

Pauling three-electron bonds and increased-valence structures as components of the "intellectual heritage" of qualitative valence bond theory

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ABSTRACT

The symbolisms used by Shaik and Hiberty (2003, *Helvet. Chim. Acta*, 86, 1063) to provide valence-bond (VB) structures for the Pauling three-electron bond (or three-electron two atomic orbital bond) and the ground-state of O₂, are compared with those provided by Green and Linnett (1960, *J. Chem. Soc.* 4949). The incorporation of the Green-Linnett VB structure for O₂ into the VB structures for numerous diamagnetic as well as paramagnetic tri- and polyatomic molecules, to generate increased-valence structures, is re-described. Illustrative examples include molecular systems of the types R-O₂ and R-O₂-R, with for either or both species, R = F, NO, Co^{II}(*S* = 1/2), O(*S* = 1), Fe^{II}(*S* = 1), O₂(*S* = 1), and Cu^I(*S* = 1). The use of increased-valence structures to provide VB formulations of S_N2 reactions is also re-described. The origin of the existence of a triplet-spin (*S* = 1) ground-state for O₂ is re-examined, with attention given to two-electron delocalisation (exchange) resonance which is associated with reduced electron-electron repulsion.

KEYWORDS: Bond Theory, Increased-Valence Structures, Three-Electron Bonds, Valence Bond (VB) Theory, S_N2 Reactions

1. INTRODUCTION

In their forceful discussion of "myth and reality in the attitude toward valence-bond (VB) theory...",

Shaik and Hiberty [1] give consideration to the Pauling three-electron bond (or three-electron two atomic orbital (AO) bond) and the ground-state of O₂ with two Pauling three-electron bonds. We agree with the Shaik-Hiberty conclusions that "taken together, molecular orbital (MO) and VB theories constitute a valuable arsenal in the hands of the chemists. In fact, insistence to understand electronic structure without this complimentary knowledge is crippling, and discarding any one of the two theories undermines the intellectual heritage of chemistry." However when discussing the Pauling three-electron bond and O₂, the Shaik and Hiberty case for the use of VB theory would have been strengthened if they had given effective recognition to the extensive literature which exists with regard to (a) the best type of VB structures for the Pauling three-electron bond and the ³Σ_g⁻(*S* = 1 spin) ground-state of molecular O₂, (b) the equivalence which occurs between the MO and VB descriptions of the ³Σ_g⁻ ground-state of molecular O₂ with two Pauling three-electron bonds, and (c) the pivotal role that can be played by the Pauling three-electron bond in the provision of VB representations for the electronic structures of diamagnetic as well as paramagnetic electron-rich molecules. These topics have formed the subjects for a large number of publications since the early 1960's; a monograph and reviews for (c) include those of refs. [2-5]. The latter publications provide many examples of how the VB theory is able to provide "primitive patterns of understanding" [6] of the electronic structures of

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the large class of electron-rich molecules. Inclusion of these topics in VB discussions of electronic structure, should strengthen substantially "the intellectual heritage" of qualitative VB theory. Here, we provide previously-published examples for each of (a), (b) and (c). For (c), the examples chosen from our publications, with little comment here, incorporate the Green-Linnett [7] VB structure for O₂ into the VB structures for tri- and polyatomic molecules. The latter types of VB structures are designated as "increased-valence" structures [2-5].

2. The Pauling three-electron bond

The molecular orbital (MO) configuration for the Pauling three-electron bond involves two bonding electrons and one antibonding electron. With a and b as overlapping AOs centred on two atomic centres (A and B) such that the AO overlap integral $\langle a|b \rangle$ is greater than zero, the (orthogonal) bonding and antibonding MOs that accommodate these electrons are given by $\psi_{ab} = a + kb$ and $\psi^*_{ab} = k^*a - b$ respectively, (for which $k > 0$ and $k^* = (k + \langle a|b \rangle)/(1 + k\langle a|b \rangle)$). Green and Linnett [7] demonstrated that the MO configuration $(\psi_{ab})^2(\psi^*_{ab})^1$ is proportional to $(a)^1(\psi_{ab})^1(b)^1$, in which the spins of the a and b electrons are parallel and opposed to the spin of the ψ_{ab} electron. If the antibonding ψ^*_{ab} electron has an α spin wavefunction, then the a and b electrons also have α spin wavefunctions. In Figure 1 [2, 4, 5, 8], orbital occupancies for the identity

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

are displayed for $k = 1$ with an α spin ψ^*_{ab} electron.

Green and Linnett used crosses and circles (x and o) to represent $m_s = +1/2$ and $m_s = -1/2$ spin electrons with α and β spin wavefunctions. For the $(a)^1(\psi_{ab})^1(b)^1$ configuration, the Green-Linnett VB structures¹⁾ are **1** and **2** for $m_s = +1/2$ and $m_s = -1/2$ spin antibonding ψ^*_{ab} electrons [7, 9-11].

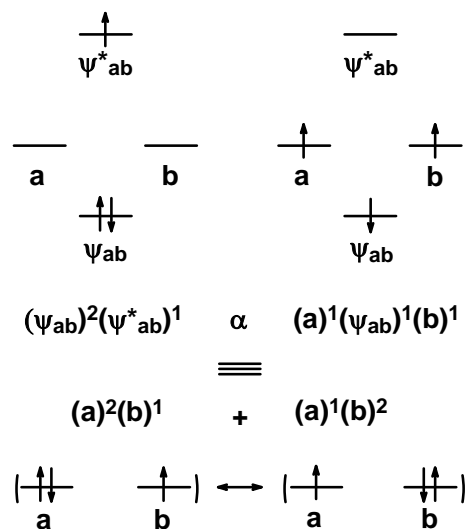
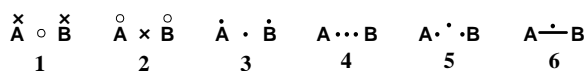
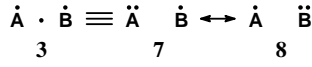


Figure 1. Orbital occupations for the *Pauling* three-electron bond [2, 4, 5(a), 8].

When electron spins are not indicated, the Green-Linnett symbolism for the Pauling three-electron bond is **3** [7, 9-11]. Each of these three VB structures shows more clearly than do any of the Pauling [12, 13], Shaik and Hiberty [1] and (earlier) Shaik [14] structures **4-6** that the Pauling three-electron bond involves effectively only one bonding electron. Therefore as discussed by Linnett [9, 10] the Pauling "three-electron bond" designation is a misnomer; it gives a misleading idea of the electron pattern in space [9, 10]. Although alternative designations such as "three-electron two AO", "3-electron 2-centre" and "three-electron hemi/half" bond have been proposed [15], Pauling's designation is more widely known, and we shall continue to use it here. But of course, as recognised by Linnett, a "true" three-electron bond involves three bonding electrons; the six $(\sigma_{CC})^2(\pi_{CC})^1$ C-C bonds for C₆H₆, as in Linnett's non-paired spatial orbital structure [9] provide examples of these types of bonds. The ground-state of O₂⁻ with a MO bond order of 1.5 which is associated with the valence-shell $(\sigma_s)^2(\sigma^*_s)^2(\sigma_p)^2(\pi_x)^2(\pi^*_x)^2(\pi_y)^2(\pi^*_y)^1$ MO configuration, involves a "true" three-electron bond, with an electron-pair σ -bond and a Pauling three-electron π_y -bond!

With electron spins not indicated, as in VB structure **3** for example, each of the Pauling

three-electron bond VB structures **1-6** is equivalent to resonance between the Lewis structures **7** and **8**,



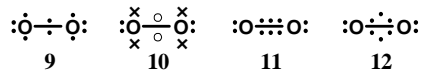
with $(a)^2(b)^1$ and $(a)^1(b)^2$ AO configurations. For $S = M_S = +1/2$, the Slater determinantal wavefunction formulations of the Pauling three-electron bond identities are those of equation 1 [2-5(a), 11, 16].

$$|\psi_{ab}^{\alpha} \psi_{ab}^{\beta} \psi_{ab}^{\gamma}| \propto |a^{\alpha} \psi_{ab}^{\beta} b^{\alpha}| \equiv |a^{\alpha} a^{\beta} b^{\alpha}| + k |a^{\alpha} b^{\beta} b^{\alpha}| \quad (1)$$

Pauling three-electron bonds and the electronic structures of high-spin (or hypoligated) transition metal complexes, F^+ type colour centres, high-temperature superconductors, n-type semiconductors, and electron conduction in alkali metals and $(\text{SN})_x$ polymers have been described in refs. [2-4, 17-21].

3. VB structures for the ground-state of O_2

The $^3\Sigma_g^-$ ground-state MO configuration for O_2 involves a $(\pi_x)^2(\pi_x^*)^1(\pi_y)^2(\pi_y^*)^1$ configuration for the six π -electrons, with parallel spins for the electrons that occupy the antibonding π_x^* and π_y^* MOs. Two Pauling three-electron bonds are present in this configuration. The remaining six valence-shell electrons, which form the $(\sigma_s)^2(\sigma_s^*)^2(\sigma_p)^2$ MO configuration, generate an electron-pair σ -bond and a lone-pair of electrons associated with each atomic centre [2-5(a), 7, 9-11]. The resulting Green-Linnett VB structures are [2-5(a), 7, 9-11, 22] **9** with electron spins not indicated, and **10** for $S = M_S = +1$.



Each of these structures indicates more clearly than does either the Pauling structure **11** [12, 13] or the Shaik-Hiberty structure **12** [1] that the O_2 ground-state involves a $(\sigma)^2(\pi_x)^1(\pi_y)^1$ double bond with parallel spins for the two π -electrons.

¹As in refs. [2-5], atomic formal charges are not indicated in the generalised VB structures **1-30** of this paper.

² π -electron CI-methods are discussed in refs. [11, 22].

4. Electronic states for O_2

Without configuration interaction² (CI), and with the remaining electrons - in particular the $(\pi_x)^2(\pi_y)^2$ electrons not indicated - the $M_S = 0$ and $M_S = \pm 1$ $^3\Sigma_g^-$ wavefunctions for the antibonding π^* -electrons are given by equation 2,

$$\begin{aligned} \Psi_1 = & (|\pi_x^* \alpha \pi_y^* \beta| - |\pi_y^* \alpha \pi_x^* \beta|)/\sqrt{2}, |\pi_x^* \alpha \pi_y^* \alpha|, \\ & |\pi_x^* \beta \pi_y^* \beta| \\ = & [\{\pi_x^*(1)\pi_y^*(2) - \pi_y^*(1)\pi_x^*(2)\}/\sqrt{2}]T(\text{spin}) \end{aligned} \quad (2)$$

in which $T(\text{spin}) = [\{\alpha(1)\beta(2) + \beta(1)\alpha(2)\}/\sqrt{2}]$ ($S = 1$, $M_S = 0$), $\alpha(1)\alpha(2)$ ($S = 1$, $M_S = 1$) or $\beta(1)\beta(2)$ ($S = 1$, $M_S = -1$), i.e. the π_x^* and π_y^* electrons have parallel spins.

The MO description of the $^1\Delta_g$ first excited state involves the two degenerate $S = M_S = 0$ configurations (cf. refs. [2, 23] for example) of equations 3 and 4,

$$\begin{aligned} \Psi_2 = & (|\pi_x^* \alpha \pi_y^* \beta| + |\pi_y^* \alpha \pi_x^* \beta|)/\sqrt{2} \\ = & [\{\pi_x^*(1)\pi_y^*(2) + \pi_y^*(1)\pi_x^*(2)\}/\sqrt{2}]S(\text{spin}) \end{aligned} \quad (3)$$

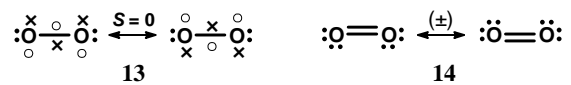
$$\begin{aligned} \Psi_3 = & (|\pi_x^* \alpha \pi_x^* \beta| - |\pi_y^* \alpha \pi_y^* \beta|)/\sqrt{2} \\ = & [\{\pi_x^*(1)\pi_x^*(2) - \pi_y^*(1)\pi_y^*(2)\}/\sqrt{2}]S(\text{spin}) \end{aligned} \quad (4)$$

with $S(\text{spin}) = [\{\alpha(1)\beta(2) - \beta(1)\alpha(2)\}/\sqrt{2}]$ ($M_S = 0$), i.e. opposed spins for the π_x^* and π_y^* .

A second $S = M_S = 0$ excited state with the π -electron MO wavefunction of equation 5 has $^1\Sigma_g^+$ symmetry.

$$\begin{aligned} \Psi_4 = & (|\pi_x^* \alpha \pi_x^* \beta| + |\pi_y^* \alpha \pi_y^* \beta|)/\sqrt{2} \\ = & [\{\pi_x^*(1)\pi_x^*(2) + \pi_y^*(1)\pi_y^*(2)\}/\sqrt{2}]S(\text{spin}) \end{aligned} \quad (5)$$

For Ψ_2 , the associated VB structures are the Linnett structures of **13** with a $(\sigma)^2(\pi_x)^1(\pi_y)^1$ double bond, and opposed spins for the π_x and π_y bonding electrons.



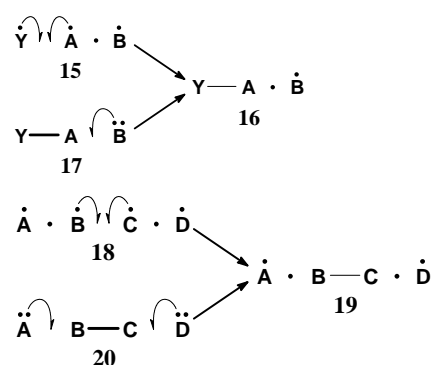
The VB structures which are associated with Ψ_3 and Ψ_4 are the Lewis structures of **14** with $(\sigma)^2(\pi_x)^2$ and $(\sigma)^2(\pi_y)^2$ double bonds. Hund's rule of maximum spin multiplicity for orthogonal orbitals determines that **13** is of higher energy than **10**. Because Ψ_2 for structure **13** and Ψ_3 for the (-) of **14** are degenerate components of the $^1\Delta_g$ state, the Lewis structures of **14** are also of higher energy than **10**. Therefore the simplest VB-type rationalisation for the existence of a triplet-spin ground state can be provided via reference to the MO rationalisation through the equivalence which exists between the $^3\Sigma_g^-$ MO and VB wavefunctions and between the $^1\Delta_g$ MO and VB wavefunctions [9-11].

In the Appendix, we explore further the origins of the energy differences that exist between the $^3\Sigma_g^-$, $^1\Delta_g$ and $^1\Sigma_g^+$ states of O_2 when the same MOs are used to construct the wavefunctions of equations 2-5. It is deduced that the electron-electron repulsion is less for Ψ_1 than it is for any of Ψ_2 - Ψ_4 . However here it can be noted that the argument used by Shaik and Hiberty [1] to compare the energies of VB structures **12** and **14** ignores inter-electronic repulsion between the $(\pi_x)^2(\pi_x^*)^1$ and the $(\pi_y)^2(\pi_y^*)^1$ Pauling three-electron bond configurations. Therefore their π -electron energy for their $^3\Sigma_g^-$ structure **12** is the same as that for resonance between the ($S = 0$) structures of **13**.

5. Increased-valence structures

The use of the Green-Linnett VB structures for the O_2 ground-state to help provide VB structures for O-O containing molecules has been described on many occasions [2-5, 11, 24]. Here, we shall re-present some of them, in order to provide examples of how the (paramagnetic, $S = 1/2$) Pauling three-electron bond can be incorporated into the VB structures for (diamagnetic, $S = 0$) 4-electron 3-centre and 6-electron 4-centre bonding units. (Extension to longer electron-rich bonding units is possible - cf. for example the polymer $(SN)_x$ [2-5, 18], but will not be considered here).

In general, we obtain the 4-electron 3-centre and 6-electron 4-centre VB structures by spin-pairing the antibonding ψ_{ab}^* electron of the A-B Pauling three-electron bond with the unpaired electron of either an atom (designated as Y) or a second three-electron bond (designated as CD), when ψ_{ab}^* overlaps with the associated odd-electron orbitals y and ψ_{cd}^* [2-5(a), 25]. The orbital occupancies for the y- ψ_{ab}^* and ψ_{ab}^* - ψ_{cd}^* spin-pairings are displayed in Figure 2 [2, 3(a), (c), 5(a), 25]. In **15** \rightarrow **16** and **18** \rightarrow **19**,



we utilise the equation 1 type of identity, for example $|\psi_{ab}^{\alpha}\psi_{ab}^{\beta}\psi_{ab}^{\gamma}\psi_{ab}^{\delta}| \propto |a^{\alpha}b^{\beta}b^{\gamma}b^{\delta}|$ and $|\psi_{cd}^{\beta}\psi_{cd}^{\alpha}\psi_{cd}^{\gamma}\psi_{cd}^{\delta}| \propto |c^{\beta}d^{\alpha}d^{\gamma}d^{\delta}|$, and indicate only the nearest-neighbour y-a or b-c components of the y- ψ_{ab}^* and ψ_{ab}^* - ψ_{cd}^* spin-pairings. However it is to be understood that y-b or a-c, a-d and b-d spin-pairings also occur simultaneously. The latter spin-pairings will be made explicit in the identities that are presented in Section 6 below.

The VB structures **16** and **19** are designated as increased-valence structures [2-5, 25]. They can also be obtained from the standard Lewis structures **17** and **20** (which involve nearest-neighbour electron-pair bonds and lone-pairs of electrons) via one-electron delocalisations of non-bonding electrons into bonding MOs (ψ_{ab} for **17**, and ψ_{ab} and ψ_{cd} for **20**), as indicated in these structures [2-5, 25]. The thin bond lines which are present in the increased-valence structures represent fractional electron-pair bonds [2-5, 25], cf. also the identities that are presented in Section 6. When the atoms A and D of structure

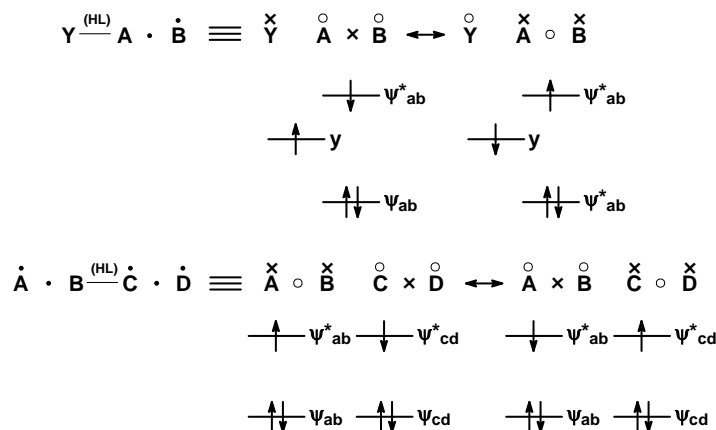


Figure 2. Orbital occupations and electron spins for increased-valence structures **16** and **19**, with Heitler-London (HL) type $S = 0$ spin-pairings for the unpaired electrons, i.e. $\Psi(\mathbf{16}, \text{HL}) = |\psi_{ab}^{\alpha} \psi_{ab}^{\beta} y^{\alpha} \psi_{ab}^{\beta}| + |\psi_{ab}^{\alpha} \psi_{ab}^{\beta} \psi_{ab}^{\alpha} y^{\beta}|$, and $\Psi(\mathbf{19}, \text{HL}) = |\psi_{ab}^{\alpha} \psi_{ab}^{\beta} \psi_{cd}^{\alpha} \psi_{cd}^{\beta} \psi_{ab}^{\alpha} \psi_{cd}^{\beta}| + |\psi_{ab}^{\alpha} \psi_{ab}^{\beta} \psi_{cd}^{\alpha} \psi_{cd}^{\beta} \psi_{cd}^{\alpha} \psi_{ab}^{\beta}|$.

19 are adjacent, a cyclic increased-valence structure is obtained (cf. O_4 of Figure 6 below), with two nearest-neighbour fractional electron-pair bonds [2-5, 26].

Either or both of these two types of generalised techniques is used in Figures 3-6 to construct increased-valence structures for FO_2 , FO_2F , $\text{Co}^{\text{II}}\text{O}_2$ and $\text{Fe}^{\text{I}}\text{O}_2$ (Figure 3, [2-5(a), 11, 24, 27]), O_3 [2-5(a), 28] and $\text{Fe}^{\text{II}}\text{O}_2$ (Figure 4, [2, 3(d), 24, 27, 29]), $\text{NO} + \text{O}_2 \rightarrow \text{ONOO}$ (Figure 5, [2, 3(a), 4, 30]), $2\text{O}_2 \rightarrow \text{O}_4$ (Figure 6, [3(b), 31]). Figures 3 and 4

involve type **16** increased-valence structures whereas extended and cyclic type **19** increased-valence structures are present in the VB structures for ONOO and O_4 in Figures 5 and 6.

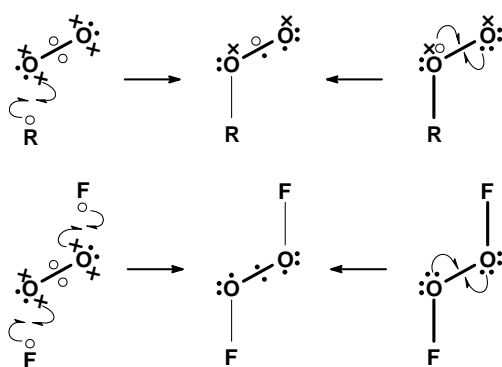


Figure 3. Increased-valence and Lewis VB structures R-O_2 with $\text{R} = \text{F}$, $\text{Co}^{\text{II}}(S=1/2)$ and $\text{Fe}^{\text{I}}(S=1/2)$, and $\text{F-O}_2\text{-F}$.

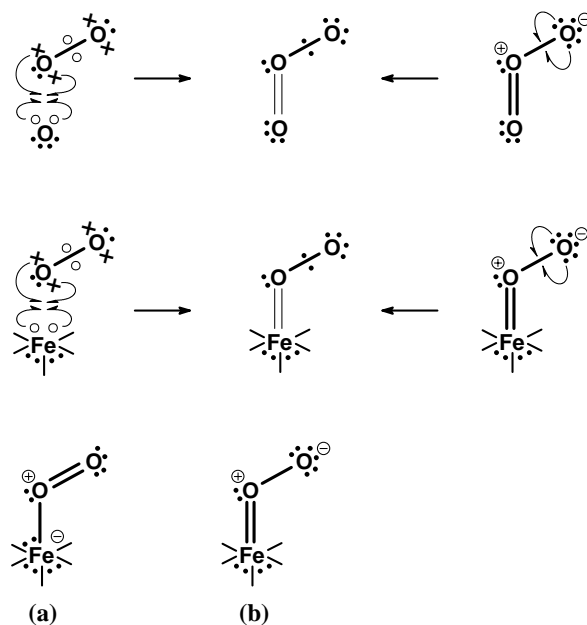


Figure 4. Increased-valence and Lewis VB structures for O_3 and the $\text{Fe}^{\text{II}}\text{O}_2$ substituent of oxyhaemoglobin.

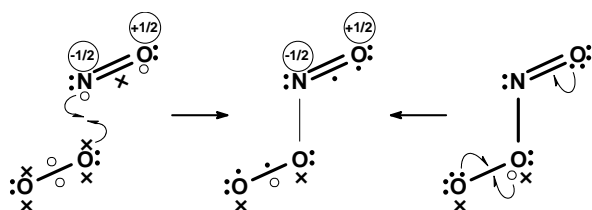


Figure 5. Increased-valence and Lewis VB structures for ONOO.

In Figures 7-11, we also display proposed mechanisms for the following reactions: $2\text{Fe}^{\text{II}} + \text{O}_2 \rightarrow 2\text{Fe}^{\text{II}}\text{OFe}^{\text{II}}$ (Figure 7, [2, 3(d), 4, 29, 32]), $\text{Fe}^{\text{II}} + \text{Cu}^{\text{I}} + \text{O}_2 \rightarrow 2\text{Fe}^{\text{II}}\text{OCu}^{\text{I}}$ (Figure 8, [2, 3(d), 4, 29]), $\text{NO} + \text{O}_3 \rightarrow \text{NO}_2 + \text{O}_2(^3\Sigma_g^-)$ (Figure 9, [2, 3(a), 4, 30]), $2\text{NO} + \text{O}_2 \rightarrow 2\text{NO}_2$ (Figure 10, [3(b), (c)]) and $\text{FNO}_2 + \text{O}_3 \rightarrow 2\text{O}_2(^3\Sigma_g^-) + \text{FNO}$ (Figure 11, [5(a), 33]). Figures 5, 9 and 10 use the Green-Linnett symbolism for the Pauling three-electron bond VB structure for NO [7] as well as for O_2 . Mirror-image increased-valence structures for O_3 are not displayed. The VB structures for paramagnetic NO_2 involve a diamagnetic 4-electron 3-centre increased-valence representation of type **16**, and a paramagnetic Pauling three-electron bond.

In Figure 3, the unpaired electron of each univalent radical (F, or low-spin ($3d^7$) Co^{II} and Fe^{I}) is spin-paired with one of the unpaired electrons of $^3\Sigma_g^- \text{O}_2$. It has been suggested [24] that the $\text{Fe}^{\text{I}}\text{O}_2$ could replace either the $\text{Fe}^{\text{III}}\text{O}_2^{2-}$ or the $\text{Fe}^{\text{II}}\text{O}_2^-$ in formulations of the reaction cycle for

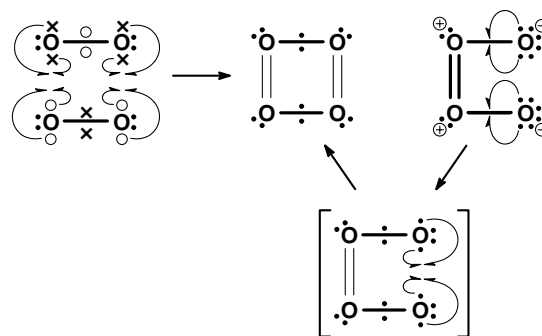


Figure 6. Increased-valence and Lewis VB structures for O_4 .

cytochrome P-450-dependent mono-oxygenases. Contrasts between the VB descriptions for FOOF and HOOH are provided in refs. [2, 3(b), 5].

In Figure 4, the increased-valence structure for the $\text{Fe}^{\text{II}}\text{O}_2$ linkage is obtained by spin-pairing the unpaired electrons of $^3\Sigma_g^- \text{O}_2$ with those of intermediate-spin ($S = 1$) Fe^{II} . It provides the VB structure which is appropriate for McLure's theory of the bonding of O_2 to haemoglobin [34]. The Pauling-Coryell VB structures for the $\text{Fe}^{\text{II}}\text{O}_2$ linkage are (a) and (b) of Figure 4 [35]. Structure (b) is also used to construct the increased-valence structure. Shaik and co-workers [36] have used structure (a), with an O_2 VB structure of **14** coordinated to low-spin Fe^{II} , to represent $\text{Fe}^{\text{II}}\text{O}_2$ linkages. Figure 10 provides a VB formulation for the McKee mechanism for $2\text{NO} + \text{O}_2 \rightarrow 2\text{NO}_2$, namely $\text{NO} + \text{NO} + \text{O}_2 \rightarrow \text{ON} \cdots \text{O}_2 \cdots \text{NO}(\text{ts}) \rightarrow \text{ONOONO} \rightarrow \text{ONO} \cdots \text{ONO}(\text{ts}) \rightarrow 2\text{NO}_2$ [37].

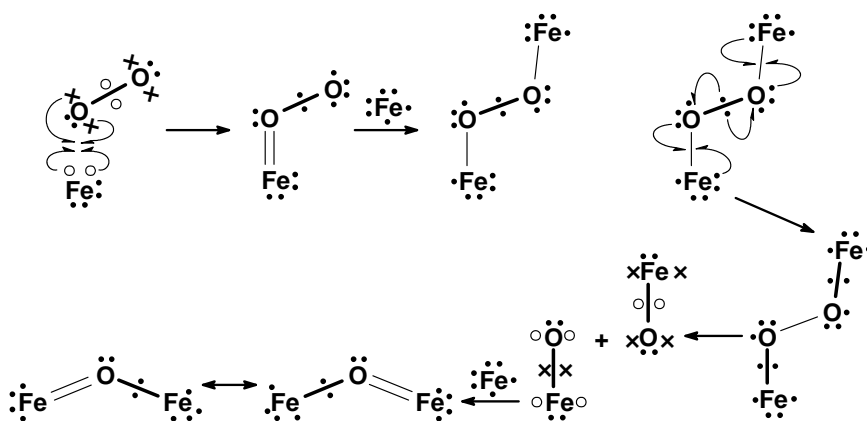
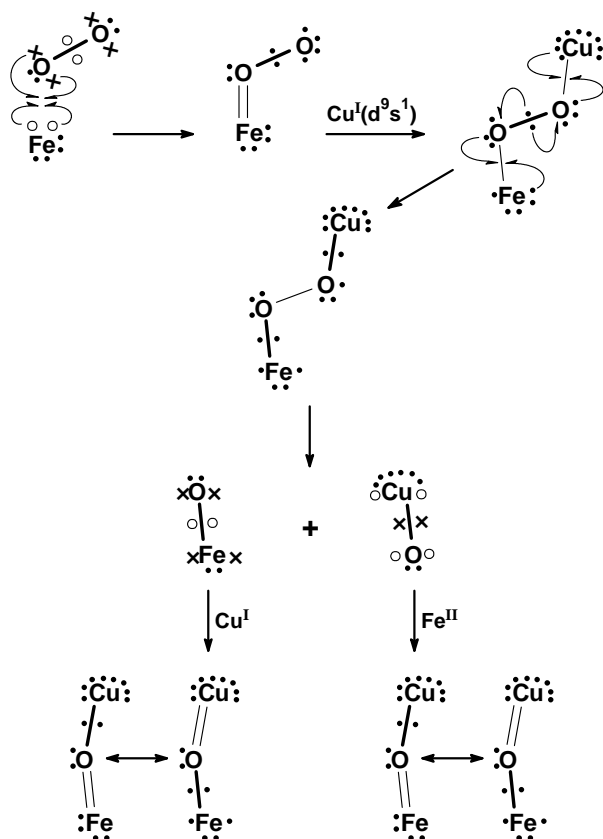
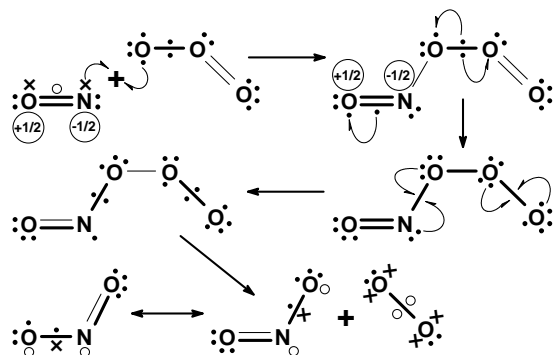


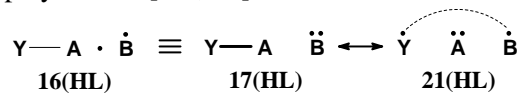
Figure 7. $2\text{Fe}^{\text{II}} + \text{O}_2 \rightarrow 2\text{Fe}^{\text{II}}\text{OFe}^{\text{II}}$

Figure 8. $\text{Fe}^{\text{II}} + \text{Cu}^{\text{I}} + \text{O}_2 \rightarrow 2\text{Fe}^{\text{II}}\text{OCu}^{\text{I}}$ Figure 9. $\text{NO} + \text{O}_3 \rightarrow \text{NO}_2 + \text{O}_2(^3\Sigma_g^-)$

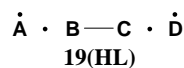
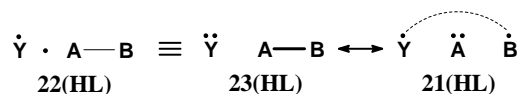
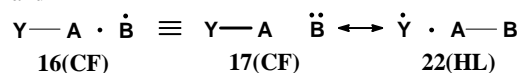
6. Some identities for increased-valence structures

Further chemical applications, theorems, identities and definitions of atomic valence for increased-valence structures are discussed in the references provided. Different types of identities are obtained when an electron-pair bond is formulated according to either the Heitler-London (HL) AO

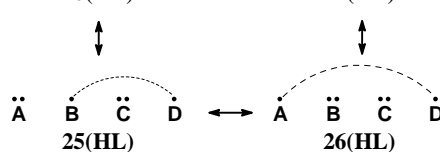
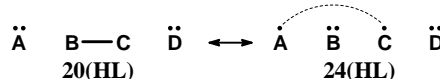
procedure (i.e. $|a^\alpha b^\beta| + |b^\alpha a^\beta|$), or the more-general Coulson-Fischer (CF) [38] procedure (i.e. $|(a + k'b)^\alpha(b + k''a)^\beta| + |(b + k'a)^\alpha(a + k'b)^\beta|$). Some examples of these identities are those displayed here [2-5, 39].



and



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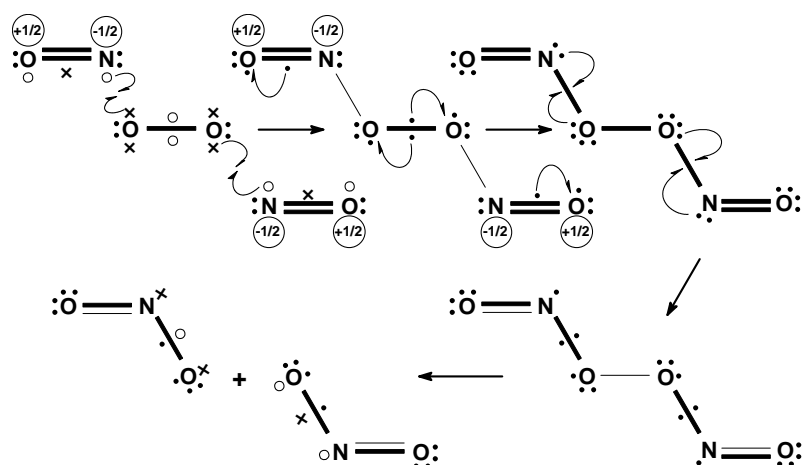
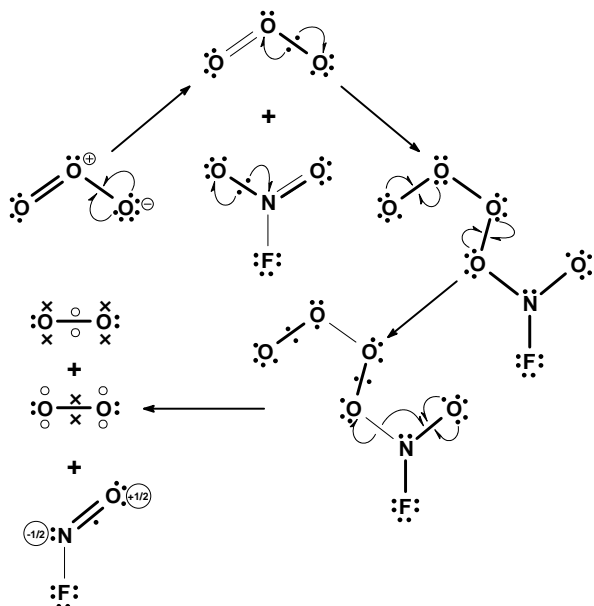
For symmetrical 6-electron 4-centre bonding units, it has been deduced on several occasions [2, 3(c), 40] that the VB wavefunction for increased-valence structure **19**, with a HL formulation for its wavefunction (cf. Caption for Figure 2), is equivalent to the covalent component of the lowest-energy 6-electron 4-centre MO configuration $|\psi_1\alpha\psi_1\beta\psi_2\alpha\psi_2\beta\psi_3\alpha\psi_3\beta| = \Psi_{\text{covalent}} + \Psi_{\text{ionic}}$ with the 4-centre MOs given by equation 6.

$$\begin{aligned} \psi_1 &= a + d + \lambda(b + c), \\ \psi_2 &= a - d + \mu(b - c), \\ \psi_3 &= \lambda^*(a + d) - (b + c) \end{aligned} \quad (6)$$

With $\psi_4 = \mu^*(a - d) - (b - c)$, the lower-energy $\Psi(\text{CI})$ of equation 7,

$$\begin{aligned} \Psi(\text{CI}) &= C_1|\psi_1\alpha\psi_1\beta\psi_2\alpha\psi_2\beta\psi_3\alpha\psi_3\beta| \\ &\quad + C_2|\psi_1\alpha\psi_1\beta\psi_2\alpha\psi_2\beta\psi_4\alpha\psi_4\beta| \end{aligned} \quad (7)$$

increases the importance of Ψ_{covalent} relative to Ψ_{ionic} [2, 3(c), 40].

Figure 10. $2\text{NO} + \text{O}_2 \rightarrow 2\text{NO}_2$.Figure 11. $\text{FNO}_2 + \text{O}_3 \rightarrow 2\text{O}_2(^3\Sigma_g^-) + \text{FNO}$

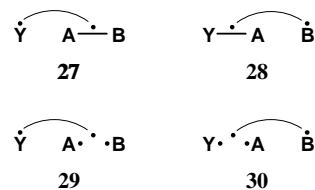
Definitions of the A-atom atomic valence, $V_a = V_{ay} + V_{ab}$, for **16**(HL) and **16**(CF) are provided in refs. [2, 41, 42]. In each case, the A-atom valence in these increased-valence structures can exceed the maximum value of unity which can occur in any of the Lewis structures **17**(HL) and **17**(CF), for which $V_{ab} = 0$. Similarly for increased-valence structure **19**(HL), the B and C-atom valencies, $V_b = V_{ba} + V_{bc}$ and $V_c = V_{cb} + V_{cd}$, can exceed unity [2, 25(c)].

7. Some additional comments

Subsequent to the publication of ref. [1], Shaik and Hiberty have published papers entitled (a) "A Conversation on VB vs. MO THEORY: A Never-Ending Controversy?" (with Hoffmann) [43], and (b) "Valence Bond Theory, Its History, Fundamentals and Applications - A Primer" [44].

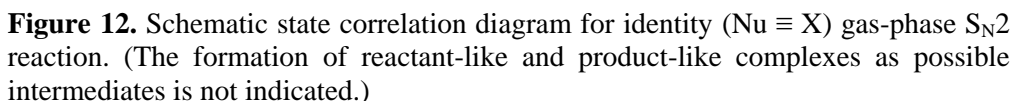
Except for the inclusion of ref. [2] in the supporting material of [43], and to a passing reference to refs. [2, 3(d)] in [44], these authors do not give consideration to the use of increased-valence structures to provide qualitative VB representations of the electronic structures for the large class of electron-rich molecules. As implied by the present review, a substantial literature exists on the subject of increased-valence structures, which commenced with a 1964 publication [40(a)] on VB structures for N_2O_4 .

In [44], Shaik and Hiberty continue to use **6** as the VB representation for the Pauling three-electron bond, and **12** as the VB structure for the ground-state of O_2 . When VB structures of type **6** are incorporated into the VB structures for 4-electron 3-centre bonding units, via the spin-pairing of their odd-electron with the odd electron of a third



indicated that **(b)** and **(c)** are equivalent to **(a)** \leftrightarrow **(e)** and **(d)** \leftrightarrow **(f)** respectively, in which **(e)** and **(f)** are particular examples of **16(HL)** and **22(HL)**. Thus the present paper focuses attention on different types of VB symbolism.

Recently, the electronic structure of O_3 has been studied by Pakiari and Nazari [47]. In their Figure 3, they have displayed the Linnett double quartet structure for this molecule, which is a special case [28] of resonance between two equivalent increased-valence structures of the type displayed in Figures 3, 10 and 11 here. See for example refs. [2-5, 28] for further increased-valence descriptions of the electronic structure of O_3 .



8. CONCLUSIONS

The references and examples which we have provided indicate that on many occasions since the early 1960's, it has been stressed that (a) the Green-Linnett symbolism is the preferred VB symbolism for the Pauling three-electron bond, and (b) the Pauling three-electron bond plays a pivotal role in the provision of VB structures for a large class of diamagnetic as well as paramagnetic electron-rich molecules. It has been remarked that the Pauling three-electron bond "probes the ultimate limits of chemical valence for electron-rich molecules" [48]. Therefore Pauling three-electron bonds, and increased-valence structures with Pauling three-electron bonds as components, can be considered to be components of the "intellectual heritage" [1] of qualitative VB theory.

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APPENDIX

When the same MOs³ are used to construct the wavefunctions of equations 2-5, their energies are given by equations 8-11.

$$E_1 = 2H(\pi^*_x, \pi^*_x) + J(\pi^*_x, \pi^*_y) - K(\pi^*_x, \pi^*_y) \quad (8)$$

$$E_2 = 2H(\pi^*_x, \pi^*_x) + J(\pi^*_x, \pi^*_y) + K(\pi^*_x, \pi^*_y) \quad (9)$$

$$E_3 = 2H(\pi^*_x, \pi^*_x) + J(\pi^*_x, \pi^*_x) - K(\pi^*_x, \pi^*_y) \quad (10)$$

$$E_4 = 2H(\pi^*_x, \pi^*_x) + J(\pi^*_x, \pi^*_x) + K(\pi^*_x, \pi^*_y) \quad (11)$$

in which

$$H(\pi^*_x, \pi^*_x) = \langle \pi^*_x(1) | H^{\text{core}}(1) | \pi^*_x(1) \rangle,$$

$$J(i, j) = \langle i(1)j(2) | 1/r_{12} | i(1)j(2) \rangle \text{ and}$$

$$K(i, j) = \langle i(1)j(2) | 1/r_{12} | j(1)i(2) \rangle.$$

The energy separations ${}^1E_2 - {}^3E_1$ and ${}^1E_4 - {}^1E_3$ are both equal to twice the electron-electron repulsion exchange

integral $K(\pi^*_x, \pi^*_y) = \langle \pi^*_x(1)\pi^*_y(2) | 1/r_{12} | \pi^*_y(1)\pi^*_x(2) \rangle$. Because no change in electron spin occurs during an electronic excitation from Ψ_3 to Ψ_4 , the exchange integral does not arise from spin correlation effects, as is sometimes assumed. Rather it arises from two-electron delocalisations (exchange) between the π^*_x and π^*_y MOs; $\pi^*_y(1)\pi^*_y(2)$ as well $\pi^*_x(1)\pi^*_x(2)$ contributes to the (symmetry-adapted) Ψ_3 and Ψ_4 . Similarly delocalisation between the π^*_x and π^*_y MOs ensures that $\pi^*_y(1)\pi^*_x(2)$ as well $\pi^*_x(1)\pi^*_y(2)$ contributes to the construction of the wavefunctions Ψ_1 and Ψ_2 .

The π^*_x and π^*_y MOs are orthogonal. Therefore each of $\langle \pi^*_x(1)\pi^*_x(2) | H | \pi^*_y(1)\pi^*_y(2) \rangle$ and $\langle \pi^*_x(1)\pi^*_y(2) | H | \pi^*_y(1)\pi^*_x(2) \rangle$ is equal to the exchange integral $K(\pi^*_x, \pi^*_y)$. When off-diagonal Hamiltonian matrix elements are not equal to zero, electron delocalisation leads to a lower-energy state as well as to a higher-energy state. Because $K(\pi^*_x, \pi^*_y)$ is greater than zero, the negative linear combinations of $\pi^*_x(1)\pi^*_y(2)$ with $\pi^*_y(1)\pi^*_x(2)$ and $\pi^*_x(1)\pi^*_x(2)$ with $\pi^*_y(1)\pi^*_y(2)$ must generate the lower-energy states.

When comparing the energies of equations 7 and 9 for the two negative linear combinations, Ψ_1 and Ψ_3 , the energy separation $E_3 - E_1 = J(\pi^*_x, \pi^*_x) - J(\pi^*_x, \pi^*_y)$ is associated with electron charge correlation. Two electrons that occupy different MOs (π^*_x and π^*_y) are better separated spatially than when they occupy the same MO (π^*_x or π^*_y). Therefore the energy of repulsion between the electrons is less for either $\pi^*_x(1)\pi^*_y(2)$ or $\pi^*_y(1)\pi^*_x(2)$ than it is for either $\pi^*_x(1)\pi^*_x(2)$ or $\pi^*_y(1)\pi^*_y(2)$. (Using an alternative procedure, this result has also been deduced by Shaik and Hiberty [1]). Similarly the same energy separation exists between the two positive linear combinations, Ψ_2 and Ψ_4 .

It can be deduced [23] that $J(\pi^*_x, \pi^*_x) - J(\pi^*_x, \pi^*_y) = 2K(\pi^*_x, \pi^*_y)$, and therefore the ${}^1\Delta_g$ wavefunctions Ψ_2 and Ψ_3 are degenerate.

The symmetry (symmetric or antisymmetric with regard to the interchange of electrons) of the

³An analysis with complex antibonding MOs, which are eigenfunctions of the angular momentum operator L_z , can also be provided. When different, variationally-determined orbitals are used, differences in electron-nuclear attraction energies also affect the energies of these states [49]. This factor will not be examined here.

spatial wavefunction for the two-electron configurations and the Pauli exclusion principle determine which electron spin-wavefunction is to be associated with each spatial wavefunction. But it is the reduced electron-electron repulsion which determines why the ground-state of O_2 involves a triplet spin state.

To conclude this section, it is noted that for H_2 , with overlapping AOs a and b , the integrals $\langle a(1)b(2)|H|b(1)a(2)\rangle$ and $\langle a(1)a(2)|H|b(1)b(2)\rangle$, both of which are equivalent to $2\langle a(1)|b(1)\rangle\langle a(1)|H^{core}(1)|b(1)\rangle + \langle a(1)b(2)|1/r_{12}|b(1)a(2)\rangle$, are negative. Therefore the positive linear combinations $a(1)b(2) + b(1)a(2)$ and $a(1)a(2) + b(1)b(2)$ generate lower energies than do the corresponding negative linear combinations $a(1)b(2) - b(1)a(2)$ and $a(1)a(2) - b(1)b(2)$. The above treatment for O_2 , in which the overlapping AOs a and b are replaced by the orthogonal MOs π^*_x and π^*_y , represents a particular case of the H_2 -type theory.

Note

See (a) Harcourt R. D. 2005, *Aust. J. Chem.*, 58, 573 and Harcourt, R. D. *Trends. Phys. Chem.*, Vol. 11, 2006, for development of increased-valence theory for the diatomic one electron bond; (b) Karafiloglou, P. and Harcourt, R. D. 2005, *J. Mol. Struct. THEOCHEM.*, 729, 155, for the results of some recent VB calculations for systems with three-electron two-centre bonds; (c) Harcourt R. D. and Klapötke, T. M. 2006, *Environ. Chem.*, 3, 355, 457 for increased-valence formulations of mechanisms for the formation and decomposition of N_2O_5 .

REFERENCES

1. Shaik, S., and Hiberty, P. C. 2003, *Helv. Chim. Acta*, 86, 1063.
2. Harcourt, R. D. 1982, *Qualitative Valence Bond Descriptions of Electron-Rich Molecules: Pauling "3-electron Bonds" and "Increased-Valence" Theory*, Lecture Notes in Chemistry, Vol. 20, Springer-Verlag, Berlin, pp.1-260. A 2003 Addendum is available from the author.
3. Harcourt, R. D. in (a) 1990, *Valence Bond Theory and Chemical Structure*, (eds. Klein, D., and Trinajstić, N.) Elsevier, p. 251.
4. Harcourt, R. D. 2000, *Eur. J. Inorg. Chem.*, 1901.
5. Harcourt, R. D., and Klapötke, T. M. 2003, *J. Fluor. Chem.* (a) 123(1), 5 (addition: 2004, 125, 785); (b) 123, 273. See also Schulz, A. 1999, *Trends Inorg. Chem.* 6, 137.
6. Coulson, C. A. 1960, *Revs. Mod. Phys.*, 32, 170.
7. Green, M., and Linnett, J. W. 1960, *J. Chem. Soc.*, 4959.
8. Fourré, I., Silvi, B., Sevin, A., and H. Chevreau 2002, *J. Phys. Chem.(A)*, 106, 2561.
9. Linnett, J. W. (a) 1961, *J. Am. Chem. Soc.*, 83, 2643. (b) 1972, *Sci. Progress*, Oxford, 60, 1.
10. Linnett, J. W. 1964, *The Electronic Structures of Molecules*, Methuen, London.
11. Harcourt, R. D. 1985, *J. Chem. Ed.* 62, 95.
12. Pauling, L. (a) 1931, *J. Am. Chem. Soc.* 53, 1367; (b) 1931, *J. Am. Chem. Soc.* 53, 3225.
13. Pauling, L. 1960, *The Nature of the Chemical Bond*, Cornell University Press, Ithaca, New York.
14. Shaik, S., and Shurki, A. 1999, *Angew. Chem. (Int. Ed.)*, 38, 586.
15. (a) Gregory, A. R., and Malatesta, V. 1980, *J. Org. Chem.*, 45, 122; (b) Kiang, T., and Zare, R. N. 1980, *J. Am. Chem. Soc.* 102, 4024. (c) Gill, P. M. W., and Radom, L. 1988, *J. Am. Chem. Soc.*, 110, 4931.
16. Harcourt, R. D. (a) 1978, *Aust. J. Chem.*, 31, 199. (b) 1988, *Chem. Eng. News*, 66, October 3, p. 5. (c) 1997, *J. Phys. Chem. A*, 101, 2496. Corrections: 1997, 101, 5962. (*N.B.* A non-three-electron bond description of the electronic structure of H_2^- (Harcourt, R. D. 1987, *J. Phys. B*, 20, L617) has been shown to be fallacious, *cf.* refs. 39 and 42 therein of ref. (c) here.)
17. Harcourt, R. D., and Scollary, G. R. 1975, *Inorg. Nucl. Chem. Letts.*, 11, 821.
18. Skrezenek, F. L., and Harcourt, R. D. (a) 1984, *J. Am. Chem. Soc.*, 106, 3984; (b) 1987, *J. Mol. Struct. THEOCHEM*, 151, 203.

19. Harcourt, R. D. 1989, *J. Mol. Struct. THEOCHEM*, 186, 131.
20. Harcourt, R. D. 1974, *J. Phys. B*, **7**, L41.
21. Harcourt, R. D., and Styles, M. L. 2003, *J. Phys. Chem. A*, 107, 3877.
22. Harcourt, R. D. 1992, *J. Phys. Chem.*, 96, 7616.
23. Hurley, A. C., Harcourt, R. D., and Taylor, P. R. 1980, *Israel J. Chem.*, 19, 215.
24. Harcourt, R. D. 1977, *Int. J. Quantum Chem. Quantum Biol. Symp.*, 4, 143.
25. Harcourt, R. D. (a) 1971, *J. Mol. Struct.*, 9, 221; (b) 1978, *J. Am. Chem. Soc.*, 100, 8060; (c) 1980, *J. Am. Chem. Soc.*, 102, 5195; 1981, 103, 5623; (d) 1991, *J. Phys. Chem.*, 95, 6916.
26. Harcourt, R. D. 1985, *THEOCHEM*, 122, 235; (b) 1993, *J. Phys. Chem.*, 97, 1351.
27. Harcourt, R. D. (a) 1973, *Inorg. Nucl. Chem. Letts.*, 9, 475; (b) 1990, *Chem. Phys. Letts.*, 167, 374.
28. Harcourt, R. D., Skrezenek, F. L., Wilson, R. M., and Flegg, R. H. 1986, *J. Chem. Soc. Faraday Trans. 2*, 82, 495; (b) Harcourt, R. D., 1992, *J. Mol. Struct. THEOCHEM*, 259, 155.
29. van der Putten, A., Elzing, A., Visscher, W., Barendrecht, E., and Harcourt, R. D. 1988, *J. Mol. Struct. THEOCHEM*, 180, 309; See Reed, C. A., and Landrum, J. T. 1979, *Fed. Eur. Biochem. Soc. Letts.* 106, 156, for the basis of the mechanism for Figure 8.
30. Harcourt, R. D. (a) 1971, *J. Mol. Struct.*, 11, 1; 1972, 18, 515; (b) 1991, *Croat. Chem. Acta*, 64, 399.
31. Harcourt, R. D. 1997, *Int. J. Quantum Chem.*, 63, 547; (b) Harcourt, R. D., and Pyper, N. 1998, *Int. J. Quantum Chem.*, 68, 129.
32. Harcourt, R. D. 1977, *J. Inorg. Nucl. Chem.*, 39, 243.
33. Harcourt, R. D., and Wolyneć, P. P. 2001, *J. Phys. Chem. (A)*, 105, 4974.
34. McClure, D. S. 1960, *Radiation Res. Suppl.* 2, 218.
35. Pauling, L., and Coryell, C. D. 1936, *Proc. Natl. Acad. Science USA*, 22, 210.
36. Ogliaro, F., de Visser, S. P., Cohen, S., Sharma, D. K., and Shaik, S. 2002, *J. Am. Chem. Soc.*, 124, 2806.
37. McKee, M. L. 1995, *J. Am. Chem. Soc.*, 117, 1629.
38. Coulson, C. A., and Fischer, I. 1949, *Phil. Mag.*, 40, 396.
39. Harcourt, R. D. (a) 1975, *Aust. J. Chem.*, 28, 881; (b) 1999, *J. Phys. Chem. A*, 103, 4923 and refs. [2(d), 3(g,h), 17] therein (2003, 107, 11260).
40. Harcourt, R. D. (a) 1964, *Theoret. Chim. Acta*, 2, 437; 1966, 4, 202; (b) 1979, *Aust. J. Chem.*, 32, 933.
41. Harcourt, R. D. 1993, *J. Mol. Struct.*, 300, 243.
42. Harcourt, R. D. 2003, *J. Mol. Struct. THEOCHEM*, 634, 265; 2004, 684, 167; 2005, 716, 99.
43. Hoffmann, R., Shaik, S., and Hiberty, P. C. 2003, *Acc. Chem. Res.*, 36, 750.
44. Shaik, S., and Hiberty, P. C. 2004, *Revs. Comp. Chem.*, 20, 1-100.
45. Harcourt, R. D. (a) 1992, *New J. Chem.*, 16, 667; (b) 1996, *Int. J. Quantum Chem.*, 60, 553.
46. Harcourt, R. D., *J. Mol. Struct. THEOCHEM* (a) 1991, 229, 39; (b) 1992, 253, 363; (c) 1997, 398-399, 93.
47. Pakiari, A. H., and Nazari, F. 2003, *J. Mol. Struct. THEOCHEM*, 640, 109.
48. Williams, F. 1989, *Chem. Eng. News*, 67, January 9, 2.
49. See for example Boyd, R. J. 1984, *Nature*, 310, 480, and refs. therein.