas structures (**2**) and (**3**) are ionic. The $\mathbf{B\!:}\ \mathbf{\cdot C} \leftrightarrow \mathbf{B\cdot}\ \mathbf{:\!C}$ resonance for (**1**) ↔ (**2**), or (**3**) ↔ (**4**) and the $\mathbf{A\cdot}\ \mathbf{:\!D} \leftrightarrow \mathbf{A\!:}\ \mathbf{\cdot D}$ resonance for (**1**) ↔ (**3**) or (**4**) ↔ (**2**) generate the Pauling "3-electron bond" structures $\mathbf{B\cdot\!\cdot\!\cdot C}$ and $\mathbf{A\cdot\!\cdot\!\cdot D}$, respectively.

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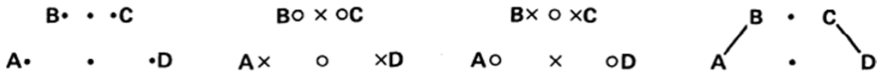
Resonance between structures (**1**)-(**4**) generates two Pauling "3-electron bonds" as in (**5**), with the spin distributions of (**6**) and (**7**), in which the crosses (×) and circles (○) represent electrons with +½ and –½ s_z spin quantum numbers. The molecular orbital configuration for each of the structures (**5**)-(**7**) involves two **B-C** and two **A-D** bonding electrons, and one **B-C** and one **A-D** antibonding electron. On spin-pairing the two antibonding electrons, "increased-valence" structure (**8**) is obtained.



(5) (6) (7) (8)

In Section 7-2, we have constructed the delocalized molecular orbitals for a symmetrical 6-electron 4-centre bonding unit. The lowest-energy configuration is given by Eqn. (1),

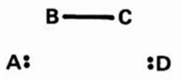
$$\Psi_1(\mathrm{MO}) = \left|(\psi_1)^2(\psi_2)^2(\psi_3)^2\right| \tag{1}$$

$$\equiv \left|(s_1)^2\left(\frac{s_4+\mu s_2}{(1+\mu^2)^{\frac{1}{2}}}\right)^2(s_3)^2\right| \tag{2}$$

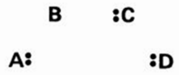
$$= \{\left|(s_1)^2(s_4)^2(s_3)^2\right| + \mu^2\left|(s_1)^2(s_2)^2(s_3)^2\right| + \mu^2(\left|(s_1)^2(s_4^\alpha)^1(s_2^\beta)^1(s_3)^2\right| + \left|(s_1)^2(s_2^\alpha)^1(s_4^\beta)^1(s_3)^2\right|)\}/(1+\mu^2) \tag{3}$$

for which the molecular orbitals (ψ_i) and symmetry orbitals (s_i) are defined as in Section 7-2, with overlapping orbitals χ_1, χ_2, χ_3 and χ_4 located on the **A**, **B**, **C** and **D** atomic centres. Algebraic expansion of Eqn. (2) generates the linear combination of the symmetry-orbital configurations given in Eqn.(3) (cf. Ref. 1).

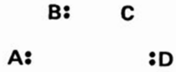
The $\left|(s_1)^2(s_4)^2(s_3)^2\right|$ and $\left|(s_1)^2(s_2)^2(s_3)^2\right|$ configurations of Eqn. (3) generate the covalent and ionic structures (**9**)-(**11**), and (**12**)-(**14**), respectively, with **B-C** and **A-D** electron-pair bonds in the covalent structures (**9**) and (**12**). The remaining Slater determinants of Eqn. (3) are associated with the Pauling "3-electron bond" structures (**6**) and (**7**), in which the crosses and circles represent electrons with α and β spins. Therefore the molecular orbital configuration of Eqn. (1) for 6-electron 4-centre bonding is concomitant with covalent-ionic resonance of both the electron-pair bond and Pauling "3-electron bond" types.



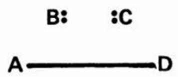
(9)



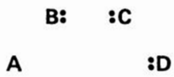
(10)



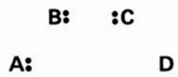
(11)



(12)



(13)

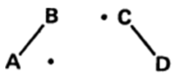


(14)

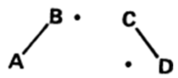
When $\Psi_1(\mathrm{MO})$ of Eqn. (1) is linearly combined with the excited configuration $\Psi_2(\mathrm{MO})$ of Eqn. (4), $\Psi_2(\mathrm{MO}) = \left|(\psi_1)^2(\psi_2)^2(\psi_4)^2\right|$ (4)

$$\equiv \left| \left(\frac{s_3 + \lambda s_1}{(1+\lambda^2)^{\frac{1}{2}}} \right)^2 (s_3)^2 (s_4)^2 \right| \tag{5}$$

to give a lower-energy configuration-interaction wave-function, the contributions to resonance of the ionic structures (**2**), (**3**), (**10**), (**11**), (**13**) and (**14**) are reduced relative to those of the covalent structures (**1**), (**4**), (**9**) and (**12**). The Pauling "3-electron bond" structures (**5**)-(**8**) then acquire polarity for the 1-electron bonds. The "increased-valence" structure (**8**) is then replaced by resonance between (**15**) and (**16**).



(15)



(16)

We shall conclude by noting that covalent-ionic resonance for the electron-pair bond, $\mathbf{X - Y} \leftrightarrow \overset{(-)}{\mathbf{X:}}\ \overset{(+)}{\mathbf{Y}} \leftrightarrow \overset{(+)}{\mathbf{X}}\ \overset{(-)}{\mathbf{:Y}}$ is equivalent to resonance between the 1-electron bond structures $\dot{\mathbf{X}} \cdot \mathbf{Y}$ and $\mathbf{X} \cdot \dot{\mathbf{Y}}$. This is because $\dot{\mathbf{X}} \cdot \mathbf{Y} \equiv \overset{(-)}{\mathbf{X:}}\ \overset{(+)}{\mathbf{Y}} \leftrightarrow \mathbf{X - Y}$ and $\mathbf{X} \cdot \dot{\mathbf{Y}} \equiv \mathbf{X - Y} \leftrightarrow \overset{(+)}{\mathbf{X}}\ \overset{(-)}{\mathbf{:Y}}$.

With these identities, all electron-pair bonds that have both covalent and ionic character may be expressed in terms of 1-electron bond structures[2], i.e. for any molecule, valence-bond structures may be constructed that involve only 1-electron bonds. Application to the π-electron structure of N_2 is described in Refs. 3 and 4.

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Chapter 25 Some Additional Topics

1. Recoupled-Pair Bonding

The concept of **recoupled-pair bonding** was introduced in 2009[1], and applied in a number of subsequent publications – see for example Refs. 1-4. A recoupled-pair bond forms when an electron in a singly occupied ligand orbital recouples the pair of electrons in a doubly occupied lone pair orbital on the central atom, leading to a central atom-ligand bond[1-4]. A **recoupled-pair bond dyad** occurs when a second ligand forms a bond with the orbital left over from the initial recoupled pair bond[1-4].

In Ref. 5, it is shown that for a 4-electron 3-centre bonding unit with one overlapping atomic orbital per atomic centre, recoupled pair bonding *always* occurs when an electron is delocalized from a doubly-occupied atomic orbital into either a bonding molecular orbital or an antibonding molecular orbital, to form a 1-electron bond and a fractional electron-pair bond. (This effect always occurs – see Addendum for Chapter 3 – regardless of how the wavefunction for the electron-pair bond is constructed from two overlapping atomic orbitals.) These delocalizations, shown in Fig. 25-1, give increased-valence structures **2** and **5** of Fig. 25-1[5], i.e. structures (**11**) and (**12**) of Section 23-5.

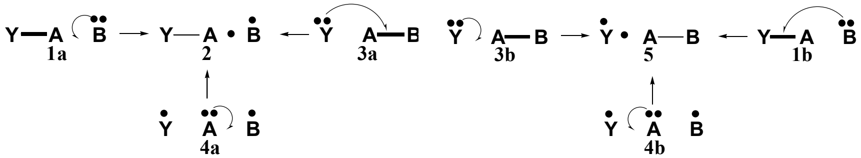

Figure 25-1: 1a → 2, 4a → 2, 3b → 5 and **4b → 5**: delocalization into an **A-B** or **Y-A** bonding molecular orbital. **1b → 5** and **3a → 2**: delocalization into a **Y-A** or **A-B** antibonding molecular orbital.

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2. "Increased-Valence" Structures for 3-Electron 3-Centre Bonding Units

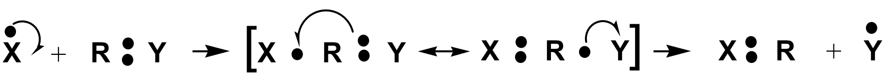
Although 3-electron 3-centre bonding units with three overlapping atomic orbitals are not electron-rich, for them increased-valence structures of the general types **X • R :Y** and **X : R • Y** (with atomic formal charges omitted) can be constructed. With one atomic orbital (x, r and y) per atomic centre, their electrons occupy the orbitals of Eqs. (2) and (3), respectively.

$$\phi_{xr} = x + lr,\ \phi_{ry} = r + k_1 y,\ \phi_{yr} = y + k_2 r \tag{2}$$

$$\phi_{yr} = y + kr,\ \phi_{rx} = r + l_1 x,\ \phi_{xr} = x + l_2 r \tag{3}$$

In Section 13-9, increased-valence structures are displayed for H_3.

The mechanism for the radical transfer reaction $\mathbf{X^\bullet} + \mathbf{R : Y} \rightarrow \mathbf{X : R} + \mathbf{Y^\bullet}$ has been formulated[6-8] (without atomic formal charges) as



Reactants Reactant-like Complex Product-like Complex Products

With each pair of **R:Y** and **X:R** electrons singlet spin-paired, the reactant-like and product-like wave-functions Ψ(**RC**) and Ψ(**PC**) wavefunctions are equivalent to[6-8]

Ψ(**RC**) = Ψ(**Reactants**) + *l*Ψ(**Reactants***), i.e.

and

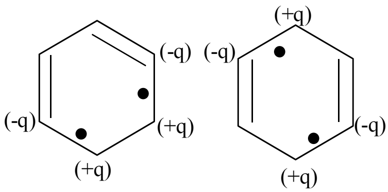
Ψ(**PC**) = Ψ(**Products**) + *k*Ψ(**Products***), i.e.

As for S_N2 reactions (cf. Addendum, Chapter 21), without the formation of the intermolecular one-electron bond that are present in the reactant-like and product-like complexes, the valence-bond mechanism for $\mathbf{X^\bullet} + \mathbf{R : Y} \rightarrow \mathbf{X : R} + \mathbf{Y^\bullet}$ involves a 2-step mechanism[6c]. The origin of electronic hypervalence for the reactant-like and product-like complexes is associated[5,6c,9] with the contributions of the excited state wavefunctions Ψ(**Reactants***) and Ψ(**Products***) to the Ψ(**RC**) and Ψ(**PC**), respectively. The excited state wavefunctions are those for Pauling "3-electron bonds".

With $\Psi = \Psi(\mathbf{RC}) + \rho\Psi(\mathbf{PC})$, there are seven variational parameters when $0 < |\rho| < \infty$. A variationally-better $\Psi = \Psi(\mathbf{RC}) + \rho\Psi(\mathbf{PC})$ is of course obtained when the atomic orbitals for the $\Psi(\mathbf{RC})$ and $\Psi(\mathbf{PC})$ differ.

3. The Electronic Structure of C_6H_6

In Ref. 6c, the six π-electrons of C_6H_6 are partitioned to form two sets of 3-electron 3-centre bonding units. Two increased-valence structures of the type **Y • A : B** have been incorporated[5] into the valence-bond structures, to give six Kekulé- and six Dewar increased-valence structures of types **III** and **IV** (cf. Figure 4 of Ref. 5).



III **IV**

The results of STO-6G VB calculations[6c] for the 2pπ-electrons of C_6H_6 and the six 1s σ-electrons of H_6 with D_{6h} symmetry show that resonance between the Dewar-type increased-valence structure generates a lower energy than does resonance between the Kekulé-type increased-valence structures. This result has been associated[5] with the more favourable distribution of the atomic formal charges in structure **IV** relative to that for structure **III**.

4. p and n Type Semiconductors and High T_c Superconductors

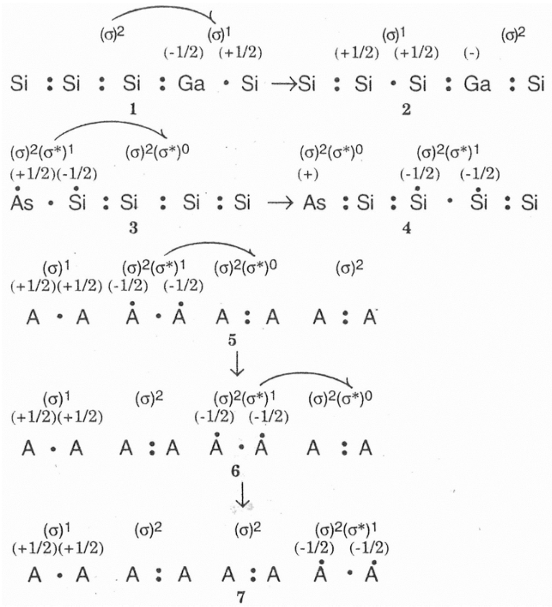


Figure 25-4: Electron conduction in p and n type semiconductors, and alkali metals.

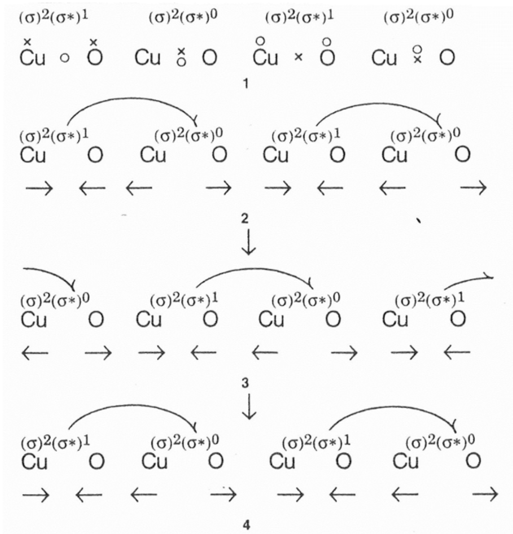


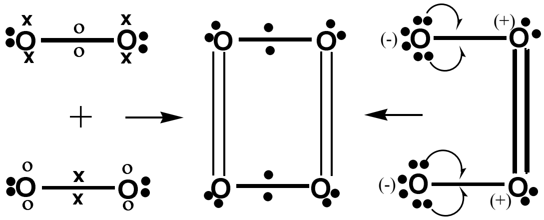
Figure 25-5: Lattice vibrations and electron conduction for …$(CuO)(CuO)^+(CuO)(CuO)^+$…→…$(CuO)(CuO)^+(CuO)(CuO)^+$…

In Fig. 25-4, electron conduction mechanisms[10] are displayed for *p* and *n* type semiconductors, which involve silicon doped with gallium and arsenic, respectively. Figure 25-5 gives the following speculative mechanism[10] for electron conduction in the high temperature superconductor $YBa_2Cu_3O_7$. It makes use of the instability of Pauling "3-electron bonds" under compression (cf. Section 3-10).

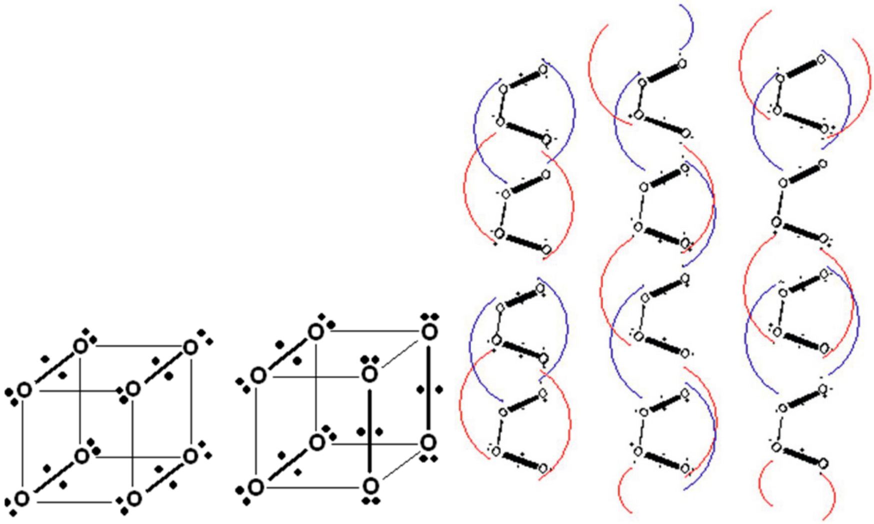
One formulation of an A type layer of $YBa_2Cu_3O_7$ involves a $(CuO)(CuO)^+(CuO)(CuO)^+$... arrangements of copper and oxygen ions. Each (CuO) component involves a Pauling "3-electron bond", which arises from the overlap of the singly-occupied $3d_{x^2-y^2}$ atomic orbital of Cu^{2+} with the doubly-occupied $2p\sigma$ AO of O^{2-}, to give the $(\sigma_{CuO})^2(\sigma^*_{CuO})^1$ molecular orbital configuration. Each $(CuO)^+$ component involves the $(\sigma_{CuO})^2$ molecular orbital configuration. In Fig. 25-5, the electron spins are indicated in structure (**1**), and each $(CuO)(CuO)^+$ component involves a 5-electron 4-centre bonding unit. Lattice vibrations of the type indicated in structure (**2**) involve a compression of the (CuO) Pauling "3-electron bonds" and expansion of the $(CuO)^+$ electron-pair bonds. The resulting (CuO) instability would lead to transfer of electrons from the singly-occupied antibonding molecular orbitals into the vacant antibonding molecular orbitals of the $(CuO)^+$, as indicated in structure (**2**), to generate structure (**3**). If a unidirectional flow of electrons is able to be established, i.e. if the next vibration is able to generate structure (**4**) rather than structure (**2**), the process (**2**) $\rightarrow$ (**3**) $\rightarrow$ (**4**) provides a speculative mechanism for the superconductivity. At any stage of a vibration, the electronic wavefunction can be expressed as $\Psi = \Psi_2 + \mu\Psi_3$.

5. Dimerization and Polymerization of O_2

A computational study[11] predicts that at high pressures, O_2 forms an insulating spiral-chain O_4 polymer structure. Figure 25-6 displays[12] (a) the formation of increased-valence structure (**2**) for the O_2 dimer from the O_2 monomers of (**1**) and the O_2 dimer Lewis structure (**3**); (b) types of increased-valence structures for O_8 ((**4**) and (**5**)) and spiral chain O_4 polymers ((**6**), (**7**) and (**8**)).



(1) **(2)** **(3)**



(4) **(5)** **(6)** **(7)** **(8)**

Figure 25-6: Increased-valence structures for O_2 and O_4 dimers, and spiral chain O_4 polymer. Reproduced from Ref. 12, with permission.

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Appendix

Atomic Orbital Overlap and Resonance Between Standard and "Long-Bond" Lewis Structures

As well as relative energy considerations, atomic orbital overlap via the off-diagonal matrix elements (H_{ij}) of the secular equations (Section 1-3) helps promote the importance of "long-bond" structures for *N*-centre electron-rich bonding units[1]. We shall demonstrate this by consideration of 4-electron 3-centre bonding, for which the standard and "long-bond" Lewis structures are structures (**1**), (**2**) and (**3**) of Section 23-1. With Heitler-London type wave-functions for the electron-pair bonds, the wave-functions for these structures are the Ψ_1, Ψ_2 and Ψ_3 of Eqn. 23-2.

The extent to which Ψ_j will linearly combine with Ψ_i, and the magnitude of the concomitant resonance stabilization energy, depend on the magnitude of the Hamiltonian matrix element H_{ij} for $i \neq j$, as well as on the energy separation $H_{jj} - H_{ii}$. The off-diagonal H_{ij} is atomic orbital overlap dependent, directly through the overlap integrals S_{ya}, S_{ab} and S_{yb}, and indirectly through the core Hamiltonian and electron repulsion integrals of the general types $H^{\mathrm{o}}_{\mu\nu}$, $(\mu\nu|\lambda\lambda)$ and $(\mu\nu|\lambda\sigma)$. (The μ, ν, λ and σ are any of the atomic orbitals y, a and b, with $\mu \neq \nu$; see for example Ref. 2 for integral definitions). With the Ψ_i of Eqn. 23-2, it may be deduced (see for example Ref. 3 for procedure) that the dominant terms for H_{13} and H_{23} are functions of S_{ya} and S_{ab}, respectively. However because the atomic orbitals y and b are located on non-adjacent centres, the magnitude of the overlap integral S_{yb} is small, and therefore the dominant terms for H_{12} are functions of the product $S_{\mathrm{ya}}S_{\mathrm{ab}}$. Consequently, because all overlap integrals are less than unity in magnitude, H_{13} and H_{23} will have appreciably larger magnitudes than has H_{12}.

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These H_{ij} considerations show that with respect to atomic orbital overlap, a pair of standard and "long-bond" structures (i.e. structures (**1**) and (**3**), or (**2**) and (**3**)) are better suited for resonance than are the pair of standard structures (**1**) and (**2**), i.e. the "long-bond" structure (**3**) helps the standard structures (**1**) and (**2**) to interact by functioning as a "bridge" between them. One may envisage the conversion of structure (**1**) into (**2**) to occur via structure (**3**), by transferring a **Y** electron of structure (**1**) into the **A** atomic orbital to afford structure (**3**), and then the transfer of an **A** electron of structure (**3**) into the **B** atomic orbital to obtain structure (**2**), i.e. the "long-bond" structure forms a connecting link between the standard structures.

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