Increased-Valence Structures for Qualitative Valence-Bond Representations of Electronic Structure for Electron-Rich Molecules

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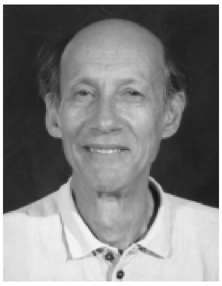
Whereas familiar Lewis-type valence-bond structures for singlet-spin systems involve electron-pair bonds and lone-pairs of electrons, increased-valence structures involve one-electron bonds and fractional electron-pair bonds. An increased-valence structure may be easily derived from a familiar Lewis structure via one-electron delocalizations of lone-pair electrons into two-centre bonding molecular orbitals. The increased-valence structure is equivalent to resonance between several Lewis structures, including the familiar Lewis structure from which it was derived, and therefore it is more stable than the latter structure. Some of the properties of increased-valence structures, and their associated Pauling three-electron bonds as diatomic components of these structures, are discussed, with specific reference to N_2O and the $Fe^{II}O_2$ linkages of oxyhaemoglobin. Applications to numerous other systems that involve 4-electron 3-centre, 6-electron 4-centre, and 6-electron 5-centre bonding units are presented. Brief consideration is also given to a speculative Bohr approach to electronic structure.

Introduction

Over the last two decades, there has been a resurgence of interest in valence-bond (VB) descriptions of the electronic structures of molecules.[1−5] My research has been concerned primarily with the qualitative development of the subject, particularly through the formulation of the *increased-valence* theory[4,5] for the large class of electron-rich molecules. For these molecules, the theory enables their familiar, traditional Lewis-type VB structures, with lone-pairs of electrons and electron-pair bonds, to be stabilized by means of one-electron delocalizations into bonding molecular orbitals (MOs). The resulting increased-valence structures are then able to provide new insights into the origins of bond properties, and how molecules react. Using an $Fe^{II}O_2$ linkage for oxyhaemoglobin, and N_2O, as examples, I shall redescribe some essential features of this theory, and give consideration to a number of the many applications that we have made to inorganic systems. Recent reviews that discuss a variety of examples include those of ref.[5,6] The reader who is more interested in the applications may omit those sections of this review that involve detailed formulations of VB wavefunctions. I shall also briefly redescribe aspects of a speculative approach to qualitative descriptions of electronic structure via Bohr circular orbit theory.[7] The essential purpose of both types of approach to electronic structure is to help provide "primitive patterns of understanding",[8] using mostly qualitative VB methods.

The simplest definition of an electron-rich bonding unit is that it involves N overlapping (hybrid or non-hybrid) atomic orbitals (AOs) centred on N atomic centres, with n electrons occupying these AOs, when $N < n < 2N$. Familiar examples involve 3-electron 2-centre, 4-electron 3-centre, and 6-electron 4-centre bonding, and we shall give primary attention to them here. Pauling designated the 3-electron 2-centre bonding unit as a "three-electron bond",[9] and this designation has continued to be used very widely. Although modifications to the term,[10] such as "three-electron two-orbital bond" and "three-electron hemi-bond" or "three-



Richard Harcourt was born in Melbourne, Australia. In 1963, he received a Ph.D. degree in Chemistry from Monash University, under the supervision of Professor R. D. Brown. At the end of 1993, he took early retirement from his appointment as a Senior Lecturer in Physical Chemistry at the University of Melbourne, where he has continued to work as a Research Associate. His research has involved primarily valence-bond studies of the electronic structures of molecules, with particular emphasis given to the development and application of the increased-valence theory which he formulated three decades ago. Related research has involved energy transfer studies. A reformulation of Bohr orbit descriptions of electronic structure has also provided a fruitful (speculative) area of research.

MICROREVIEWS: This feature introduces the readers to the authors' research through a concise overview of the selected topic. Reference to important work from others in the field is included.

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electron half-bond” provide more accurate descriptions of its bonding properties, we shall use Pauling’s designation here. Some of the properties of three-electron bonds will be discussed in the next Section. As will be discussed below, increased-valence structures for 4-electron 3-centre and 6-electron 4-centre bonding units involve three-electron bonds as diatomic components.

The Three-Electron Bond, or Three-Electron Half-Bond

In MO theory, the diatomic three-electron bond involves two bonding electrons and one antibonding electron. Thus if a and b are the overlapping AOs centred on the atomic nuclei A and B, the MO configuration is $(\psi_{ab})^2(\psi^*_{ab})^1$, in which $\psi_{ab} = a + kb$ and $\psi^*_{ab} = k^*a - b$ are orthogonal bonding and antibonding MOs. The k is a variationally controlled polarity parameter with $k^* = (k + <a|b>)/(1 + k<a|b>)$, and the maximum bond-order of 0.5 occurs when $k = 1$, thereby indicating that the designations “three-electron hemi-/half-bond[10]” provide a clearer description of the bonding properties.

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

It is easy to demonstrate[4,5,11] that the identities of Equation (1) obtain, or in terms of Slater determinants [cf. Equation (2)], in which α and β are the $m_s = +1/2$ and $m_s = -1/2$ electron-spin wavefunctions, and the antibonding ψ^*_{ab} electron is assumed to have an $m_s = +1/2$ spin quantum number. (The identity $|\psi_{ab}{}^{\alpha}\psi_{ab}{}^{\beta}\psi^*_{ab}{}^{\alpha}| \propto |a^{\alpha}\psi_{ab}{}^{\beta}b^{\alpha}|$ was deduced by Linnett.[12]) The $(a)^1(\psi_{ab})^1(b)^1$ configuration involves parallel spins for the a and b electrons, and therefore these two electrons are non-bonding (more accurately, net antibonding[13]); the responsibility for bonding belongs solely with the ψ_{ab} electron, whose spin is opposed to the spin for each of the a and b electrons. In Figure 1, the orbital diagrams that pertain to the identities of Equations (1) or (2) are displayed for $k = k^* = 1$ in the MOs. These identities form the basis for much of the discussion of the properties of increased-valence structures.

$$|\psi_{ab}{}^{\alpha}\psi_{ab}{}^{\beta}\psi^*_{ab}{}^{\alpha}| \propto |a^{\alpha}\psi_{ab}{}^{\beta}b^{\alpha}| \equiv |a^{\alpha}a^{\beta}b^{\alpha}| + k|a^{\alpha}b^{\beta}b^{\alpha}| \qquad (2)$$

Various VB symbolisms have been used to represent the three-electron bond,[4,5,11]. These include VB structures **1−6** and **7** ↔ **8**.

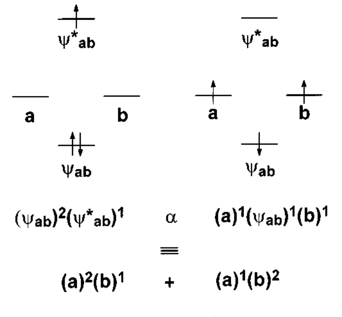
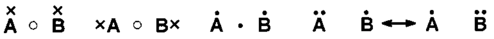


Figure 1. Orbital diagrams for the identities of Equation(1); ↑ ≡ $m_s = +1/2$, ↓ ≡ $m_s = -1/2$

1 **2** **3**



4 **5** **6** **7** **8**

(Atomic formal charges have been omitted from all generalized VB structures that use any of the symbols Y, A, B, C, and D to designate atomic centres.)

The symbolism of structure **1** was introduced by Pauling[9] in 1931, but since then, symbolisms such as **2** and **3** have sometimes been used.[3f,14] However because the equivalent MO theory indicates that the three-electron bond has a maximum bond order of 0.5, structure **2** is unsatisfactory and structures **1** and **3** do not make clear that two of the electrons are non-bonding (more-accurately, net antibonding) in character. Structures **4** and **5** (with spins, **x** for $m_s = +1/2$ and **o** for $m_s = -1/2$) and **6** (without spins) were introduced by Linnett,[12] and with only one bonding electron, they are more-clearly associated with the $|a^{\alpha}\psi_{ab}{}^{\beta}b^{\alpha}|$ configuration than are structures **1−3**. Therefore the Linnett symbolism is the preferred[4,5,11] VB symbolism for the three-electron bond. The second identity of Equation (1) shows that each of the three-electron bond VB structures **1−6** is equivalent to resonance between the canonical Lewis structures **7** and **8**.

When the odd-electron has $m_s = +1/2$ spin for example, each of the Lewis structures **7** and **8** may be used to generate the three-electron bond VB structure by delocalizing the $m_s = -1/2$ spin lone-pair electron into the ψ_{ab} bonding MO, as is indicated in **9** → **10** and **11** → **12**.

9 **10** **11** **12**

One-electron delocalizations of this type lead to stabilization of the Lewis structures **7** and **8**, and they will be used extensively throughout the paper to generate increased-valence structures from familiar Lewis-type VB structures for triatomic and polyatomic systems. When the extent of delocalization, via the value of the MO polarity parameter k, is determined variationally, a one-electron delocalization from an AO into a bonding MO, *always* generates a stabilization of the increased-valence structure relative to the Lewis structure from which it was derived.

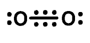
Theory for the three-electron bond may be elaborated further by increasing the number of AOs which are used to accommodate the electrons.[11b] With three AOs (a′,a′′, and b) to accommodate the electrons of the Lewis structure **7**, and three additional AOs (a, b′, and b′′) to accommodate the electrons of the Lewis structure **8**, it has been deduced that a wavefunction of the form $\Psi = \Psi_1(VB) + \Psi_2(VB) = \Psi_1(MO) + \Psi_2(MO)$ may be constructed from each set of three AOs, for which the Ψ_1 and Ψ_2 are three-electron bond wavefunctions. The equivalence has been illustrated[11b] via the results of some ab initio calculations for the $^2\Sigma_u^-$ ground-states of H_2^- and He_2^+. The simplest example involves four AOs, (i.e. for $a' = a'' = a$, $b = b_0$, and $a = a_0$, $b' = b'' = b$) to give the $(a)^2(b_0)^1$ and $(a_0)^1(b)^2$ configurations for structures **7** and **8**, respectively. With H_2^- as the example, use of these AOs is sufficient to ensure that the dissociation products are H^- + H or H + H^-, rather than the $H^{-0.5}$ + $H^{-0.5}$ for a three-electron bond with two equivalent AOs. For H_2^-, the use of canonical double-zeta molecular orbitals constructed from 1s′ and 1s″ atomic orbitals on each atomic centre must lead to ionization of this anion[11b] to form H_2 + e^- when the exponents of the diffuse (1s″) orbital components of these molecular orbitals are energy-optimized.

The relevance of three-electron bonds for VB descriptions of the electronic structures of high-spin transition metal complexes, F^+-type colour centres, *n*-type semiconductors and high T_c superconductors is described in ref.[5c], and references 26, 28, and 30 therein.

Linnett-type VB structures with electron-spins either indicated, or not indicated, as in structures **4** for example, and structure **6**, will be used in this Review to provide VB representations of the Pauling three-electron bond.

The Oxygen Molecule

The $^3\Sigma_g^-$ ground-state for the oxygen molecule O_2, has an electron-pair σ-bond and two three-electron π bonds, $(\pi_x)^2(\pi^*_x)^1$ and $(\pi_y)^2(\pi^*_y)^1$ with parallel spins for the antibonding π^*_x and π^*_y electrons. The Pauling and Linnett VB structures[9,12] for this molecule are **13**,[9] **14**[12] without spins, and **15**[12] with spins when it is assumed that the antibonding π^*_x and π^*_y electrons have m_s = +1/2 spin quantum numbers.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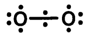
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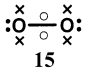
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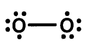
Each of these structures is equivalent to resonance between the canonical Lewis structures **16–19**.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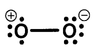
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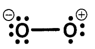
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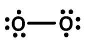
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The results of ab initio VB calculations for O_2 from several laboratories[15,16] indicate that the uncharged VB structures **16** and **19** have larger weights than have the polar VB structures **17** and **18**. This result, which is not unexpected, reflects the operation of the electroneutrality principle.[9b]

Bonding of O_2 to Haemoglobin

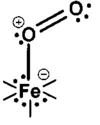
Theories of the bonding of O_2 to haemoglobin or myoglobin will be used here to introduce the concept of an increased-valence structure.

Haemoglobin (Hb) involves four iron atoms, each of which is formally high-spin (S = 2 spin) Fe^{II}, with four unpaired, parallel-spin electrons. When oxyhaemoglobin (HbO_2) is formed, four paramagnetic (S = 1 spin) O_2 molecules bind to the iron atoms, to give four S = 0 spin iron-O_2 linkages. Ever since this effect was first observed by Pauling and Coryell[17] in 1936, there has been debate with regard to how the electronic structure of each S = 0 spin iron-O_2 linkage should be (approximately) formulated.[18,19] The three primary models[17,20,21] that are usually considered are the following:

(a) Low-spin $Fe^{II}((t_{2g})^6, S = 0)$ + $O_2^*((\pi^*_x)^2(\pi^*_y)^0, S = 0)$ (Pauling and Coryell);[17]

(b) Intermediate-spin $Fe^{II}((t_{2g})^5(e_g)^1, S = 1)$ + $O_2((\pi^*_x)^1(\pi^*_y)^1, S = 1)$ (McClure, 1960),[20] with antiparallel spin-coupling of the unpaired antibonding π^*_x and π^*_y electrons of ground-state O_2 with those for the Fe^{II};

(c) Low-spin $Fe^{III}(S = 1/2)$ + $O_2^-(S = 1/2)$ (Weiss, 1964),[21] with anti-parallel spin coupling for the unpaired electrons of Fe^{III} and O_2^-.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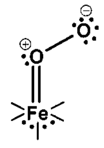
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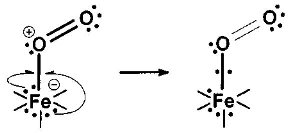
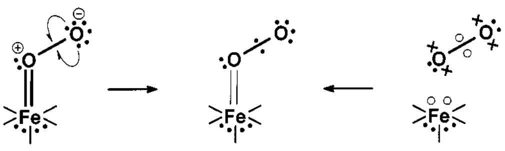
Attention will be given to models (a) and (b). The Pauling-Coryell model (a) involves[17] resonance between the familiar standard (or *Kekulé*-type) Lewis structures **20** and **21**, for which an S = 0 spin excited valence-state of O_2 $:\ddot{O}=\ddot{O}:$ is coordinated with the low-spin Fe^{II} in structure **20**. From VB structures **20** and **21**, we can generate[18] VB structures **23** and **25** via the one-electron delocalizations indicated in **22** and **24** (cf. **9** → **10** and **11** → **12**).

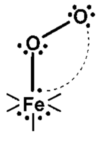

22 **23**


24 **25** **26**

VB structure **25** can also be constructed[18] by spin-pairing the two unpaired electrons of ground-state O_2 with the two unpaired electrons of intermediate-spin Fe^{II}, as in **26** → **25**.

The latter procedure involves e_g-π^*_x and t_{2g}-π^*_y spin-pairings for the appropriate pairs of overlapping orbitals, and it provides the VB representation for the McClure model of (b). We shall focus attention on VB structure **25**, but of course it will participate in resonance with the higher-energy structure **23**, (which involves the O_2 excited state). For reasons that will be discussed later when the general theory of 4-electron 3-centre bonding is outlined, VB structures **23**, **25**, and **31** below for N_2O, are examples of *increased-valence* structures.[4,5]

Because the three-electron bond structure for the O_2 ground-state is equivalent to resonance between four canonical Lewis structures, via the identity **14** ≡ **16**↔**17**↔**18**↔**19**, it follows[18] that the $Fe^{II}O_2$ VB structure **25** for model (b) is equivalent to resonance between the canonical Lewis structures **24** and **27–29** when it is assumed that the four electrons of the Fe^{II}=O_2 bond of structure **24** occupy AOs, i.e. a Heitler-London type formulation of the wavefunction [a(1)b(2) + b(1)a(2) with a and b overlapping AOs] is used for each $Fe^{II}-O$ electron-pair bond. Because structures **27−29** do not involve Fe=O double bonds, the Fe=O bond-number or bond-order for increased-valence structure **25** is less than two. Thin bond lines are used to represent the fractional electron-pair bonds which are present in this structure, and in all increased-valence structures.[4−6] The extent to which structures **24** and **27−29** contribute to the equivalent Lewis structure VB resonance scheme determines the strength of the Fe=O bond.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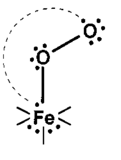
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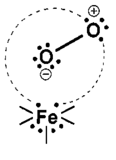
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Each of the VB structures **27−29** is an example of a "*long-bond*" or "*formal-bond*", or *Dewar*-type canonical Lewis structure. A "long" or formal bond has negligible strength, and therefore the function of the pecked bond-line (----) which is sometimes used to represent this type of bond[22] is to indicate that the associated pair of electrons are spin-paired. Some workers do not show the presence of formal bonds, and the VB structure is then designated as a *singlet diradical* or *spin-paired diradical* structure. The formal bonding is not indicated in the increased-valence structure. The more-familiar Lewis structures of types **20** and **21**, are designated as *standard* or *Kekulé*-type canonical Lewis structures.

Increased-valence structures for electron-rich systems are equivalent to resonance between Kekulé- and Dewar-type Lewis structures. Therefore when the polarity parameters that are associated with the one-electron bonds of the increased-valence structures are chosen variationally, use of increased-valence structures *must provide a more stable VB representation of electronic structure* than does use of only the more familiar Kekulé-type Lewis structures alone.

Structure **27** is equivalent to the singlet-biradical structure which Goddard and Olafson have used[23] to represent the electronic structures of the $Fe^{II}O_2$ linkages of oxyhaemoglobin, via the McClure model (b). Because increased-valence structure **25** is equivalent to resonance between structures **24** and **27−29**, structure **25** must provide a lower-energy representation of the electronic structure than does either **24** or **27** alone.

The observed reduction[24] in the value of the O−O stretching frequency in HbO_2, namely from 1556 cm^{-1} (free O_2) to 1107 cm^{-1} (HbO_2), is sometimes cited as evidence for the Weiss model (c), but the results of MO calculations[25] indicate that little Fe → O_2 charge-transfer occurs.

O−O Bond Making and Breaking

Either an $Mn^{V}=O$ or an $Mn^{IV}=O$ species has been implicated in the formation of an O−O bond in the photosynthetic process.[26] We give consideration to the $Mn^{IV}=O$ here. An $S = 1/2$ spin VB structure for this species is usually represented as **I** of Figure 2.

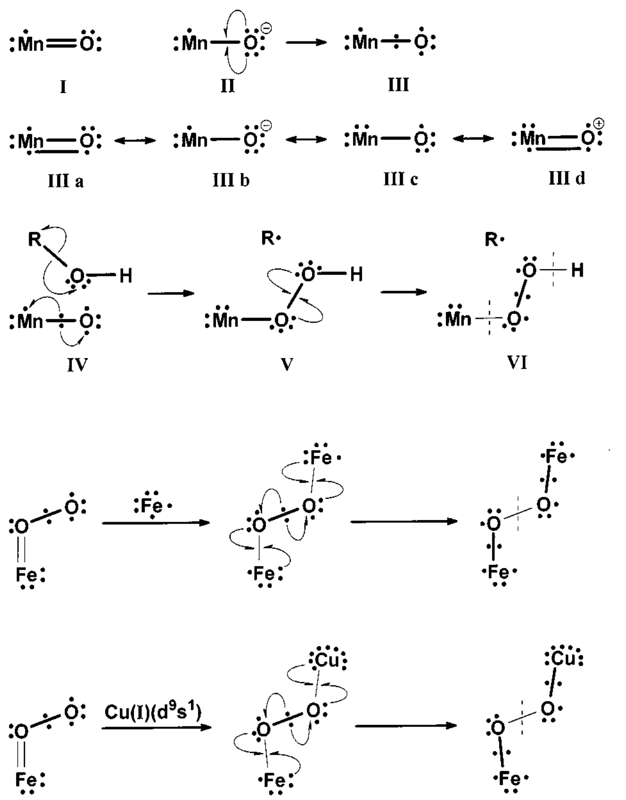


Figure 2. O−O bond-making via $Mn^{IV}O$ + ROH for photosyntheses, and O−O bond-breaking for $Fe^{II}O_2Fe^{II} \rightarrow 2\ Fe^{II}O$ and Cu^{I}-$O_2Fe^{II} \rightarrow Cu^{I}O + Fe^{II}O$ decompositions; the $Fe^{II}O_2$ structure corresponds to the increased-valence structure **25**; formal charges are not indicated on the transition metal ions

However it may also be formulated as **II**, from which we may generate VB structure **III** with a three-electron bond. VB structure **III** has an Mn = O double bond whose electronic structure $((\sigma)^2(\pi_x)^1(\pi_y)^1)$ is similar to that of VB structure **15** for the O_2 ground-state. VB structure **III** is equivalent to resonance between the canonical Lewis structures **IIIa−IIId**, (with **IIIa** and **IIIb** corresponding to structures **I** and **II**), and therefore **III** is more stable than is either structure **I** or structure **II** alone. With a nitrogen atom replacing the Mn in these VB structures, a similar type of VB representation is relevant for the ground-state of NO.

Unlike structure **I**, the three-electron bond structure **III** locates unpaired electron spin-density on the oxygen atom. Therefore the $Mn^{IV}=O$ is able to react with ROH to generate $Mn^{III}OOH$ ($S = 1/2$) according to **IV** → **V**. The $Mn^{III}OOH$ has been postulated[26b] to be the precursor for O_2 formation. Further electronic reorganization, as indicated in **V** → **VI**, weakens the Mn-O and O-H bonds to generate O_2 + Mn^{II} + H. The **IV** → **V** → **VI** mechanism for the formation of the postulated $Mn^{III}OOH$ species provides an alternative to those provided in references 26b,c.

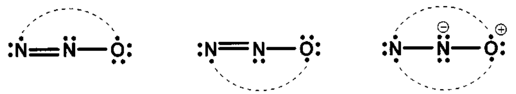
In Figure 2, increased-valence structures[4,6a] are also displayed for $Fe^{II}-O_2-Fe^{II}$ and $Cu^{I}-O_2-Fe^{II}$, in which the O_2 ground-state is bonded to $Fe^{II}(S = 1, (t_{2g})^5(e_g)^1)$ and $Cu^{I}(S = 1,(t_{2g})^6(e_g)^3(4s)^1)$. The electronic reorganization for the $Fe^{II}-O_2-Fe^{II} \rightarrow 2\ Fe^{II}O$ and $Cu^{I}-O_2-Fe^{II} \rightarrow Cu^{I}O + Fe^{II}O$ decomposition processes, which have been associated with the oxidation of Fe^{II} porphyrin complexes[4,6a] and cytochrome c oxidase catalysis[4,6a] of $4\ H^+ + 4e + O_2 \rightarrow 2\ H_2O$, are indicated. Each of these decomposition processes involves the breaking of O−O three-electron bonds as well as the O−O σ-bond.

Increased-Valence Structures and N_2O

Ab initio VB calculations on the $Fe^{II}O_2$ linkage have yet to be performed in order to determine which of the canonical Lewis structures are of primary importance. However the results of both semi-empirical[27] and ab-initio[28,29] calculations have been reported for N_2O, whose Kekulé-type Lewis structure **30** is similar to **24** for $Fe^{II}O_2$. By delocalizing an oxygen $p\pi_x$ and an oxygen $p\pi_y$ electron into bonding π_x(ON) and π_y(ON) MOs respectively, we obtain increased-valence structure **31**, which is similar in type to VB structure **25** for the $Fe^{II}O_2$ linkage.

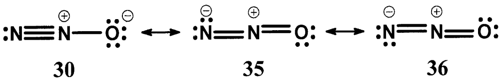
30 **31**

Using the three-electron bond identity, $\dot{A} \cdot \dot{B} \equiv \ddot{A}\quad \dot{B} \longleftrightarrow \dot{A}\quad \ddot{B}$, it is easy to deduce that increased-valence structure **31** is equivalent to resonance between the Kekulé-type Lewis structure **30**, and the Dewar-type Lewis structures **32**−**34**, when the wavefunctions for the N−N π_x and π_y bonds are formulated using the Heitler−London type procedure (cf. discussion above for the $Fe{=}O_2$ bond of VB structure **25**).



32 **33** **34**

The results obtained from a variety of ab initio VB calculations for N_2O are reported in ref.[29] These results, which are in agreement with those obtained from our earlier semi-empirical VB studies,[27] show that the Dewar structures **32** and **33** in particular have an importance which is comparable with those for the familiar Kekulé-type structures **30**, **35**, and **36**.



30 **35** **36**

Resonance between the latter three structures is usually used to provide the primary qualitative VB representation of the electronic structure of N_2O, and of course increased-valence structures can also be generated[5,27,29] from the Lewis structures **35** and **36**, as well as from structure **30**.

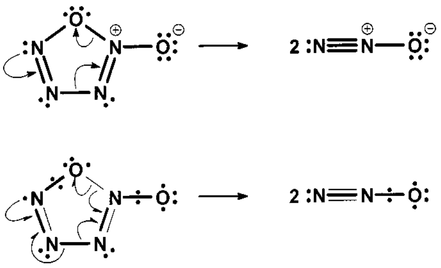


Figure 3. Standard Lewis VB and increased-valence representations for cyclic $N_4O_2 \rightarrow 2\ N_2O$ decomposition; the increased-valence representation involves lower energies for reactant and products

The conclusion that N_2O has appreciable singlet diradical character has been exploited to develop VB mechanisms for a variety of reactions which involve this molecule. These reactions include: (a) thermal decomposition[29,30a] to generate either $N_2 + O^*$ or $2\ N_2 + O_2^*$, (b) $N_2O + X \rightarrow N_2 + OX$, for which X is a univalent radical,[29,30a,30b] (c) 1,3-dipolar cycloaddition reactions,[29,30a] (d) a unimolecular $C_{\infty v} \rightarrow C_{2v} \rightarrow D_{\infty h}$ isomerization process[31] and (e) $NO + NCO \rightarrow N_2O + CO$.[5b] For each case, the primary "active space" involves four singly-occupied orbitals, and for them, the Rumer diagrams[30a,30b] allow for the existence of two $S = 0$ spin-pairing schemes − one for a reactant-like species and one for a product-like species. Therefore a crossing of potential energy curves is involved when proceeding from reactants to products[4,30a,30b,32]. The VB representation for the diradical mechanism for decomposition reactions of type (a) is contrasted[30b] with the usual type of polar mechanism that would be used to indicate how electronic reorganization might proceed, via the shifting of pairs of electrons. In Figure 3, these two types of VB representations[30b] are illustrated here for the decomposition of cyclic $N_4O_2 \rightarrow 2\ N_2O$, which has been calculated[33] to arise as an intermediate in the thermal decomposition of N_3-NO_2.

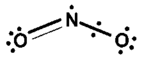
Some ab initio STO-6G VB calculations for N_2 have been performed,[34] in order to illustrate the effect of AO hybridization on the length of the N−N bond of N_2 relative to those of HN_3 and N_2O. For N_2, the electron-pair N−N σ-bond arises from the overlap of hybrid AOs of the form $h \approx 2p\sigma + 0.18(2s)$, whereas for N_2O, this bond involves the overlap of $2p\sigma + 0.18(2s)$ and $2p\sigma + 2s$ hybrid AOs. The results of calculations for N_2 with these two pairs of AOs give a bond shortening of 0.03 Å for the latter pair relative to the former pair. With this estimate, the N−N bond length of 1.13 Å for N_2O is ≈ 0.06 Å longer than is that for an N_2 with $2p\sigma + 0.18(2s)$ and $2p\sigma + 2s$ hybrid AOs. The fractionality of the N−N triple bond in increased-valence structure **31** is in agreement with the appreciable lengthening of the N−N bond of N_2O relative to that of an N_2 with the same AO hybridization.

Inspection of increased-valence structure **31** for N_2O reveals that more than eight electrons appear to be involved in bonding to the central nitrogen atom, i.e. an *apparent violation of the Lewis-Langmuir octet rule* occurs for this atom. In each of references 34 and 35, it is demonstrated that this effect is a consequence of the inclusion of the Dewar-type Lewis structures **32**−**34** as well as the Kekulé structure **30** in the canonical structure resonance scheme.

Increased-Valence Structures for NO_2, O_3, and SO_2

Increased-valence structures **37**−**40** for NO_2 and O_3 have now been derived − either from Lewis VB structures via one-electron delocalizations, or from three-electron bond

VB structures for the reactants O + NO and O + O_2 − and displayed on numerous occasions.[4,5,35,36] These increased-valence structures will be used in subsequent discussions.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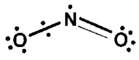
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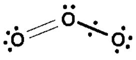
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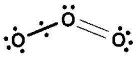
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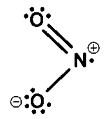
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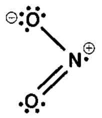
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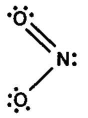
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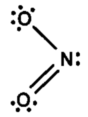
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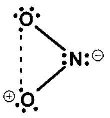
With $\sigma_v\Psi_{37} = \Psi_{38}$ and $\sigma_v\Psi_{38} = \Psi_{37}$, the $\Psi(^2A_1) = \Psi_{37} + \Psi_{38}$ resonance between increased-valence structures **37** and **38** for the ground-state of NO_2 is equivalent[35] to resonance between the canonical Lewis structures **41**−**47**.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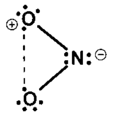
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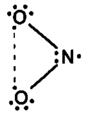

47

When the O−N−O bond-angle of NO_2 is near to the experimental value of 134°, a significant contribution from the Dewar-type Lewis structure **47** has been calculated to occur.[36] This structure is considered[35] to be primarily responsible for the retention of C_{2v} point-group symmetry for the experimentally-observed ground-state. For small bond-angles, the ground-state is calculated[37] to have $^2B_2$ symmetry in the C_{2v} point-group, and structure **47** then does not contribute[35] to the equivalent Lewis structure resonance scheme for $\Psi(^2B_2) = \Psi_{37} - \Psi_{38}$. Consequently for this state, one N−O bond can be stretched relative to the other, and $NO_2 \rightarrow NO + O$ dissociation then becomes possible.[35,36] Similar considerations may be used[35] to account for the $O_3 \rightarrow O_2 + O$ and $CO_2 \rightarrow CO + O$ thermal dissociations.

In Figure 4, increased-valence structures for NO_2 and O_3 are used to indicate how electronic reorganization can proceed for other reactions with these molecules as reactants.[4,5] The mechanisms displayed exploit the singlet diradical character which is present in the increased-valence structures. SO_2 and S_2O are homoelectronic with O_3, and with similar types of increased-valence structures, VB representations[38] for some reactions that involve these sulfur-containing molecules are displayed in Figure 4.

Spin-Coupled Valence-Bond Calculations

Other workers have used their *spin-coupled* VB techniques[3a,3b,39] to study the electronic structures of NO_2, N_2O, and other 1,3-dipolar (or zwitterionic-diradical hybrid)[32a] molecules, such as O_3, CH_2N_2, and HCNO. The calculations allocate a separate orbital for each active-space electron, and consider the different spin-pairing schemes that are available for these electrons. No orthogonality constraints are required for each pair of active-space orbitals in the spin-coupled calculations. These orbitals are designated as "distorted AOs" and may involve two or more atomic centres. Therefore they do not correspond to the one-centre AOs which are associated with the active-space electrons of the canonical Lewis structures.

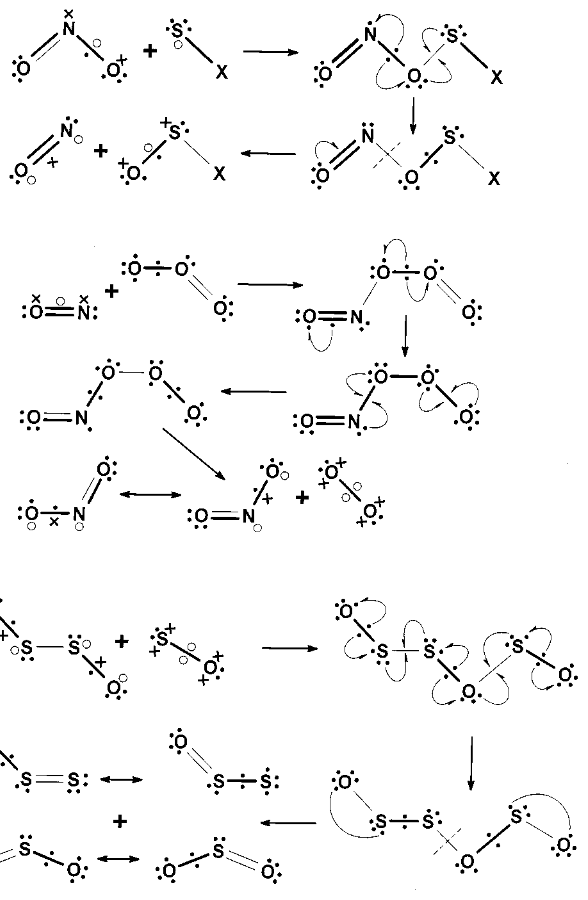


Figure 4. Increased-valence representations for $NO_2 + SX \rightarrow NO + OSX$ (X = halogen), $NO + O_3 \rightarrow NO_2 + O_2$, and $3\,SO \rightarrow SO_2 + S_2O$ via an $S = 1$ spin intermediate S_2O_2 (each of O_2, SO and S_2 has a $^3\Sigma_g^-$ ground-state; therefore an $S = 0 \leftarrow S = 1$ electronic excitation of one of the SO monomers must occur to obtain the $S = 1$ spin intermediate for S_2O_2; the reaction $2\,SO + S_2 \rightarrow 2\,S_2O$ may be similarly represented)

The results of spin-coupled VB calculations have been interpreted to imply that 1,3-dipolar molecular species possess very little singlet diradical character.[3a,3b,39] For some of these molecules, such as N_2O, a similar conclusion was obtained from *biorthogonal* VB calculations.[40] In contrast, classical VB studies[27−29,36,41] indicate that singlet-diradical canonical Lewis structures can contribute appreciably to the ground-state resonance schemes. The difference in interpretation is associated[5a,28,35] with the use of the 2-centre or multicentre "distorted" AOs to accommodate at least some of the active-space electrons in the spin-coupled VB calculations. The use of these AOs conceals[5a,28,35] the presence of appreciable singlet-diradical character, which manifests itself in VB representations for reactions that involve 1,3-dipolar molecules[29−32] (for example, $NO + O_3 \rightarrow NO_2 + O_2$ in Figure 4).

$N\equiv N=O$
48

$:N\equiv N-\underset{\cdot\cdot}{O}: \longleftrightarrow :N\equiv N=\ddot{O}:$
49 **50**

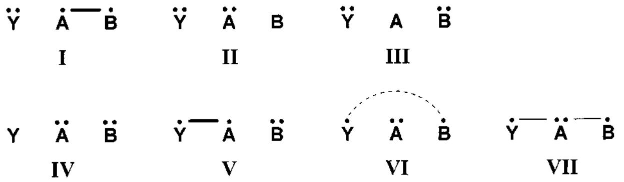


Figure 5. Canonical Lewis VB structures for $S = 0$ spin 4-electron 3-centre bonding unit, with three overlapping AOs; $\Psi_{\mathbf{I}} = |y^{\alpha}y^{\beta}a^{\alpha}b^{\beta}| + |y^{\alpha}y^{\beta}b^{\alpha}a^{\beta}|$, $\Psi_{\mathbf{II}} = |y^{\alpha}y^{\beta}a^{\alpha}a^{\beta}|$, $\Psi_{\mathbf{III}} = |y^{\alpha}y^{\beta}b^{\alpha}b^{\beta}|$, $\Psi_{\mathbf{IV}} = |a^{\alpha}a^{\beta}b^{\alpha}b^{\beta}|$, $\Psi_{\mathbf{V}} = |y^{\alpha}a^{\beta}b^{\alpha}b^{\beta}| + |a^{\alpha}y^{\beta}b^{\alpha}b^{\beta}|$, $\Psi_{\mathbf{VI}} = |y^{\alpha}a^{\beta}a^{\alpha}b^{\beta}| + |a^{\alpha}y^{\beta}b^{\alpha}a^{\beta}|$; with either a (non-orthogonal) double-zeta basis set, or an (orthogonal) expanded valence-shell AO basis set (a,d) for the two electrons on atom A in structure **VI**, canonical Lewis structure **VII** will also contribute to the VB resonance scheme; using the (a,d) basis, y-a and d-b spin-pairings give $\Psi_{\mathbf{VII}} = |y^{\alpha}a^{\beta}d^{\alpha}b^{\beta}| + |y^{\alpha}a^{\beta}b^{\alpha}d^{\beta}| + |a^{\alpha}y^{\beta}b^{\alpha}d^{\beta}| + |a^{\alpha}y^{\beta}d^{\alpha}b^{\beta}|$; a second $S = 0$ spin wavefunction, with a-d and y-b spin-pairings, may also be constructed

A 19th century-type of VB representation for N_2O is **48**, and a 20th century equivalent, **49** ↔ **50**, involve an apparent quinquevalence for the central nitrogen atom. VB structures of type **48** have been used frequently in discussions of the results of spin-coupled VB calculations. With a minimal basis set, it has been calculated that increased-valence structure **31** is more stable than the **49** ↔ **50** resonance.[42]

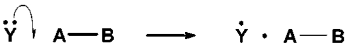
Increased-Valence Structures and 4-Electron 3-Centre Bonding

I shall now redescribe and develop further some of the general VB theory for 4-electron 3-centre bonding units, i.e. for four electrons distributed amongst three overlapping AOs located on three atomic centres.[4,5,30a,34,35,43]

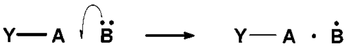
For each of $Fe^{II}O_2$ and N_2O, there are two 4-electron 3-centre bonding units. For the purpose of the following discussion, it is easier to focus attention on those for N_2O. These bonding units arise from the presence of four π_x electrons and four π_y electrons, which are distributed between three overlapping $2p_x$ and three overlapping $2p_y$ AOs, respectively. For each $S = 0$ spin 4-electron 3-centre bonding unit, there are six[42,43] canonical Lewis VB structures, namely **I**−**VI** of Figure 5, in which Y, A, and B are the atomic centres, and y, a, and b are the associated (normalized) overlapping AOs. Each of the structures **I**, **V**, and **VI** has two singly occupied AOs, and their $S = 0$ spin wavefunctions are indicated in the caption for Figure 5.

Structures **I** and **V** are Kekulé-type structures, structure **VI** is a Dewar-type structure, and structures **II**−**IV** are of the polar type.

For any 4-electron 3-centre bonding unit, increased-valence structures[4,5,30a,34,35,43] may be constructed from Kekulé-type Lewis structures by delocalizing a non-bonding Y or B electron into a bonding Y−A or A−B MO, as is indicated in **51** → **52** and **53** → **54**.



51 **52**



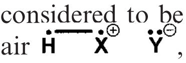
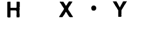
53 **54**

The delocalized electron occupies the bonding localized MO (LMO) $\psi_{ay} = a + ly$ in structure **52** and the bonding LMO $\psi_{ab} = a + kb$ in structure **54**. When $\Psi_{\mathbf{I}}$ and $\Psi_{\mathbf{V}}$ are assumed to be the wavefunctions (cf. Figure 5) for structures **51** and **53** it follows that **52** ≡ **I** ↔ **VI** and **54** ≡ **V** ↔ **VI**, i.e. in each case, the increased-valence structure is equivalent to resonance between the Kekulé and Dewar canonical Lewis structures. Because of the absence of either an A−B or a Y−A electron-pair bond in the Dewar structure **VI**, the A−B bond in **52** and the Y−A bond of **54** are fractional electron-pair bonds.

The increased-valence structure **54** involves the $(y)^1(a)^1(\psi_{ab})^1(b)^1$ configuration. We have already demonstrated that the A-B three-electron bond configuration $(a)^1(\psi_{ab})^1(b)^1$ is proportional to the MO configuration $(\psi_{ab})^2(\psi^*_{ab})^1$, [cf. Equations (1) and (2), and Figure 1]. Therefore $(y)^1(a)^1(\psi_{ab})^1(b)^1$ is proportional to $(y)^1(\psi_{ab})^2(\psi^*_{ab})^1$, i.e. increased-valence structure **54** involves the spin-pairing of the y electron with the antibonding ψ^*_{ab} electron of the A-B three-electron bond. [In terms of Slater determinants, the $S = 0$ spin wavefunction is give by Equation (3).]

$$\begin{aligned}\Psi_{\mathbf{54}} &= |y^{\beta}a^{\alpha}\psi_{ab}{}^{\beta}b^{\alpha}| + |y^{\alpha}a^{\beta}\psi_{ab}{}^{\alpha}b^{\beta}| \\ &\propto |y^{\beta}\psi_{ab}{}^{\alpha}\psi_{ab}{}^{\beta}\psi^*{}_{ab}{}^{\alpha}| + |y^{\alpha}\psi_{ab}{}^{\beta}\psi_{ab}{}^{\alpha}\psi^*{}_{ab}{}^{\beta}| \qquad (3)\end{aligned}$$

Consideration has been[34] given to the evaluation of atomic valencies for increased-valence structure **54**, with AO overlap integrals both excluded and included in the definition of valence. It has been demonstrated that the A-atom valence is able to exceed unity in this structure, whereas in each of the Kekulé-type Lewis structures, **I** and **V**, the A-atom valence is unity. Therefore with regard to its A-atom valence, VB structure **54** (and also **52**) may exhibit "increased-valence" relative to the Kekulé-type Lewis structures.

The results of experimental and theoretical studies of HXY-type rare-gas molecules (X = Kr or Xe; Y = Cl, Br, I, CN, ...) have been reviewed recently.[45] The H, X, and Y then correspond to the Y, A, and B of Figure 5. With X = Xe and Y = Cl, the origin of bonding is considered to be described[45,46] best as primarily an ion pair , which is equivalent to structure **V** of Figure 5. However at non-dissociative interatomic distances, it will interact with , which corresponds to structure **VI** of Figure 5. Resonance between these canonical Lewis structures generates increased-valence structure **54** as .

Increased-Valence Structures and Expansion of Valence-Shell

To stabilize further a 4-electron 3-centre bonding unit, additional AOs may be included on the atomic centres. We focus attention on the A-atom of increased-valence structure **54** by including a second orthogonal AO, which we designate as d. We now define a new A−B bonding MO as $\psi_{a'b} = a + kb + k'd = \psi_{ab} + k'd$. The resulting

$(y)^1(a)^1(\psi_{a'b})^1(b)^1$ configuration, (whose $S = 0$ spin wavefunction involves four Slater determinants, cf. $\Psi_{\mathbf{VII}}$ of Figure 5), may then be expressed according to Equation (4).

$$(y)^1(a)^1(\psi_{a'b})^1(b)^1 = (y)^1(a)^1(\psi_{ab})^1(b)^1 + k'(y)^1(a)^1(d)^1(b)^1 \tag{4}$$

$$\rightarrow \Psi_{\mathbf{54}}(k'=0) + k'\Psi_{\mathbf{VII}} \tag{5}$$

For $\Psi_{\mathbf{54}}(k' = 0)$, spin-pairing occurs between the y and ψ^*_{ab} electrons, whereas $\Psi_{\mathbf{VII}}$ involves y-a and d-b spin-pairings. Introduction of the d AO enables allowance for expansion of the A-atom valence-shell to occur via use of an increased-valence structure. To provide an example, we consider the axial F−Cl−F σ-bonding for ClF_3 of Figure 6.

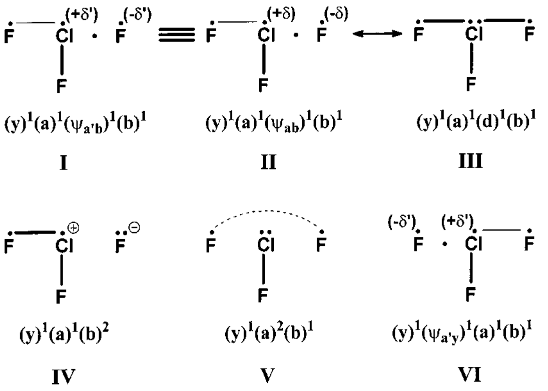


Figure 6. Increased-valence structures **I** and **VI** for ClF_3 with expanded valence-shell on the Cl atom; for the axial three-centre bonding, y, a, b and d are 2pσ(F), 3pσ(Cl), 2pσ(F) and $3d_z{}^2$(Cl) AOs; $\psi_{a'b} = a + kb + k'd = \psi_{ab} + k'd$, $\psi_{a'y} = a + ky + k'd = \psi_{ay} + k'd$, with y-a and $\psi_{a'b}$-b spin-pairings for structure **I** and b-a and $\psi_{a'y}$-y spin-pairings for structure **VI** (cf. $\Psi_{\mathbf{VII}}$ for structure **VII** in Figure 5)

If y = $F(2p_z)$, a = $Cl(3p_z)$, b = $F(2p_z)$, and d = $Cl(3d_{z^2})$, then increased-valence structure **I** for ClF_3 is equivalent to resonance between the increased-valence structure **II** ($k' = 0$) and the expanded valence-shell structure **III**. In turn, increased-valence **II** ($k' = 0$) is equivalent to resonance between the canonical Lewis structures **IV** and **V** of Figure 6. A similar type of identity may be developed for the mirror-image increased-valence structure **VI** of Figure 6.

In ref.[35], analagous theory has also been developed for a double-zeta basis set (with a′ and a″ AOs replacing the a and d AOs) on the A-atom. In subsequent discussions we shall not consider explicitly either double-zeta basis sets or expansion of the valence shell, but recognize that when appropriate, these types of basis sets may be introduced into the wavefunction for an increased-valence structure.

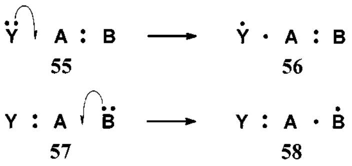
Numerous MO studies of the phenomenon of valence-shell expansion have been reported.[47] The difficulty for atoms of first-row elements to form many stable hypercoordinate compounds has been associated[34,43] with large values for the ionization energies of A-atoms in Lewis structures of type **VI** in Figure 5, when A is a first-row atom.

Localized MO Increased-Valence Structures

The identities **52** ≡ **I** ↔ **VI** and **54** ≡ **V** ↔ **VI** utilize the a and b AOs to accommodate the electrons of the fractional A-B electron-pair bond in increased-valence structure **52**, and the y and a AOs of the fractional Y−A electron-pair bond in increased-valence structure **54**. For a more general formulation of these bonds, these AOs are replaced by the Coulson−Fischer-type[48] LMOs of Equations (6) and (7) for the fractional A−B and Y−A bonds, respectively. The LMO VB structures that correspond to the canonical Kekulé structures **I** and **V** and the increased-valence structures **52** and **54**, are symbolized[5,30a,43] as **55** and **57**, and **56** and **58**, respectively, for which **55** ≡ **I**↔**II**↔**III**, **57** ≡ **V**↔**IV**↔**III**, and structures **I**−**V** here are those of Figure 5.

$$\psi''_{ab} = a + k''b,\ \psi'_{ba} = b + k'a \tag{6}$$

$$\psi''_{ay} = a + l''y,\ \psi'_{ya} = y + l'a \tag{7}$$



In the LMO Kekulé-type structures **55** and **57**, the one-electron delocalization that is needed to generate the LMO increased-valence structures **56** or **58** is indicated. As is the case for the (Heitler−London-type) increased-valence structures **52** and **54**, the delocalized electron occupies the Y−A bonding LMO $\psi_{ay} = a + ly$ in increased-valence structure **56**, and the A−B bonding LMO $\psi_{ab} = a + kb$ in increased-valence structure **58**. The A-atom valence in the LMO increased-valence structures **56** and **58** can exceed unity,[30a,43] and a demonstration of this result is provided again in the Appendix.

LMO Increased-Valence Structures and Donor-Acceptor Complexes

The simplest types of $S = 0$ spin wavefunctions for the LMO increased-valence structures **56** and **58** are those of Equations (8) and (11) respectively.[30a,43]

$$\Psi_{\mathbf{56}} = |\psi'_{ba}{}^{\alpha}\psi''_{ab}{}^{\beta}\psi_{ay}{}^{\alpha}y^{\beta}| + |\psi''_{ab}{}^{\alpha}\psi'_{ba}{}^{\beta}y^{\alpha}\psi_{ay}{}^{\beta}| \tag{8}$$

$$\Psi_{\mathbf{56}} = l\{(1 + k'k'')\Psi_{\mathbf{I}} + 2k'\Psi_{\mathbf{II}} + 2k''\Psi_{\mathbf{III}}\} + k''\Psi_{\mathbf{V}} + \Psi_{\mathbf{VI}} \tag{9}$$

$$\Psi_{\mathbf{56}} = l\Psi_{\mathbf{55}} + \Psi_{\mathbf{54''}} \tag{10}$$

$$\Psi_{\mathbf{58}} = |\psi'_{ya}{}^{\alpha}\psi''_{ay}{}^{\beta}\psi_{ab}{}^{\alpha}b^{\beta}| + |\psi''_{ay}{}^{\alpha}\psi'_{ya}{}^{\beta}b^{\alpha}\psi_{ab}{}^{\beta}| \tag{11}$$

$$\Psi_{\mathbf{58}} = k\{(1 + l'l'')\Psi_{\mathbf{V}} + 2l'\Psi_{\mathbf{IV}} + 2l''\Psi_{\mathbf{III}}\} + l''\Psi_{\mathbf{I}} + \Psi_{\mathbf{VI}} \tag{12}$$

$$\Psi_{\mathbf{58}} = k\Psi_{\mathbf{57}} + \Psi_{\mathbf{52''}} \tag{13}$$

When the AO expressions for ψ_{ay}, ψ_{ab} and the LMOs of Equations (6) and (7) are substituted into Equations (8) and (11), we obtain the linear combinations of Equations (9) and (12) respectively. These linear combinations show that the Dewar structure **VI** of Figure 5 is included in the equivalent canonical structure resonance schemes for the LMO increased-valence structures **56** and **58**. Equations (9) and (12) are also equivalent to Equations (10) and (13) respectively, in which the the $\Psi_{\mathbf{54}''}$ and $\Psi_{\mathbf{52}''}$ correspond to $\Psi_{\mathbf{54}}$ and $\Psi_{\mathbf{52}}$ when k'' and l'' replace k and l in the latter configurations.

The lower-energy linear combination of $\Psi_{\mathbf{56}}$ and $\Psi_{\mathbf{58}}$, via Equation (14), has seven variational parameters (k, l, k', k'', l', l'', and μ) whereas the lowest-energy linear combination of the $\Psi_{\mathbf{I}}-\Psi_{\mathbf{VI}}$ of Figure 5 involves five independent variational parameters. One type of correspondence between the two linear combinations is obtained when l' and l'' are set equal to k' and k'' respectively.

$$\Psi(\text{Increased-valence, LMO}) = \Psi_{\mathbf{56}} + \mu\Psi_{\mathbf{58}} \tag{14}$$

Each of Equations (10) and (13) represents a Mulliken-type wavefunction[30a,43] for either an intra- or an intermolecular complex when the complex involves an n-type donor (D), and a sacrificial acceptor (A). The simplest Mulliken-type representation for such a complex involves resonance between a "no bond" (D,A) and a dative (D^+-A^-) VB structure.[22] Thus when $\ddot{\mathrm{Y}}$ and A : B are identified as an electron-donor and an electron-acceptor, the VB structures **55** and **54** correspond to the (D,A) and (D^+-A^-) structures respectively, and according to Equation (10), increased-valence structure **56** is equivalent to resonance between these two structures. Similarly, increased-valence structure **58** is equivalent to resonance between (D,A) and (D^+-A^-) types of VB structures, with D = $\ddot{\mathrm{B}}$, A = Y : A, (D,A) = **57** and (D^+-A^-) = **52**. In each of the increased-valence structures, a one-electron bond links the donor to the acceptor.

One-Electron and Concerted Two-Electron Delocalizations into Bonding and Antibonding Molecular Orbitals

When $k'' = 1/k' = k$ in Equation (6), an approximate LMO wavefunction for VB structure **55** is given by Equation (15).

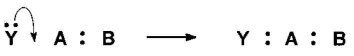
$$\psi_{\mathbf{55}} = |y^{\alpha}y^{\beta}\psi_{ab}{}^{\alpha}\psi_{ab}{}^{\beta}| \tag{15}$$

Some (concerted) delocalization of the y electrons into the antibonding MO $\psi^*_{ab} = k^*a - b$ generates the *approximate* MO wavefunction[49,50] of Equation (16), which provides the usual approximate MO formulation for the anomeric effect[51] and negative hyperconjugation.[52]

$$\Psi_1(\text{MO}) = |(y + \lambda\psi^*_{ab})^{\alpha}(y + \lambda\psi^*_{ab})^{\beta}\psi_{ab}{}^{\alpha}\psi_{ab}{}^{\beta}| \tag{16}$$

$$\begin{aligned}\Psi_1(\text{MO}) \equiv {} & |y^{\alpha}y^{\beta}\psi_{ab}{}^{\alpha}\psi_{ab}{}^{\beta}| + \lambda(|y^{\alpha}\psi^*_{ab}{}^{\beta}\psi_{ab}{}^{\alpha}\psi_{ab}{}^{\beta}| \\ & + |\psi^*_{ab}{}^{\alpha}y^{\beta}\psi_{ab}{}^{\alpha}\psi_{ab}{}^{\beta}|) + \lambda^2|\psi^*_{ab}{}^{\alpha}\psi^*_{ab}{}^{\beta}\psi_{ab}{}^{\alpha}\psi_{ab}{}^{\beta}|\end{aligned} \tag{17}$$

When the y electrons of structure **55** are delocalized into the Y−A bonding MO $\psi_{ya} = y + la$, according to **55** → **59**, the resulting wavefunction is given by Equation (18).



55 **59**

$$\psi_{\mathbf{59}} = |\psi_{ya}{}^{\alpha}\psi_{ya}{}^{\beta}\psi_{ab}{}^{\alpha}\psi_{ab}{}^{\beta}| \tag{18}$$

$$\begin{aligned}\psi_{\mathbf{59}} \equiv {} & |y^{\alpha}y^{\beta}\psi_{ab}{}^{\alpha}\psi_{ab}{}^{\beta}| + l\{|y^{\alpha}a^{\beta}\psi_{ab}{}^{\alpha}\psi_{ab}{}^{\beta}| \\ & + |a^{\alpha}y^{\beta}\psi_{ab}{}^{\alpha}\psi_{ab}{}^{\beta}|\} + l^2|a^{\alpha}a^{\beta}\psi_{ab}{}^{\alpha}\psi_{ab}{}^{\beta}|\end{aligned} \tag{19}$$

Introduction of the identities $|\psi^*_{ab}{}^{\alpha}\psi_{ab}{}^{\alpha}| = (kk^* + 1)|a^{\alpha}b^{\alpha}|$ and $|\psi^*_{ab}{}^{\beta}\psi_{ab}{}^{\beta}| = (kk^* + 1)|a^{\beta}b^{\beta}|$ into Equation (17), and the identities $|a^{\alpha}\psi_{ab}{}^{\alpha}| = k|a^{\alpha}b^{\alpha}|$ and $|a^{\beta}\psi_{ab}{}^{\beta}| = k|a^{\beta}b^{\beta}|$ into Equation (19), we obtain[49] Equations (20) and (21), in which $\Psi_{\mathbf{IV}}$ is the wavefunction for VB structure **IV** of Figure 5. The Ψ_1(MO) and $\psi_{\mathbf{59}}$ are equivalent[49] when $\lambda = kl/(kk^* + 1)$. Therefore some concerted delocalization of the two lone-pair electrons of donor $\ddot{\mathrm{Y}}$ of VB structure **55** into the vacant *antibonding* MO of acceptor A : B is equivalent to the concerted delocalization of these electrons into the Y−A *bonding* MO, to give VB structure **59**.

$$\Psi_1(\text{MO}) \equiv \Psi_{\mathbf{55}} + \lambda(kk^* + 1)\Psi_{\mathbf{54}} + (kk^* + 1)^2\lambda^2\Psi_{\mathbf{IV}} \tag{20}$$

$$\psi_{\mathbf{59}} \equiv \Psi_{\mathbf{55}} + kl\Psi_{\mathbf{54}} + k^2l^2\Psi_{\mathbf{IV}} \tag{21}$$

VB Representations for Gas-Phase Nucleophilic Substitution Reactions

If $\ddot{\mathrm{Y}}$ is a nucleophile and A:B is a substrate, then at each stage along the reaction coordinate, resonance between the LMO increased-valence structures **56** and **58** can be used to provide a "variationally-best" VB representation [cf. Equation (14)] for a gas-phase nucleophilic substitution reaction. In several publications,[5,30a,43,53] the generalized VB representation for this type of reaction has been presented. Here we consider a specific example, namely that of **I** → [**II** ↔ **III**] → **IV** of Figure 7 for the (Grotthuss) proton-transfer reaction $H_2O + H_3O^+ \rightarrow H_3O^+ + H_2O$. The LMO increased-valence structures **II** and **III** of Figure 7 are VB structures for reactant-like and product-like complexes respectively, and are formed via the one-electron delocaliz-

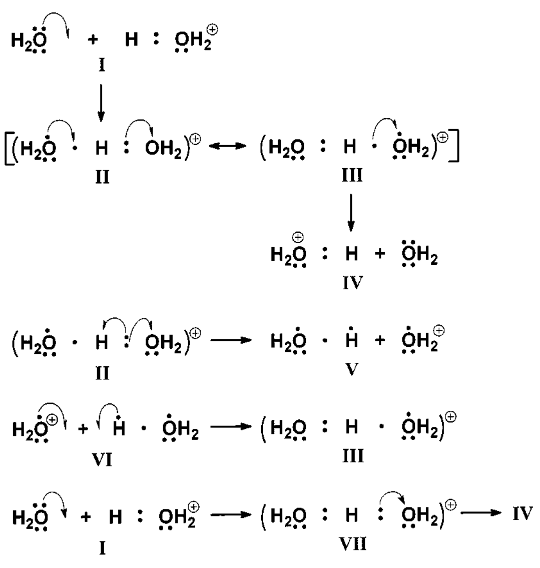


Figure 7. Valence-bond representations for the gas-phase proton-transfer reaction $H_2O + H_3O^+ \rightarrow H_3O^+ + H_2O$

ations that are indicated in this Scheme. At the conclusion of the reaction, the reactant-like complex **II** would dissociate according to **II** → **V** of Figure 7, whereas near the commencement of the reaction, the formation of the product-like complex **III** proceeds according to **VI** → **III** of Figure 7.

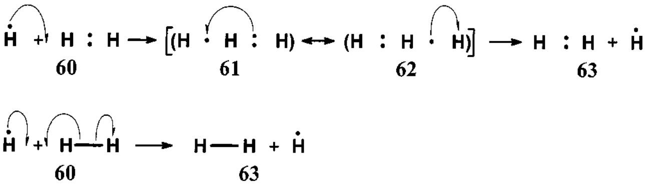
In ref.[5b,30a,53], the generalized forms of VB structures **I**−**VI** of Figure 7 have been used to construct state correlation diagrams for the conversion of reactants into products. These diagrams use a VB symbolism which differs from the symbolism used by Shaik and co-workers[3f] for this purpose. Shaik and co-workers[3f] use VB structures of type **2** to represent the three-electron bond structures − for example $HO_2\overset{\bullet}{—}H$ and $H\overset{\bullet}{—}OH_2$ for the H_3O structures **V** and **VI**.

A qualitative MO description for nucleophilic substitution reactions is often formulated approximately according to the Ψ_1(MO) of Equation (16), i.e. electrons delocalize from the nucleophile orbital (y) into the antibonding MO (ψ^*_{ab}) of the substrate. As has been deduced above, this delocalization is equivalent to the concerted delocalization of the y electrons into the bonding MO (ψ_{ya}), according to **55** → **59**, or **I** → **VII** of Figure 7 here. According to Equation (20), the Ψ_1(MO) configuration of Equation (16) alone cannot generate the $H_3O^+ + H_2O$ products; the inclusion of the Ψ_{IV} (of Figure 5) of this Equation, to give an $H_2O^{2+}H_3O^-$ structure, prevents this from occurring. To obtain the correct dissociation products, it is then necessary to form[49] the linear combination $\Psi = C_1\Psi_1(MO) + C_2\Psi_2(MO)$, with Ψ_2(MO) given by Equation (22), in which $\psi_{ay} = a + \kappa y$ and $\psi^*_{ay} = \kappa^*a - y$. The LMO equivalent for this type of linear combination is examined in ref.[43], where it is demonstrated that the formation of the primary contributor to the VB representation of a reactant-like complex must proceed according to an initial *one-electron* delocalization, as in **I** → **II** of Figure 7, rather than by the *concerted electron-pair* delocalization which is associated with the Ψ_1(MO) of Equation (16).

$$\Psi_2(MO) = |(b + \lambda'\psi^*_{ay})^{\alpha}(b + \lambda'\psi^*_{ay})^{\beta}\psi_{ay}{}^{\alpha}\psi_{ay}{}^{\beta}| \tag{22}$$

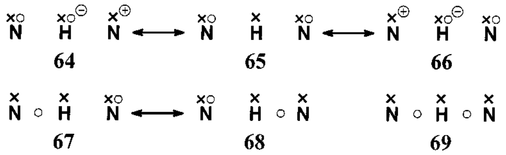
Three-Electron Three-Centre Bonding and VB Representations for Gas-Phase Radical Transfer Reactions

Although 3-electron 3-centre bonding units are not electron-rich, it is possible to construct increased-valence structures for them. The LMO VB structures **61** and **62** for H_3 in the formulation[54] **60** → [**61** ↔ **62**] → **63** for the radical transfer reaction $H + H_2 \rightarrow H_2 + H$, provide examples. These structures represent reactant-like and product-like intermolecular species, respectively. The formulation **60** → [**61**↔**62**] → **63** indicates succinctly the nature of the electronic reorganization which may be involved in the conversion of reactants into products for a radical transfer reaction. This formulation is equivalent to the variationally best resonance between the eight (S = 1/2 spin) canonical Lewis structures that may be constructed from three overlapping AOs.[54] The electronic reorganization is also equivalent to the more familiar formulation of **60** → **63**.



Five-Electron Three-Centre Bonding

Each of NO_2, SO_2^-, and ClO_2 has a 5-electron 3-centre bonding unit;[5c,36,55] five electrons are distributed amongst three overlapping σ AOs (NO_2) or π-electron AOs (SO_2^- and ClO_2, when it is assumed that sulfur and chlorine 3d AOs do not participate in π-bonding as hybridization functions). For this type of bonding unit, three equivalent VB representations may be constructed,[5c,36,55] which we illustrate here for the NHN linkage[56] that arises when two nitrogen atoms are linked by a hydrogen atom in medium-ring bicyclic compounds.



(a) Resonance between the canonical Lewis structures **64**, **65**, and **66**.

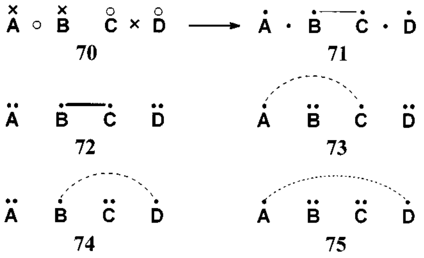
(b) Resonance between the three-electron bond structures **67** and **68**.

(c) The VB structure **69**, with two (non-independent) three-electron bonds.

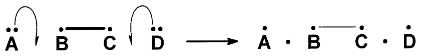
The wavefunction for each of these sets of VB structures is also equivalent[4,5c,36,55] to the 3-centre MO configuration $(\psi_1)^2(\psi_2)^2(\psi_3)^1$ for the five electrons.

Six-Electron Four-Centre Bonding: Theory

Six-electron 4-centre bonding units involve six electrons distributed amongst four overlapping AOs[4,5,57] located around four atomic centres. An increased-valence structure for an extended 6-electron 4-centre bonding unit is obtained[4,5,57a,57b] by spin-pairing in a Heitler−London manner the odd electrons of two three-electron bonds structures AB and CD, as is indicated in **70** → **71**.



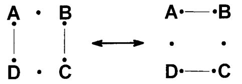
Increased-valence structure **71** is equivalent to resonance between the canonical Kekulé structure **72** and the canonical Dewar structures **73**−**75**, and may also be derived[4,5,57] from the Kekulé structure **72** by delocalizing a non-bonding a and a non-bonding d electron into the A-B bonding MO and the C-D bonding MO, respectively.



72 **71**

For symmetrical 6-electron 4-centre bonding units it has been deduced[4,5c,57a] that Ψ_{71} is equivalent to the covalent component of the MO configuration $|\psi_1{}^{\alpha}\psi_1{}^{\beta}\psi_2{}^{\alpha}\psi_2{}^{\beta}\psi_3{}^{\alpha}\psi_3{}^{\beta}|$ with $\psi_1 = a + d + \lambda(b + c)$, $\psi_2 = a - d + k(b - c)$, $\psi_3 = \lambda^*(a + d) - (b + c)$, when the MO configuration is expressed as $\Psi_{\text{covalent}} + \Psi_{\text{ionic}}$. Configuration interaction increases the importance of Ψ_{covalent} relative to Ψ_{ionic}. Theory for non-symmetrical 6-electron 4-centre bonding units is described in ref.[57d]

For a cyclic 6-electron 4-centre bonding unit, increased-valence structures **76** and **77** may be constructed.[4,5][57c] Resonance between these structures corresponds to the covalent component of a three-configuration MO-CI wavefunction.[5c,57c] It is also equivalent to resonance between four canonical Kekulé-type Lewis structures and two canonical Dewar-type Lewis structures.



76 **77**

Six-Electron Four-Centre Bonding: Some Applications

Over the last decade, we have studied the following systems, each of which involves one or more 6-electron 4-centre bonding units.

(a) $OClOClO_2$, to demonstrate that the existence of long intermolecular O−Cl bonds between the two ClO_2 moieties[58] is associated[55] with the presence of a Cl−O three-electron bond in each of these moieties.

(b) N_2O_4, N_2O_3, and N_2O_2 to account for variations in their N−N bond lengths (1.78 Å, 1.86 Å and 2.24 Å)[5b,59a,59b,60c] relative to the 1.45 Å for N_2H_4. The bond lengthenings are shown to be due primarily to (i) delocalization of oxygen lone-pair electrons into the AOs of the N−N σ-bond (N_2O_4), (ii) delocalization of NO_2-oxygen lone-pair electrons into the AOs of the N−N σ-bond and the orientations of the NO-nitrogen AOs, to give a (fractional) bent N−N σ-bond (N_2O_3), and (iii) orientations of the NO-nitrogen AOs to give a (fractional) bent N−N σ-bond, together with the consequent strong non-bonded repulsions between the nitrogen lone-pair electrons (N_2O_2).

(c) The D_{2h} and D_{2d} isomers of N_2O_4, in order to demonstrate[59c,60a] that *cis* O−O overlap in the planar conformer is primarily responsible for the barrier to rotation around the N−N bond of this species. The *cis* O−O overlap manifests itself in a stabilizing manner by appreciable delocalization of oxygen lone-pair electrons into the AOs of the N−N σ-bond, and covalent-ionic resonance (i.e. $O_2N{-}NO_2 \leftrightarrow O_2N^+NO_2{}^- \leftrightarrow O_2N^-NO_2{}^+$) is calculated to be needed to enhance this stabilizing effect.

(d) $S_2Cl_4{}^{2+}$,[57b] the linear cation $ICNI^+$,[57d] the N−N dimer of HNO,[60b] the D_{2h} dimer of O_2,[60d] and S_2N_2.[60e]

In Figure 8, increased-valence structures **I-III** are displayed for S_2O_2, $S_2O_4{}^{2-}$, and $S_2I_4{}^{2+}$, together with experimental estimates[4,38] for their bond lengths and those for S_2, SO, I_2^+, and "normal" S−S and S−I single bonds.The increased-valence structures are derived from either or both of the **70** → **71** or the **72** → **71** types processes for 6-electron 4-centre bonding units. Inspection of structures **I**−**III** reveals that the bond-orders implied by them are in qualitative accord with the experimental S−S, S−O, S−I, and I−I bond lengths for S_2O_2, $S_2O_4{}^{2-}$, and $S_2I_4{}^{2+}$. For example, the S−S bond order is less than two in **I**, less than unity in **II**, and equal to two in **III**, and the S-S lengths for S_2O_2, $S_2O_4{}^{2-}$, and $S_2I_4{}^{2+}$ are respectively longer than a double bond, longer than a single bond and somewhat shorter than a double bond.

In Figure 9, increased-valence structures for cyclic S_2N_2 are derived[60e] from the familiar zwitterionic Lewis structures via **72** → **71** type delocalizations. VB representations[38,61] for $S_2N_2 \rightarrow (SN)_x$ polymerization and electron conduction in the $(SN)_x$ polymer, are also displayed in Figure 9.

The Antiferromagnetism of the Copper Acetate Dimer

A 6-electron 4-centre bonding unit[5a,5c,62] is present in each $Cu^{II}(CH_3COO^-)Cu^{II}$ component of antiferromagnetic[63] $Cu_2(CH_3COO)_4 \cdot 2\,H_2O$, for which $J = (E_{\text{singlet}} - E_{\text{triplet}})/2 = -143\ \text{cm}^{-1}$.[63] It arises from the overlap of singly occupied $3d_{x^2-y^2}$ AOs on the Cu^{II} ions with a lone-pair AO on each oxygen atom of the CH_3COO^- ligand

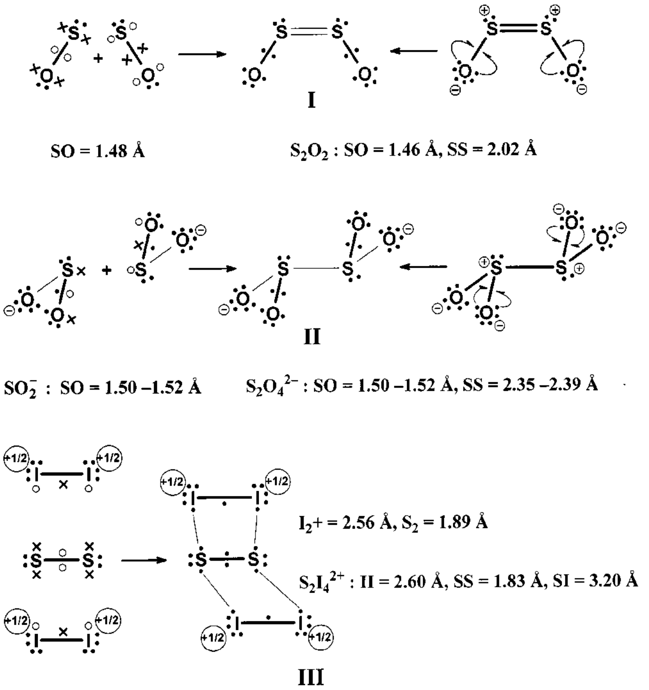


Figure 8. VB structures and bond-lengths for SO, S_2, $SO_2{}^-$, $I_2{}^+$, S_2O_2, $S_2O_4{}^{2-}$, and $S_2I_4{}^{2+}$ with 6-electron 4-centre bonding units; the increased-valence structure for $SO_2{}^-$ is obtained by replacing the halogen X by O^- in the increased-valence structure displayed for XSO in Figure 4; estimates of the lengths of "normal" S−O, S−S, S−I, and I−I single bonds are 1.70, 2.06, 2.37, and 2.67 Å, respectively[4]

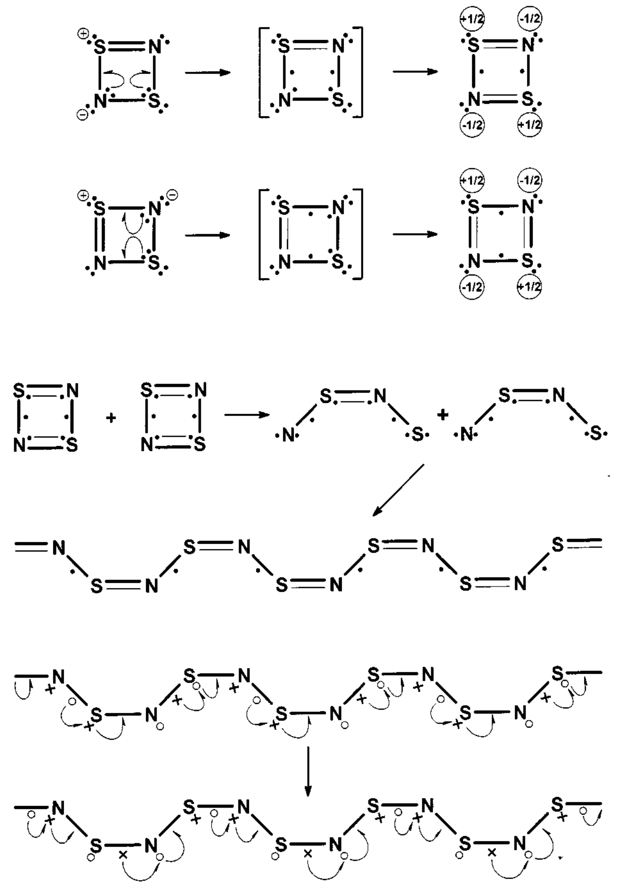


Figure 9. Derivation of increased-valence structures for S_2N_2, and VB representations for $S_2N_2 \rightarrow (SN)_x$ polymerization and electron conduction in $(SN)_x$

(Figure 10). The A and D atoms of VB structure **72** are the oxygen atoms, and B and C are the copper atoms. The oxygen lone-pair AOs overlap to a small extent, as do the $3d_{x^2-y^2}$ AOs. The origin of the antiferromagnetism has been associated primarily with superexchange, i.e. some delocalization of the oxygen lone-pair electrons into the singly-occupied $3d_{x^2-y^2}$ AOs, together with covalent-ionic resonance $[(CuO)(CuO) \leftrightarrow (CuO)^-(CuO)^+ \leftrightarrow (CuO)^+(CuO)^-]$.[5a,5c,62]

The primary type of covalent-ionic resonance involves[5a,5c,62] the $S = 0$ and $S = 1$ spin VB structures of Figure 10. These structures arise by the delocalization of one oxygen lone-pair electron into a singly-occupied copper AO. The $S = 0$ spin covalent and ionic structures correspond to the generalized Lewis structures of types **73** and **74** above, and **78** and **79**, respectively. (For the corresponding $S = 1$ structures, the two electrons that singly occupy AOs have parallel spins.) Because the AO overlap between the singly occupied non-adjacent AOs is small, the covalent VB structures are essentially degenerate, i.e. $^3E_{cov} \approx {}^1E_{cov} = E_{cov}$. It may be deduced[64] that the resulting expression for the magnetic exchange parameter that arises from these types of covalent-ionic resonance is approximately given by $J = (\beta_{bc} + \beta_{ad})^2 J_{CuO}/({}^1E_{ion} - E_{cov})^2$, in which β_{bc} and β_{ad} are O−O and Cu−Cu overlap-dependent resonance integrals, and J_{CuO} is the (negative) exchange integral for the Cu−O electron-pair bond of each $S = 0$ spin ionic structure.

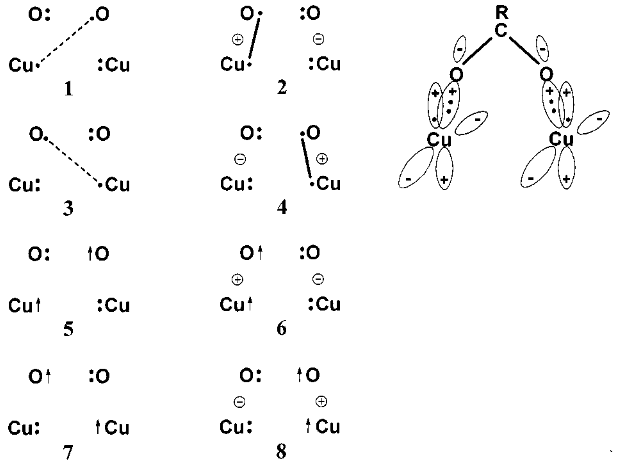
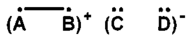


Figure 10. AOs for a 6-electron 4-centre bonding unit of $Cu^{II}(CH_3COO^-)Cu^{II}$,[5c] and the associated primary Lewis-type VB structures for a VB rationalization of the origin of the antiferromagnetism of Cu^{II} carboxylate dimers[5c]



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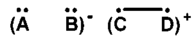


79

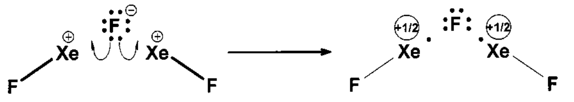
Of course, covalent structures of types **72** and **75**, together with their ionic partners, also participate in resonance with the VB structures of types **73**, **74**, **78**, and **79**, and their contributions to the magnetic exchange parameter will modify the above expression for it. With $\psi_{ab} = a + kb$ and $\psi_{dc} = d + kc$, the *simplest* expression for J is then given by[64] Equation (23).

$$J = -2\{(\beta_{bc})^2/(\gamma_{bb} - \gamma_{bc}) - k^2 J_{CuO}(\beta_{bc} + \beta_{ad})^2/(\gamma_{ab} - \gamma_{ac})^2 + k^4(\beta_{ad})^2/(\gamma_{aa} - \gamma_{ad})\}/(k^2 + 1)^2 \qquad (23)$$

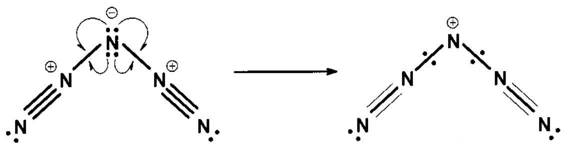
In Equation (23), k is the "superexchange" parameter, which measures the extent of delocalization of electrons from the oxygen AOs (a and d) into the copper AOs (b and c) The $\gamma_{\upsilon\nu}$ are (two-electron) Coulomb integrals which involve a pair of AOs.

Six-Electron Five-Centre Bonding: $Xe_2F_3^+$ and N_5^+

The anion H_5^-, with five overlapping 1s AOs, provides a prototype example of a molecular system with a 6-electron 5-centre bonding unit.[65] For the $\mathbf{X}_a{-}\mathbf{Y}_b$ $\mathbf{X}_c^-$ $\mathbf{Y}_d{-}\mathbf{X}_e$ type Lewis structures of the non-linear ions $H_2F_3^-$, I_5^-, and $Xe_2F_3^+$, the AO on each **Y** atom which helps to form the terminal $\mathbf{Y}_b{-}\mathbf{X}_a$ or $\mathbf{Y}_d{-}\mathbf{X}_e$ bond also overlaps with the valence-shell doubly-occupied p_x and p_y AOs of the central halide anion, to generate two (non-orthogonal) 6-electron 5-centre bonding units. For either bonding unit, an increased-valence structure may be generated, as indicated in **80** → **81** for $Xe_2F_3^+$ when the p_x electrons of the F^- are delocalized. (For linear systems, only the p_x electrons form a 6-electron 5-centre bonding unit.) In increased-valence structure **81**, the terminal and central Xe−F bonds are respectively fractional electron-pair bonds, and one-electron bonds. The lengths[66] of these bonds, 1.90 and 2.14 Å, are in agreement with these bond properties.



80 **81**



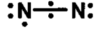
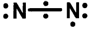
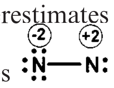
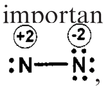
82 **83**

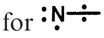
The recently prepared cation[67] N_5^+ involves two orthogonal 6-electron 5-centre bonding units, and the associated Lewis and increased-valence structures are[67b] **82** and **83**.

VB structure **83** indicates immediately that the terminal and central N−N bonds should be longer than N≡N bonds with the same AO hybridization (≈ 1.07 Å, cf. discussion for N_2O above), and substantially shorter than those for N−N bonds (≈ 1.45 Å). The calculated lengths (1.11 Å and 1.30 Å)[67] are in agreement with these deductions.

Valence Bond Alternatives to Triple Bonds

In this section and in the following two, increased-valence considerations are not needed for the primary discussion of the VB phenomena.

The results of ab initio VB calculations[68] for N_2 show that resonance between VB structures  and  with electron-pair σ bonds and one-electron π bonds, generates a lower energy than does the triple-bond structure $:N\equiv N:$ with Coulson−Fischer-type[48] LMOs to accommodate the four electrons that form the two π bonds. When the wavefunctions for these two sets of structures are expressed as linear combinations of the wavefunctions for nine canonical Lewis structures, it is found that the triple-bond structure overestimates the importance of the polar canonical structures  and , and this effect provides the explanation for the origin of the higher energy for the triple-bond structure.

In 1916, Lewis[69] was unable to accommodate the triple bond in his cubical atom model of electronic structure. In contrast cubical atom models, and Bohr orbit diagrams[7] for  and  may be constructed.

One-Electron and Two-Electron Transfer Processes

For the O_2 ground-state, two-electron transfer processes are required to convert structure **16** into structure **19**, and structure **17** into structure **18**, whereas one-electron transfers are needed to convert either structure **16** or **19** into each of structures **17** and **18**. Examples of phenomena whose origins may be rationalized in terms of either one-electron or two-electron transfer processes include:[70] (a) the mode of protonation[16] of symmetric anions such as HCO_2^- and NO_2^-, which occurs preferentially at one oxygen atom, i.e. asymmetric rather than symmetric geometries are obtained for HCOOH and HONO; (b) the asymmetry of xanthate and dithiocarbamate ligands in various complexes;[71] (c) energy transfer between donor and acceptor chromophores.[72]

Bohr Orbit Descriptions of Electronic Structure

Of course, the orbital theory forms the primary basis for modern descriptions of the electronic structure of matter. However as has been discussed on several occasions,[7,73] the Bohr orbit theory is also able to be used for this purpose. A Bohr orbit approach to electronic structure is based on a $2n \times n$ factorization of the atomic shell-structure formula $2n^2$, for which $n = 1, 2, 3, ...$ is the principal quantum number. This factorization is derived[7,73] by the application of a Heisenberg uncertainty relationship to the movement of electrons around Bohr orbits with principal quantum number n. It is deduced that there are n circular orbits (designated as $n_1, n_2, ..., n_n$) each of which can accommodate a maximum of $2n$ electrons. Two alternative derivations of the $2n^2$ formula are presented in ref.[7] The Bohr orbit theory falls outside the normal paradigm which is used to describe electronic structure, but it does provide qualitative models of electronic structure that accommodate the Lewis cubical atom model,[69] and arrangements of electrons in molecules which are appropriate for VB structures that arise in normal orbital theory. Aspects of previously published accounts of this subject have been reviewed in ref.[7], with new types of orbit diagrams provided for some of the systems considered previously.

In Figure 11, orbit diagrams are provided[7] for B_2H_6, and a variety of AF_N systems, when it is asssumed that there are N A−F electron-pair bonds in the associated VB structures. These orbit diagrams are based on the deduction that orbits with $n = 1, 2, 3, 4,$ and 5 may accommodate a maximum of 2, 4, 6, 8, and 10 electrons, respectively, and these are the occupation numbers for the equatorial n_1 orbit for the H, B, P, S, Cl, Se, Br, and I atoms in Figure 11. Examples of new types of Bohr orbit calculations of the energies for H_2^+, H_2, and the helium isoelectronic sequence are provided in ref.[7,74]

Conclusions

As indicated in the Introduction, the primary purpose of this work is to help to provide "primitive patterns of understanding" of the electronic structures of molecules. In very different ways, the work provides examples of how orbital VB theory and the Bohr orbit theory are able to do this. It is to be hoped that the approaches which have been used to provide qualitative VB descriptions of electronic structure are not difficult to comprehend − the increased-valence theory provides a natural extension of familiar Lewis theory by one-electron delocalizations − and there-

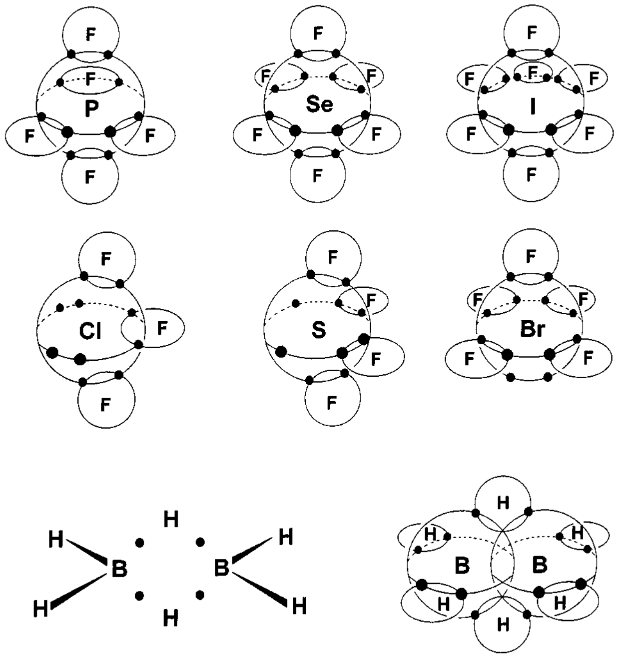


Figure 11. Bohr orbit diagrams for AF_N systems for (expanded valence-shell) Lewis VB structures with N A−F electron-pair bonds; six valence-shell electrons for each fluorine ligand are not indicated; a VB structure for B_2H_6 and the associated orbit diagram are also displayed

fore they may be useful to help bench chemists in their understanding of various aspects of chemical bonding.

Appendix: Valencies for LMO Increased-Valence Structures

For each of the LMO Kekulé structures **55** and **57**, the maximum valence for the A atom (V_a) is unity. In ref.[30a,43], expressions are deduced for the A-atom valencies for the LMO increased-valence structures **56** and **58**. The simplest definition of MO valence was used, namely that provided initally by Wiberg[75] for doubly occupied MOs, in which AO overlap integrals are omitted from the normalization constants. The derivation of the expression for V_a for increased-valence structure **56** is redescribed here.

If two electrons occupy the bonding MO $\psi_{ab} = (a + kb)/(k^2 + 1)^{05}$, the Wiberg valence[75] for the a-orbital is given by Equation (A1), in which P_{ab} is the Coulson bond order (with AO overlap integrals omitted). The maximum value for the valence is unity, which occurs when $k = 1$. However if ψ_{ab} is singly occupied, the bond-order is $k/(k^2 + 1)$, and the valence is then given by Equation (A2),[30a,43] with a maximum value of 0.5 when $k = 1$. When $k' = 1/k'' = k$ in Equation (9) for the LMO increased-valence structure **56**, we obtain Equation (A3) for the $(y)^1(\psi_{ay})^1(\psi_{ba})^2$ configuration, with $\psi_{ay} = a + ly$ and $\psi_{ba} = b + ka$. The A-atom valence is then given by Equation (A4) Pariser's procedure[76] is used to determine the P_{ay} and P_{ab} bond orders of Equations (A5) and (A6) from Equation (A3). An illustration of the use of this procedure is provided in ref.[77]

$$V_{ab} = (P_{ab})^2 = 4k^2/(k^2 + 1)^2 \qquad (A1)$$

$$V_{ab} = 2(P_{ab})^2 = 2k^2/(k^2 + 1)^2 \qquad (A2)$$

$$k\Psi_{31} = 2l(k\Psi_{I} + k^2\Psi_{II} + \Psi_{III}) + \Psi_{V} + k\Psi_{VI} \qquad (A3)$$

$$V_a = V_{ay} + V_{ab} = 2(P_{ay})^2 + (P_{ab})^2 \qquad (A4)$$

$$P_{ay} = 2l/\{2l^2(k^2 + 1) + 1\} \qquad (A5)$$

$$P_{ab} = k\{4l^2(k^2 + 1) + 1\}/[\{2l^2(k^2 + 1) + 1\}(k^2 + 1)] \qquad (A6)$$

When $k = l = 1$, $V_a = 1.13$. The maximum value for V_a is 1.212, which occurs when $k = 0.69$ and $l = 0.76$. In both cases, the A-atom valence exceeds the maximum value of unity that occurs in the Kekulé structures. Thus with regard to the valence of the A-atom, the designation "increased-valence" is appropriate for VB structure **56** (and also for VB structure **58**).

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As a consequence of the presence of four Slater determinants in the $S = 0$ spin wavefunction for Equation (4), the ψ_{ab} for the $\psi_{54}(k'=0)$ of Equation (5) is equal to $\psi_{ab} = a + 2kb$. It should also be stressed that the singlet diradical structure of type **VI** in Figure 5 contributes to the simplest canonical MO formulation of the wavefunction for a 4-electron 3-centre bonding unit (cf. C. A. Coulson, *J. Chem. Soc.* **1964**, 1442 for example). For a variety of MO and VB theorems that pertain to symmetrical 4-electron 3-centre bonding units, see R D. Harcourt, A. G. Harcourt, *J. Chem. Soc., Faraday Trans. 2* **1974**, *70*, 743.

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$$\begin{aligned}\Psi_{\mathbf{71}} &= \left|\psi_{ab}{}^{\alpha}\psi_{ab}{}^{\beta}\psi_{cd}{}^{\alpha}\psi_{cd}{}^{\beta}\psi^{*}{}_{ab}{}^{\alpha}\psi^{*}{}_{cd}{}^{\beta}\right| + \left|\psi_{ab}{}^{\alpha}\psi_{ab}{}^{\beta}\psi_{cd}{}^{\alpha}\psi_{cd}{}^{\beta}\psi^{*}{}_{cd}{}^{\alpha}\psi^{*}{}_{ab}{}^{\beta}\right| \\ &\propto \left|a^{\alpha}\psi_{ab}{}^{\beta}\psi_{cd}{}^{\alpha}d^{\beta}b^{\alpha}c^{\beta}\right| + \left|\psi_{ab}{}^{\alpha}a^{\beta}d^{\alpha}\psi_{cd}{}^{\beta}c^{\alpha}b^{\beta}\right|\end{aligned}$$

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[70] One example involves the hypothesis[16] that the stability of the genetic code under normal conditions is associated with the extent of electronic reorganization that is needed to interconvert important VB structures for different isomers of the DNA bases.

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