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Valence Bond and Molecular Orbital Descriptions of the Three-Electron Bond

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When two atomic orbitals are used to accommodate the electrons of the three-electron bond (or three-electron two-center bond), it is well-known that the valence bond ($\dot{\mathbf{A}}\cdot\dot{\mathbf{B}} \equiv \ddot{\mathbf{A}}\dot{\mathbf{B}} \leftrightarrow \dot{\mathbf{A}}\ddot{\mathbf{B}}$) and molecular orbital (one antibonding + two bonding electrons) descriptions of this type of bond are equivalent, i.e. $\Psi = \Psi(\mathrm{VB}) = \Psi(\mathrm{MO})$. With three atomic spin orbitals to accommodate the electrons of $\ddot{\mathbf{A}}\dot{\mathbf{B}}$, and three additional atomic spin orbitals to accommodate the electrons of $\dot{\mathbf{A}}\ddot{\mathbf{B}}$, it is deduced that a wave function of the form $\Psi = \Psi_1(\mathrm{VB}) + \Psi_2(\mathrm{VB}) = \Psi_1(\mathrm{MO}) + \Psi_2(\mathrm{MO})$ may be constructed from each set of three atomic spin orbitals, for which the Ψ_1 and Ψ_2 are three-electron bond wave functions. The equivalence is illustrated via the results of some *ab initio* calculations for the ground states of H_2^- and He_2^+. For H_2^-, the use of canonical double-ζ molecular orbitals constructed from 1s′ and 1s″ atomic orbitals on each atomic center must lead to ionization of this anion to form H_2 when the exponents of the diffuse (1s″) orbital components of these molecular orbitals are energy-optimized.

Introduction

The "three-electron bond" or three-electron two-center bond, as symbolized by the valence bond (VB) structure 1, was first

$$\underset{(1)}{\mathbf{A}\cdots\mathbf{B}} \qquad \underset{(2)}{\ddot{\mathbf{A}}\;\dot{\mathbf{B}}} \qquad \underset{(3)}{\dot{\mathbf{A}}\;\ddot{\mathbf{B}}} \qquad \underset{(4)}{\dot{\mathbf{A}}\cdot\dot{\mathbf{B}}} \qquad \underset{(5)}{\cdot\mathbf{A}\cdot\mathbf{B}\cdot}$$

formulated[1,2] by Pauling in 1931. The simplest orbital description of this bond involves three electrons distributed among two overlapping atomic orbitals (AOs) centered on two atomic centers. This type of bond is now receiving much attention[3−32], via both experimental and theoretical studies. Its relevance for valence bond (VB) descriptions of the electronic structures of electron-rich diamagnetic systems with four-electron three-center and six-electron four-center bonding units in particular, as well as paramagnetic systems with three-electron two-center and five-electron three-center bonding units, has been described and stressed on very many occasions.[12−25] Indeed, it is considered that the three-electron bond (together with the associated increased-valence structures for the electron-rich diamagnetic systems[12,14−25,33,34]) "probes the ultimate limit of valence for electron-rich molecules".[4b] In this paper, further consideration is provided for the theory of the three-electron bond, in particular when double-ζ AO basis sets are used to accommodate the three electrons.

Pauling's VB structure 1 for the three-electron bond is equivalent to resonance between Lewis-type VB structures 2 and 3. Because the three-electron bond involves effectively only one bonding electron, the Linnett-type symbolism[12−25,35−37] for this structure, as in 4 or 5, is to be preferred and will be used here. With one AO per atomic center, the identity of eq 1

$$\begin{aligned}\Psi(\mathrm{VB}) = \Psi_2 + k\Psi_3 &= |\mathrm{a}^{\alpha}\mathrm{b}^{\alpha}\mathrm{a}^{\beta}| + k|\mathrm{a}^{\alpha}\mathrm{b}^{\alpha}\mathrm{b}^{\beta}| \\ &\equiv |\mathrm{a}^{\alpha}\mathrm{b}^{\alpha}\psi_{\mathrm{ab}}{}^{\beta}| \equiv \Psi_1 \text{ or } \Psi_4 \text{ or } \Psi_5 \equiv \\ &\quad -(1 + kk^*)\,|\psi_{\mathrm{ab}}{}^{\alpha}\psi^*{}_{\mathrm{ab}}{}^{\alpha}\psi_{\mathrm{ab}}{}^{\beta}| = \Psi(\mathrm{MO})\end{aligned} \quad (1)$$

is obtained, in which the odd electron has an α spin wave function. The a and b are the overlapping AOs, and $\psi_{\mathrm{ab}} = \mathrm{a} + k\mathrm{b}$ and $\psi^*{}_{\mathrm{ab}} = k^*\mathrm{a} - \mathrm{b}$ are the orthogonal bonding and antibonding molecular orbitals (MOs) that may be constructed as linear combinations of these AOs. (The a and b AOs may be of the general form $\mathrm{a} = \sum c_{\mu}\chi_{\mu}{}^{\mathrm{A}}$ and $\mathrm{b} = \sum c_{\nu}\chi_{\nu}{}^{\mathrm{B}}$, in which the $\chi_{\mu}{}^{\mathrm{A}}$ and $\chi_{\nu}{}^{\mathrm{B}}$ are unhybridized AOs centered on the A and B atomic nuclei, respectively. Double-ζ and triple-ζ a and b AOs provide examples of these types of AOs.) The identity shows the equivalence that exists between the VB and MO descriptions of the three-electron bond when two AOs are used to accommodate the electrons.

It is noted here that other VB symbols have also been used[7] to represent the three-electron bond. These symbols include those of structures 6 and 7. The identity of eq 1 applies also to each of them when two AOs are used to construct the three-electron wave function.

$$\underset{(6)}{\mathrm{A}\therefore\mathrm{B}} \qquad \underset{(7)}{\mathrm{A}\overset{\bullet}{-}\mathrm{B}}$$

When more than two (hybrid or nonhybrid) AOs are used to accommodate the electrons, for example a and b_0 for the AO configuration $(\mathrm{a})^2(\mathrm{b}_0)^1$ for structure 2, and a_0 and b for the AO configuration $(\mathrm{a}_0)^1(\mathrm{b})^2$ for structure 3, it is considered that an equivalence no longer exists between the primary VB and MO formulations.[30−32,38] However when three atomic spin orbitals are used to accommodate the electrons of VB structure 2, and three additional atomic spin orbitals are used to accommodate the electrons of VB structure 3, it is still possible to formulate a three-electron bonding wave function of the form

$$\Psi = \Psi_1(\mathrm{VB}) + \Psi_2(\mathrm{VB}) = \Psi_1(\mathrm{MO}) + \Psi_2(\mathrm{MO}) \quad (2)$$

with each set of AOs. One may then use VB structures of the type 4 or 5 to provide compact VB representations of the three-electron bond. The primary purpose of this paper is to provide a derivation of eq 2 via the use of four atomic spin orbitals to accommodate the A electrons of structure 2 and the B electrons of structure 3. Aspects of this identity will be illustrated via the results of some *ab initio* VB calculations for H_2^- and He_2^+, using 1s AOs for both systems and also 1s and 2p AOs for H_2^-.

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Derivation of $\Psi = \Psi_1(\mathrm{VB}) + \Psi_2(\mathrm{VB}) = \Psi_1(\mathrm{MO}) + \Psi_2(\mathrm{MO})$

Atomic orbitals designated as a′, a″, and b_0 will be used to accommodate the three electrons of VB structure 2, with opposed spins for the a′ and a″ electrons. The corresponding AOs for VB structure 3 are b′, b″, and a_0, with opposed spins for the b′ and b″ electrons. A Linnett-type VB structure of type 4 may be constructed by delocalizing either an A electron of structure 2 into an AB bonding MO or a B electron of structure 3 into an AB bonding MO, as is indicated in 2 → 8 and 3 → 9, respectively.

(2) (8) (3) (9)

Initially we shall give attention to the 2 → 8 delocalization. Because either an a′ electron or an a″ electron may be delocalized, two bonding MOs may be constructed, namely, $\psi_{a'b_0} = a' + k'b_0$ and $\psi_{a''b_0} = a'' + k''b_0$. The resulting orbital configurations are then $(a'')^1(b_0)^1(\psi_{a'b_0})^1$ and $(a')^1(b_0)^1(\psi_{a''b_0})^1$, respectively. The two $S = M_S = 1/2$ spin wave functions of eqs 3−6 may then be constructed for each of these configurations.

$$\Psi_{\mathrm{I}}(a''b_0\psi_{a'b_0}) = 2|a''^{\alpha}b_0{}^{\alpha}\psi_{a'b_0}{}^{\beta}| - |a''^{\alpha}b_0{}^{\beta}\psi_{a'b_0}{}^{\alpha}| - |a''^{\beta}b_0{}^{\alpha}\psi_{a'b_0}{}^{\alpha}| \quad (3)$$

$$\Psi_{\mathrm{II}}(a''b_0\psi_{a'b_0}) = |a''^{\alpha}b_0{}^{\beta}\psi_{a'b_0}{}^{\alpha}| - |a''^{\beta}b_0{}^{\alpha}\psi_{a'b_0}{}^{\alpha}| \quad (4)$$

$$\Psi_{\mathrm{I}}(a'b_0\psi_{a''b_0}) = 2|a'^{\alpha}b_0{}^{\alpha}\psi_{a''b_0}{}^{\beta}| - |a'^{\alpha}b_0{}^{\beta}\psi_{a''b_0}{}^{\alpha}| - |a'^{\beta}b_0{}^{\alpha}\psi_{a''b_0}{}^{\alpha}| \quad (5)$$

$$\Psi_{\mathrm{II}}(a'b_0\psi_{a''b_0}) = |a'^{\alpha}b_0{}^{\beta}\psi_{a''b_0}{}^{\alpha}| - |a'^{\beta}b_0{}^{\alpha}\psi_{a''b_0}{}^{\alpha}| \quad (6)$$

The $\Psi_{\mathrm{I}}(a''b_0\psi_{a'b_0})$ of eq 3 is used here to demonstrate that Ψ_{I}-type wave functions involve parallel spins ($S = 1$) for the b_0 electron and either the a″ electron (eq 3) or the a′ electron (eq 5). The analysis proceeds according to eqs 7−9.

$$\Psi_{\mathrm{I}}(a''b_0\psi_{a'b_0}) = 2|a''^{\alpha}b_0{}^{\alpha}\psi_{a'b_0}{}^{\beta}| - |a''^{\alpha}b_0{}^{\beta}\psi_{a'b_0}{}^{\alpha}| - |a''^{\beta}b_0{}^{\alpha}\psi_{a'b_0}{}^{\alpha}| \quad (7)$$

$$= 2|a''^{\alpha}b_0{}^{\alpha}\psi_{a'b_0}{}^{\beta}| - |(a''^{\alpha}b_0{}^{\beta} + a''^{\beta}b_0{}^{\alpha})\psi_{a'b_0}{}^{\alpha}| \quad (8)$$

$$= 2\{(a'')^1(b_0)^1(S = M_S = 1)\}\{(\psi_{a'b_0})^1(S = 1/2, M_S = -1/2)\} - \{(a'')^1(b_0)^1(S = 1, M_S = 0)\} \times \{(\psi_{a'b_0})^1(S = 1/2, M_S = +1/2)\} \quad (9)$$

Because $S = M_S = +1/2$, the spin of the $\psi_{a'b_0}$ electron in eq 9 is opposed to those of the a″ and b_0 electrons.

The orbital spins of the Ψ_{II}-type wave functions of eqs 4 and 6 may be similarly analyzed. For example,

$$\Psi_{\mathrm{II}}(a''b_0\psi_{a'b_0}) = |a''^{\alpha}b_0{}^{\beta}\psi_{a'b_0}{}^{\alpha}| - |a''^{\beta}b_0{}^{\alpha}\psi_{a'b_0}{}^{\alpha}| \quad (10)$$

$$= |(a''^{\alpha}b_0{}^{\beta} - \alpha''^{\beta}b_0{}^{\alpha})\psi_{a'b_0}{}^{\alpha}| \quad (11)$$

$$= \{(a'')^1(b_0)^1(S = 0, M_S = 0)\}\{(\psi_{a'b_0})^1(S = 1/2, M_S = +1/2)\} \quad (12)$$

thereby indicating that the spin of the a″ electron of eq 4 is opposed to that of the b_0 electron. Similarly in eq 6, the spins of the b_0 and a′ electrons are opposed.

On substitution of the LCAO forms of $\psi_{a'b_0}$ and $\psi_{a''b_0}$ into eqs 3−6, we obtain eqs 13−16.

$$\Psi_{\mathrm{I}}(a''b_0\psi_{a'b_0}) = 2|a''^{\alpha}b_0{}^{\alpha}a'^{\beta}| - |a''^{\alpha}b_0{}^{\beta}a'^{\alpha}| - |a''^{\beta}b_0{}^{\alpha}a'^{\alpha}| + 3k'|a''^{\alpha}b_0{}^{\alpha}b_0{}^{\beta}| \quad (13)$$

$$\Psi_{\mathrm{II}}(a''b_0\psi_{a'b_0}) = |a''^{\alpha}b_0{}^{\beta}a'^{\alpha}| - |a''^{\beta}b_0{}^{\alpha}a'^{\alpha}| + k'|a''^{\alpha}b_0{}^{\beta}b_0{}^{\alpha}| \quad (14)$$

$$\Psi_{\mathrm{I}}(a'b_0\psi_{a''b_0}) = 2|a'^{\alpha}b_0{}^{\alpha}a''^{\beta}| - |a'^{\alpha}b_0{}^{\beta}a''^{\alpha}| - |a'^{\beta}b_0{}^{\alpha}a''^{\alpha}| + 3k''|a'^{\alpha}b_0{}^{\alpha}b_0{}^{\beta}| \quad (15)$$

$$\Psi_{\mathrm{II}}(a'b_0\psi_{a''b_0}) = |a'^{\alpha}b_0{}^{\beta}a''^{\alpha}| - |a'^{\beta}b_0{}^{\alpha}a''^{\alpha}| + k''|a'^{\alpha}b_0{}^{\beta}b_0{}^{\alpha}| \quad (16)$$

Inspection of the Ψ_{I} and Ψ_{II} wave functions of eqs 13 and 14 shows that they are orthogonal only when $k' = 0$ if AO overlap integrals are omitted. Similarly the wave functions of eqs 15 and 16 are orthogonal when $k'' = 0$.

We now (nonvariationally) linearly combine the Ψ_{I}-type wave functions of eqs 13 and 15, to generate eqs 17−20,

$$\Psi_{\mathrm{I}}(a''b_0\psi_{a'b_0}) + \Psi_{\mathrm{I}}(a'b_0\psi_{a''b_0}) = 3(|a''^{\alpha}b_0{}^{\alpha}a'^{\beta}| + |a'^{\alpha}b_0{}^{\alpha}a''^{\beta}| + k'|a''^{\alpha}b_0{}^{\alpha}b_0{}^{\beta}| + k''|a'^{\alpha}b_0{}^{\alpha}b_0{}^{\beta}|) \quad (17)$$

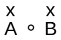
$$= 3(|a''^{\alpha}b_0{}^{\alpha}\psi_{a'b_0}{}^{\beta}| + |a'^{\alpha}b_0{}^{\alpha}\psi_{a''b_0}{}^{\beta}|) \quad (18)$$

$$= -3\{|\psi_{a''b_0}{}^{\alpha}\psi^*{}_{a''b_0}{}^{\alpha}\psi_{a'b_0}{}^{\beta}|/(1 + k''k''^*) + |\psi_{a'b_0}{}^{\alpha}\psi^*{}_{a'b_0}{}^{\alpha}\psi_{a''b_0}{}^{\beta}|/(1 + k'k'^*)\} \quad (19)$$

$$\Psi_{\mathrm{I}}(a''b_0\psi_{a'b_0}) - \Psi_{\mathrm{I}}(a'b_0\psi_{a''b_0}) = |a''^{\alpha}b_0{}^{\alpha}a'^{\beta}| - |a'^{\alpha}b_0{}^{\alpha}a''^{\beta}| + 3k'|a''^{\alpha}b_0{}^{\alpha}b_0{}^{\beta}| - 3k''|a'^{\alpha}b_0{}^{\alpha}b_0{}^{\beta}| - 2|a'^{\alpha}b_0{}^{\beta}a''^{\alpha}| \quad (20)$$

in which $\psi^*{}_{a'b_0} = k'^*a' - b_0$ and $\psi^*{}_{a''b_0} = k''^*a'' - b_0$ are antibonding MOs which are orthogonal to the bonding MOs $\psi_{a'b_0}$ and $\psi_{a''b_0}$, respectively.

Each of the Slater determinants of eq 18 may be associated with a VB structure of type 4 or 5. If the α and β spin electrons are represented by crosses and circles respectively, then these structures become 10 and 11.



(10)

(11)

In eq 19, the equivalent MO formulation is provided for the Slater determinants of eq 18. However unless a′ = a″ = a and b′ = b″ = b, each of the Slater determinants of eqs 18 and 19 is not an $S = 1/2$ spin eigenfunction of the spin operator $\hat{S}^2$; only the linear combination of the two Slater determinants corresponds to an $S = 1/2$ spin eigenstate.

Inspection of eqs 18 and 19 indicates that they provide an example of the identity of eq 2.

When a′ = a″ = a and b′ = b″ = b, eq 20 reduces to zero. Further consideration will not be given to eq 20 when a′ ≠ a″ and b′ ≠ b″.

Further Details for $\Psi = \Psi_1(\mathrm{VB}) + \Psi_2(\mathrm{VB}) = \Psi_1(\mathrm{MO}) + \Psi_2(\mathrm{MO})$

The Ψ_{II}-type wave functions of eqs 14 and 16 may be similarly linearly combined to give eqs 21−23.

$$\Psi_{\mathrm{II}}(\mathrm{a}''\mathrm{b}_0\psi_{\mathrm{a}'\mathrm{b}_0}) + \Psi_{\mathrm{II}}(\mathrm{a}'\mathrm{b}_0\psi_{\mathrm{a}''\mathrm{b}_0}) = |\mathrm{a}''^{\alpha}\mathrm{b}_0{}^{\alpha}\mathrm{a}'^{\beta}| + |\mathrm{a}'^{\alpha}\mathrm{b}_0{}^{\alpha}\mathrm{a}''^{\beta}| - k'|\mathrm{a}''^{\alpha}\mathrm{b}_0{}^{\alpha}\mathrm{b}_0{}^{\beta}| - k''|\mathrm{a}'^{\alpha}\mathrm{b}_0{}^{\alpha}\mathrm{b}_0{}^{\beta}| \tag{21}$$

$$= |\mathrm{a}''^{\alpha}\mathrm{b}_0{}^{\alpha}\phi^*{}_{\mathrm{a}'\mathrm{b}_0}{}^{\beta}| + |\mathrm{a}'^{\alpha}\mathrm{b}_0{}^{\alpha}\phi^*{}_{\mathrm{a}''\mathrm{b}_0}{}^{\beta}| \tag{22}$$

$$= -\{|\phi_{\mathrm{a}'\mathrm{b}_0}{}^{\alpha}\phi^*{}_{\mathrm{a}'\mathrm{b}_0}{}^{\alpha}\phi^*{}_{\mathrm{a}'\mathrm{b}_0}{}^{\beta}|/(1 + k'k'^*) + |\phi_{\mathrm{a}''\mathrm{b}_0}{}^{\alpha}\phi^*{}_{\mathrm{a}''\mathrm{b}_0}{}^{\alpha}\phi^*{}_{\mathrm{a}''\mathrm{b}_0}{}^{\beta}|/(1 + k''k''^*)\} \tag{23}$$

In eq 22, $\phi^*{}_{\mathrm{a}'\mathrm{b}_0} = \mathrm{a}' - k'\mathrm{b}_0$, $\phi^*{}_{\mathrm{a}''\mathrm{b}_0} = \mathrm{a}'' - k''\mathrm{b}_0$. In eq 23, $\phi_{\mathrm{a}'\mathrm{b}_0} = k'^*\mathrm{a}' + \mathrm{b}$ and $\phi_{\mathrm{a}''\mathrm{b}_0} = k''^*\mathrm{a}'' + \mathrm{b}$ are bonding MOs that are orthogonal to the antibonding MOs $\phi^*{}_{\mathrm{a}'\mathrm{b}_0}$ and $\phi^*{}_{\mathrm{a}''\mathrm{b}_0}$. Inspection of eq 23 shows that $\Psi_{\mathrm{II}}(\mathrm{a}''\mathrm{b}_0\psi_{\mathrm{a}'\mathrm{b}_0}) + \Psi_{\mathrm{II}}(\mathrm{a}'\mathrm{b}_0\psi_{\mathrm{a}''\mathrm{b}_0})$ is equivalent to a linear combination of two three-electron antibonding configurations.

As was indicated earlier, a VB structure of the type 4 may also be generated from the Lewis structure 3, by delocalizing a b′ or b″ electron into either the $\psi_{\mathrm{b}'\mathrm{a}_0} = \mathrm{b}' + l'\mathrm{a}_0$ or the $\psi_{\mathrm{b}''\mathrm{a}_0} = \mathrm{b}'' + l''\mathrm{a}_0$ bonding MO. Appropriate wave functions are those of eqs 24−27

$$\Psi_{\mathrm{I}}(\mathrm{b}''\mathrm{a}_0\psi_{\mathrm{b}'\mathrm{a}_0}) = 2|\mathrm{b}''^{\alpha}\mathrm{a}_0{}^{\alpha}\mathrm{b}'^{\beta}| + 3l'|\mathrm{b}''^{\alpha}\mathrm{a}_0{}^{\alpha}\mathrm{a}_0{}^{\beta}| + |\mathrm{b}''^{\alpha}\mathrm{b}'^{\alpha}\mathrm{a}_0{}^{\beta}| - |\mathrm{a}_0{}^{\alpha}\mathrm{b}'^{\alpha}\mathrm{b}''^{\beta}| \tag{24}$$

$$\Psi_{\mathrm{I}}(\mathrm{b}'\mathrm{a}_0\psi_{\mathrm{b}''\mathrm{a}_0}) = 2|\mathrm{b}'^{\alpha}\mathrm{a}_0{}^{\alpha}\mathrm{b}''^{\beta}| + 3l''|\mathrm{b}'^{\alpha}\mathrm{a}_0{}^{\alpha}\mathrm{a}_0{}^{\beta}| + |\mathrm{b}'^{\alpha}\mathrm{b}''^{\alpha}\mathrm{a}_0{}^{\beta}| - |\mathrm{a}_0{}^{\alpha}\mathrm{b}''^{\alpha}\mathrm{b}'^{\beta}| \tag{25}$$

$$\Psi_{\mathrm{I}}(\mathrm{b}''\mathrm{a}_0\psi_{\mathrm{b}'\mathrm{a}_0}) + \Psi_{\mathrm{I}}(\mathrm{b}'\mathrm{a}_0\psi_{\mathrm{b}''\mathrm{a}_0}) = 3(|\mathrm{b}''^{\alpha}\mathrm{a}_0{}^{\alpha}\psi_{\mathrm{b}'\mathrm{a}_0}{}^{\beta}| + |\mathrm{b}'^{\alpha}\mathrm{a}_0{}^{\alpha}\psi_{\mathrm{b}''\mathrm{a}_0}{}^{\beta}| \tag{26}$$

$$= -3\{|\psi_{\mathrm{b}''\mathrm{a}_0}{}^{\alpha}\psi^*{}_{\mathrm{b}''\mathrm{a}_0}{}^{\alpha}\psi_{\mathrm{b}'\mathrm{a}_0}{}^{\beta}|/(1 + l''l''^*) + |\psi_{\mathrm{b}'\mathrm{a}_0}{}^{\alpha}\psi^*{}_{\mathrm{b}'\mathrm{a}_0}{}^{\alpha}\psi_{\mathrm{b}''\mathrm{a}_0}{}^{\beta}|/(1 + l'l'^*)\} \tag{27}$$

and the equivalence that exists between eqs 26 and 27 provides a second example of the identity of eq 2.

Each of the four Ψ_{I}-type wave functions of eqs 13, 15, 24, and 25 involves two types of ($S = 0$ spin) AO configurations for the two-electron A or B components of the Lewis structures 2 and 3. These configurations are (i) open-shell $(\mathrm{a}')^1(\mathrm{a}'')^1$ or $(\mathrm{b}')^1(\mathrm{b}'')^1$ and (ii) closed-shell $(\mathrm{b}_0)^2$ or $(\mathrm{a}_0)^2$. The third electron for (i) occupies either a b_0 or an a_0 AO, whereas for (ii), this electron occupies one of the a′, a″, b′, or b″ AOs.

The best linear combination of the four Ψ_{I}-type wave functions is given by eq 28 or 29,

$$\Psi_{\mathrm{I}}(\mathrm{a}',\mathrm{a}'',\mathrm{b}',\mathrm{b}'') = \Psi_{\mathrm{I}}(\mathrm{a}''\mathrm{b}_0\psi_{\mathrm{a}'\mathrm{b}_0}) + \Psi_{\mathrm{I}}(\mathrm{a}'\mathrm{b}_0\psi_{\mathrm{a}''\mathrm{b}_0}) + \mu\{\Psi_{\mathrm{I}}(\mathrm{b}''\mathrm{a}_0\psi_{\mathrm{b}'\mathrm{a}_0}) + \Psi_{\mathrm{I}}(\mathrm{b}'\mathrm{a}_0\psi_{\mathrm{b}''\mathrm{a}_0})\} \tag{28}$$

$$= 3\{|\mathrm{a}''^{\alpha}\mathrm{b}_0{}^{\alpha}\psi_{\mathrm{a}'\mathrm{b}_0}{}^{\beta}| + |\mathrm{a}'^{\alpha}\mathrm{b}_0{}^{\alpha}\psi_{\mathrm{a}''\mathrm{b}_0}{}^{\beta}| + \mu(|\mathrm{b}''^{\alpha}\mathrm{a}_0{}^{\alpha}\psi_{\mathrm{b}'\mathrm{a}_0}{}^{\beta}| + |\mathrm{b}'^{\alpha}\mathrm{a}_0{}^{\alpha}\psi_{\mathrm{b}''\mathrm{a}_0}{}^{\beta}|)\} \tag{29}$$

and it is equivalent to the best linear combination of six ($S = M_S = 1/2$ spin) AO configurations for the three electrons. The latter linear combination involves five independent variational parameters, which may be related to the k', k'', l', and l'' polarity parameters and the μ of eq 28 or eq 29.

When a′ and b′, a″ and b″, and a_0 and b_0 are pairs of symmetrically equivalent AOs, the number of variational parameters reduces to two, namely, $k' = l'$, $k'' = l''$ with $\mu = \pm1$.

Values of $\mu = -1$ and $\mu = +1$ then give diatomic $^2\Sigma_u{}^+$ and $^2\Sigma_g{}^+$ states, respectively. For $\mu = -1$, Ψ_{I} of eq 27 is equivalent to eqs 30−32.

$$\Psi_{\mathrm{I}}(\mathrm{a}',\mathrm{a}'',\mathrm{b}',\mathrm{b}'') = 3\{(|\mathrm{a}''^{\alpha}\mathrm{b}_0{}^{\alpha}\psi_{\mathrm{a}'\mathrm{b}_0}{}^{\beta}| + |\mathrm{a}'^{\alpha}\mathrm{b}_0{}^{\alpha}\psi_{\mathrm{a}''\mathrm{b}_0}{}^{\beta}| - (|\mathrm{b}''^{\alpha}\mathrm{a}_0{}^{\alpha}\psi_{\mathrm{b}'\mathrm{a}_0}{}^{\beta}| + |\mathrm{b}'^{\alpha}\mathrm{a}_0{}^{\alpha}\psi_{\mathrm{b}''\mathrm{a}_0}{}^{\beta}|)\} \tag{30}$$

$$= -3\{(|\psi_{\mathrm{a}''\mathrm{b}_0}{}^{\alpha}\psi^*{}_{\mathrm{a}''\mathrm{b}_0}{}^{\alpha}\psi_{\mathrm{a}'\mathrm{b}_0}{}^{\beta}| - |\psi_{\mathrm{b}_0\mathrm{a}''}{}^{\alpha}\psi^*{}_{\mathrm{b}_0\mathrm{a}''}{}^{\alpha}\psi_{\mathrm{b}_0\mathrm{a}'}{}^{\beta}|)/(1 + k''k''^*) + (|\psi_{\mathrm{a}'\mathrm{b}_0}{}^{\alpha}\psi^*{}_{\mathrm{a}'\mathrm{b}_0}{}^{\alpha}\psi_{\mathrm{a}''\mathrm{b}_0}{}^{\beta}| - |\psi_{\mathrm{b}_0\mathrm{a}'}{}^{\alpha}\psi^*{}_{\mathrm{b}_0\mathrm{a}'}{}^{\alpha}\psi_{\mathrm{b}_0\mathrm{a}''}{}^{\beta}|)/(1 + k'k'^*)\} \tag{31}$$

$$= C_1[\psi_1\{(\mathrm{a}'\mathrm{a}'')\mathrm{b}_0\} - \psi_1\{(\mathrm{b}'\mathrm{b}'')\mathrm{a}_0\}] + C_2[\psi_2\{\mathrm{a}'(\mathrm{b}_0\mathrm{b}_0)\} - \psi_2\{\mathrm{b}'(\mathrm{a}_0\mathrm{a}_0)\}] + C_3[\psi_3\{\mathrm{a}''(\mathrm{b}_0\mathrm{b}_0)\} - \psi_3\{\mathrm{b}''(\mathrm{a}_0\mathrm{a}_0)\}] \tag{32}$$

In eq 32, the ψ_i wave functions for the Lewis VB structures of types 2 and 3 are non-normalized at this stage; for example, $\psi_1\{(\mathrm{a}'\mathrm{a}'')\mathrm{b}_0\} = |\mathrm{a}''^{\alpha}\mathrm{b}_0{}^{\alpha}\mathrm{a}'^{\beta}| + |\mathrm{a}'^{\alpha}\mathrm{b}_0{}^{\alpha}\mathrm{a}''^{\beta}|$. In terms of the associated C_i coefficients, the MO polarity parameters k' and k'' are given by eq 33.

$$k' = C_3/C_1, \quad k'' = C_2/C_1 \tag{33}$$

If $\mathrm{a}' \equiv \mathrm{a}'' \equiv \mathrm{a}$ and $\mathrm{b}' \equiv \mathrm{b}'' \equiv \mathrm{b}$, i.e. a single-$\zeta$ basis set is used to accommodate the two A electrons of VB structure 2 and the two B electrons of VB structure 3, then eqs 30−32 reduce to eqs 34−36,

$$\Psi_{\mathrm{I}}(\mathrm{a},\mathrm{b}) = 6(|\mathrm{a}^{\alpha}\mathrm{b}_0{}^{\alpha}\psi_{\mathrm{ab}_0}{}^{\beta}| - |\mathrm{b}^{\alpha}\mathrm{a}_0{}^{\alpha}\psi_{\mathrm{ba}_0}{}^{\beta}|) \tag{34}$$

$$= -6(|\psi_{\mathrm{ab}_0}{}^{\alpha}\psi^*{}_{\mathrm{ab}_0}{}^{\alpha}\psi_{\mathrm{ab}_0}{}^{\beta}| - |\psi_{\mathrm{ba}_0}{}^{\alpha}\psi^*{}_{\mathrm{ba}_0}{}^{\alpha}\psi_{\mathrm{ba}_0}{}^{\beta}|)/(1 + kk^*) \tag{35}$$

$$= C_1[\psi_1\{(\mathrm{aa})\mathrm{b}_0\} - \psi_1\{(\mathrm{bb})\mathrm{a}_0\}] + C_2[\psi_2\{\mathrm{a}(\mathrm{b}_0\mathrm{b}_0)\} - \psi_2\{\mathrm{b}(\mathrm{a}_0\mathrm{a}_0)\}] \tag{36}$$

to give a simpler type of VB−MO equivalence. Thus in each of eqs 31 and 35, each Slater determinant involves MOs that are constructed as linear combinations of only two AOs. These MOs are not the canonical MOs, simple forms of which we shall now consider.

Canonical Molecular Orbital Configuration

In the previous section it was demonstrated that when more than two (nonhybridized or hybridized) AOs are used as a basis set for VB and MO formulations of the three-electron bond, a MO−VB equivalence is obtained via resonance between several three-electron two-AO configurations, each of which may be formulated in either a VB or MO manner. The equivalence no longer exists if canonical MOs are used to accommodate the electrons. To illustrate this nonequivalence, we consider the simplest $^2\Sigma_u{}^+$ case, with the canonical MOs constructed from the AOs a and b, and a_0 and b_0. The canonical MOs and the lowest energy MO configuration are then given by eqs 37 and 38, respectively.

$$\phi_1 = \mathrm{a} + \mathrm{b} + k_1(\mathrm{a}_0 + \mathrm{b}_0),\quad \phi_2 = \mathrm{a} - \mathrm{b} + k_2(\mathrm{a}_0 - \mathrm{b}_0)$$

$$\phi_3 = \mathrm{a} + \mathrm{b} - k_3(\mathrm{a}_0 + \mathrm{b}_0),\quad \phi_4 = \mathrm{a} - \mathrm{b} - k_4(\mathrm{a}_0 - \mathrm{b}_0) \quad (37)$$

$$\begin{aligned}\Psi_1(\mathrm{CMO}) = |\phi_1{}^{\alpha}\phi_1{}^{\beta}\phi_2{}^{\alpha}| = |(\mathrm{a}+\mathrm{b})^{\alpha}(\mathrm{a}+\mathrm{b})^{\beta}(\mathrm{a}-\mathrm{b})^{\alpha}| + {}\\ k_2|(\mathrm{a}+\mathrm{b})^{\alpha}(\mathrm{a}+\mathrm{b})^{\beta}(\mathrm{a}_0-\mathrm{b}_0)^{\alpha}| + k_1{}^2|(\mathrm{a}_0+\mathrm{b}_0)^{\alpha} \times {}\\ (\mathrm{a}_0+\mathrm{b}_0)^{\beta}(\mathrm{a}-\mathrm{b})^{\alpha}| + k_1{}^2k_2|(\mathrm{a}_0+\mathrm{b}_0)^{\alpha}(\mathrm{a}_0+\mathrm{b}_0)^{\beta}(\mathrm{a}_0 - {}\\ \mathrm{b}_0)^{\alpha}| + k_1\{|(\mathrm{a}+\mathrm{b})^{\alpha}(\mathrm{a}_0+\mathrm{b}_0)^{\beta}(\mathrm{a}-\mathrm{b})^{\alpha}| + |(\mathrm{a}_0+\mathrm{b}_0)^{\alpha}(\mathrm{a} + {}\\ \mathrm{b})^{\beta}(\mathrm{a}-\mathrm{b})^{\alpha}|\} + k_1k_2\{|(\mathrm{a}+\mathrm{b})^{\alpha}(\mathrm{a}_0+\mathrm{b}_0)^{\beta}(\mathrm{a}_0-\mathrm{b}_0)^{\alpha}| + {}\\ |(\mathrm{a}_0+\mathrm{b}_0)^{\alpha}(\mathrm{a}+\mathrm{b})^{\beta}(\mathrm{a}_0-\mathrm{b}_0)^{\alpha}|\} \quad (38)\end{aligned}$$

In eq 38, only the Slater determinants $|(\mathrm{a}+\mathrm{b})^{\alpha}(\mathrm{a}+\mathrm{b})^{\beta}(\mathrm{a}-\mathrm{b})^{\alpha}|$ and $|(\mathrm{a}_0+\mathrm{b}_0)^{\alpha}(\mathrm{a}_0+\mathrm{b}_0)^{\beta}(\mathrm{a}_0-\mathrm{b}_0)^{\alpha}|$ generate $S = 1/2$ spin three-electron bond VB structures of the type 10. (It is noted that each of the Slater determinants $|(\mathrm{a}+\mathrm{b})^{\alpha}(\mathrm{a}_0+\mathrm{b}_0)^{\beta}(\mathrm{a}-\mathrm{b})^{\alpha}|$ and $|(\mathrm{a}_0+\mathrm{b}_0)^{\alpha}(\mathrm{a}+\mathrm{b})^{\beta}(\mathrm{a}_0-\mathrm{b}_0)^{\alpha}|$ corresponds to a three-electron bond structure of the type 10, but, as is the case for the Slater determinants of eqs 17, 18, 26, and 27, neither of them alone is an $S = 1/2$ spin eigenfunction). The remaining six Slater determinants, either alone or in pairs, generate a variety of $S = 1/2$ spin configurations, none of which corresponds to a three-electron bond configuration. Therefore Ψ_1(CMO) does not correspond to a linear combination of three-electron bond configurations. The same result arises when Ψ_1(CMO) is interacted variationally with the five ${}^2\Sigma_u{}^+$ excited configurations that have two bonding electrons and one antibonding electron. This configuration interaction (CI) is equivalent to the construction of the variational linear combination of eq 39,

$$\begin{aligned}\Psi(\mathrm{MOCI}) = C_1|\varphi_1{}^{\alpha}\varphi_1{}^{\beta}\varphi_2{}^{\alpha}| + C_2|\varphi_1{}^{\alpha}\varphi_1{}^{\beta}\varphi_4{}^{\alpha}| + {}\\ C_3|\varphi_3{}^{\alpha}\varphi_3{}^{\beta}\varphi_2{}^{\alpha}| + C_4|\varphi_3{}^{\alpha}\varphi_3{}^{\beta}\varphi_4{}^{\alpha}| + C_5(|\varphi_1{}^{\alpha}\varphi_3{}^{\beta}\varphi_2{}^{\alpha}| + {}\\ |\varphi_3{}^{\alpha}\varphi_1{}^{\beta}\varphi_2{}^{\alpha}|) + C_6(|\varphi_1{}^{\alpha}\varphi_3{}^{\beta}\varphi_4{}^{\alpha}| + |\varphi_3{}^{\alpha}\varphi_1{}^{\beta}\varphi_4{}^{\alpha}|) \quad (39)\end{aligned}$$

with $\varphi_1 = \mathrm{a} + \mathrm{b}$, $\varphi_2 = \mathrm{a} - \mathrm{b}$, $\varphi_3 = \mathrm{a}_0 + \mathrm{b}_0$, and $\varphi_4 = \mathrm{a}_0 - \mathrm{b}_0$.

It will now be assumed that the orbital exponents (ζ) for the a_0 and b_0 AOs are smaller than are those for the a and b AOs. For a given internuclear separation, if the energy for the three-electron bond configuration $|\varphi_1{}^{\alpha}\varphi_1{}^{\beta}\varphi_2{}^{\alpha}|$ lies above the energy for the electron-pair bond configuration $|\varphi_1{}^{\alpha}\varphi_1{}^{\beta}|$, then for fixed values of the exponents of the a and b AOs, energy optimization of the a_0 and b_0 exponents for the ${}^2\Sigma_u{}^+$ CMO configuration of eq 38 will generate values of zero for these latter exponents. This result applies also to the AO configurations $|(\mathrm{a}^{\alpha}\mathrm{b}^{\beta} + \mathrm{b}^{\alpha}\mathrm{a}^{\beta})\mathrm{a}_0{}^{\alpha}|$ and $|(\mathrm{a}^{\alpha}\mathrm{b}^{\beta} + \mathrm{b}^{\alpha}\mathrm{a}^{\beta})\mathrm{b}_0{}^{\alpha}|$, which are included in the Ψ_1(CMO) and Ψ(MOCI), and (for ${}^2\Sigma_g{}^+$ states) to $|(\mathrm{a}^{\alpha}\mathrm{a}^{\beta})\mathrm{a}_0{}^{\alpha}| + |(\mathrm{b}^{\alpha}\mathrm{b}^{\beta})\mathrm{b}_0{}^{\alpha}|$. Each of these latter wave functions generates a two-electron ${}^1\Sigma_g{}^+$ rather than a three-electron ${}^2\Sigma_u{}^+$ wave function when energy optimization of the exponents of a_0 and b_0 occurs. Thus optimization of the exponents for the double-ζ CMO configuration of eq 38 leads to the loss of the antibonding electron. This effect is illustrated via the results of some *ab initio* calculations for $H_2{}^-$ that are described in the next section. However at moderate internuclear separations, nonionization of the ${}^2\Sigma_u{}^+$ anion will occur when either the $|(\mathrm{a}^{\alpha}\mathrm{b}^{\beta} + \mathrm{b}^{\alpha}\mathrm{a}^{\beta})\mathrm{a}_0{}^{\alpha}|$ and $|(\mathrm{a}^{\alpha}\mathrm{b}^{\beta} + \mathrm{b}^{\alpha}\mathrm{a}^{\beta})\mathrm{b}_0{}^{\alpha}|$ configurations are omitted or the MO parameters k_1 and k_2 of eq 37 are set equal to each other so that the same two double-ζ AOs $(\mathrm{a} + k\mathrm{a}_0)$ and $(\mathrm{b} + k\mathrm{b}_0)$ accommodate the three electrons in each of the VB structures 2 and 3. An eq 1-type MO−VB identity then is obtained.

The considerations also indicate that fully variational VB calculations which have included $|(\mathrm{a}^{\alpha}\mathrm{b}^{\beta} + \mathrm{b}^{\alpha}\mathrm{a}^{\beta})\mathrm{a}_0{}^{\beta}|$ and $|(\mathrm{a}^{\alpha}\mathrm{b}^{\beta} + \mathrm{b}^{\alpha}\mathrm{a}^{\beta})\mathrm{b}_0{}^{\alpha}|$ type configurations must give erroneous conclusions with regard to the electronic structure of the $H_2{}^-$ anion. Such calculations, as well as the corresponding canonical MO calculations, underestimate the bond length; cf. refs 39 and 40 for example.

TABLE 1: $He_2{}^+$ VB Calculations for Eqs 32[a]

structures	$\lvert C_i\rvert$[a]	$\lvert C_i\rvert$[b]
$(\mathrm{a}'\mathrm{a}'')\mathrm{b}_0$, $(\mathrm{b}'\mathrm{b}'')\mathrm{a}_0$	0.272 820	0.421 334
$\mathrm{a}'(\mathrm{b}_0\mathrm{b}_0)$, $\mathrm{b}'(\mathrm{a}_0\mathrm{a}_0)$	0.124 835	0.049 997
$\mathrm{b}''(\mathrm{a}_0\mathrm{a}_0)$, $\mathrm{a}''(\mathrm{b}_0\mathrm{b}_0)$	0.014 236	0.009 485
$E(R_e)$/au	−4.935 76	
$E(R{=}\infty)$/au	−4.873 44	
k''	0.4576	
k'	0.0522	
R_e/au	2.2_5	

[a] Coefficients for non-normalized $S = 1/2$ spin AO configurations.
[b] Coefficients for normalized $S = 1/2$ spin AO configurations.

TABLE 2: $H_2{}^-$ VB Calculations for Eqs 32[a]

structures	$\lvert C_i\rvert$[a]	$\lvert C_i\rvert$[b]	$\lvert C_i\rvert$[a]	$\lvert C_i\rvert$[b]
$(\mathrm{a}'\mathrm{a}'')\mathrm{b}_0$, $(\mathrm{b}'\mathrm{b}'')\mathrm{a}_0$	0.362 679	0.576 752	0.365 648	0.578 267
$\mathrm{a}'(\mathrm{b}_0\mathrm{b}_0)$, $\mathrm{b}'(\mathrm{a}_0\mathrm{a}_0)$	0.032 239	0.032 165	0.036 053	0.035 895
$\mathrm{b}''(\mathrm{a}_0\mathrm{a}_0)$, $\mathrm{a}''(\mathrm{b}_0\mathrm{b}_0)$	0.006 753	0.006 553	0.009 259	0.008 919
$(\mathrm{a}'\mathrm{p}_A)\mathrm{b}_0$, $(\mathrm{b}'\mathrm{p}_B)\mathrm{a}_0$			0.055 880	0.076 571
$\mathrm{p}_A(\mathrm{b}_0\mathrm{b}_0)$, $\mathrm{p}_B(\mathrm{a}_0\mathrm{a}_0)$			0.018 717	0.017 622
$E(R_e)$/au	−1.018 75		−1.019 63	
$E(R{=}\infty)$/au	−1.012 93		−1.012 93	
k''	0.0857			
k'	0.01752			
R_e/au	$5._4$		4.9_5	

[a] Coefficients for non-normalized $S = 1/2$ spin AO configurations.
[b] Coefficients for normalized $S = 1/2$ spin AO configurations.

Calculations for $He_2{}^+$ and $H_2{}^-$ with 1s AOs

Roso's *ab initio* program[17,23,25,41,42] was used to perform elementary VB calculations for $He_2{}^+$ and $H_2{}^-$, in order to illustrate aspects of the above theory. Initially the calculations were of the single-ζ type, with two 1s AOs. The AO exponents were chosen to be those for $\mathrm{He}^{(+0.5)}$ and $\mathrm{H}^{(-0.5)}$, i.e. (2 + 1.6875)/2 and (1 + 0.6875)/2, respectively. Minimum energies of -4.903_1 and -0.970_4 au for $He_2{}^+$ and $H_2{}^-$ were calculated to occur for equilibrium internuclear separations (R_e) of $2._1$ and $3._5$ au, respectively.

Some VB calculations were then performed for $H_2{}^-$ and $He_2{}^+$ with double-ζ 1s AOs for the H^- and He. For an infinite internuclear separation, the 1s AO exponents have the following values: $H_2{}^-$: $\zeta(\mathrm{a}_0) = \zeta(\mathrm{b}_0) = 1$; $\zeta(\mathrm{a}') = \zeta(\mathrm{b}') = 1.0392$; $\zeta(\mathrm{a}'') = \zeta(\mathrm{b}'') = 0.2832$; $He_2{}^+$: $\zeta(\mathrm{a}_0) = \zeta(\mathrm{b}_0) = 2$; $\zeta(\mathrm{a}') = \zeta(\mathrm{b}') = 2.1382$; $\zeta(\mathrm{a}'') = \zeta(\mathrm{b}'') = 1.1885$. The resulting STO-6G energies for H + H^- and He^+ + He are −1.012 925 and −4.873 438 au, respectively. The ($S = 1/2$) spin Lewis structures of Table 1 were included in the molecular calculations, with no reoptimization of orbital exponents. For $H_2{}^-$, the energy is minimized (−1.018 754 au) at $R_e = 5.4$ au, to give $k' = 0.0175$ and $k'' = 0.0857$. The corresponding quantities for $He_2{}^+$ are $E = -4.935\ 76$ au, $R_e = 2.25$ au, $k' = 0.0522$, and $k'' = 0.4576$.

It is to be expected that the less firmly bound a″ and b″ electrons should delocalize more extensively than do the a′ and b′ electrons, and because k'' is calculated to be larger than k', this expectation is realized for both systems. It is also found that $He_2{}^+$ has the larger k' and k'' values. This reflects that the propensity for delocalization to occur for $He_2{}^+$ is substantially greater than it is for $H_2{}^-$, thereby providing assistance for the formation of a shorter, stronger bond in the former species.

TABLE 3: H_2^- Energies (au) and Coefficients for the Ψ(MOCI) of Eq 39, with R = 1.65 au, ξ' = 1.00, and Variable ξ''

ξ''	E	C_1	C_2	C_3	C_4	C_5	C_6
0.6875	−0.982 24	1.686	−2.085	−0.319	0.930	−0.241	−0.320
0.5500	−1.001 16	0.877	−1.662	−0.002	0.220	−0.237	0.064
0.3000	−1.042 24	0.187	−1.161	0.014	0.017	−0.077	0.082
0.1000	−1.083 95	0.003	1.008	−0.001	−0.001	0.011	−0.025
0.0100	−1.098 22	0.001	1.000	-3×10^{-7}	-1×10^{-6}	1×10^{-4}	−0.001
0.0010	−1.098 44	3×10^{-6}	1.000	0.000	1×10^{-8}	1×10^{-6}	-3×10^{-5}
0.0001	−1.098 44	1×10^{-8}	1.000	0.000	0.000	1×10^{-8}	9×10^{-7}

TABLE 4: He_2^+ Energies (au) and Coefficients for the Ψ(MOCI) of Eq 39, with R = 2.00 au, ξ' = 2.00, and ξ'' = 1.5 (Energy-Optimized) (For ξ'' = 1.4 and 1.6, E = −4.909 81 and −4.909 56)

ξ''	E	C_1	C_2	C_3	C_4	C_5	C_6
1.5	−4.909 86	0.350	−0.419	0.086	0.240	−0.529	−0.109

For H_2^-, Ψ(MOCI) of eq 39 involves a linear combination of six $S = 1/2$ spin configurations, each of which involves two bonding electrons and one antibonding electron. With a ± b = $1s'_A \pm 1s'_B$ and $a_0 \pm b_0 = 1s''_A \pm 1s''_B$, we have performed variational best calculations of linear combinations of these six configurations. The 1s′ AO exponent has been assigned a value of unity, but different values for the 1s″ AO exponent have been chosen. The results are reported in Table 3. These results show that as the 1s″ exponent is decreased, the coefficient of $|\varphi_1^{\alpha}\varphi_1^{\beta}\varphi_4^{\alpha}|$ approaches unity, and the coefficients of the remaining configurations approach zero. When $\zeta'' = 0$, the configuration $|\varphi_1^{\alpha}\varphi_1^{\beta}\varphi_4^{\alpha}|$ reduces to $|\varphi_1^{\alpha}\varphi_1^{\beta}|$, which corresponds to the single-ζ bonding MO configuration for H_2. Thus optimization of the diffuse orbital exponent of H_2^- at internuclear separations leads to ionization of the anion. This is not the case for He_2^+ (Table 4); when a value of 2.0 is assigned to the 1s′ exponent, the optimum value for ζ'' is 1.5 in the Ψ(MOCI) of eq 39 when R = 2 au for example. The resulting energy is −4.909 86 au; each of the six bonding configurations that are linearly combined in eq 39 makes a non-negligible contribution.

At R = 1.65 au, and with ζ' = 1.0, eq 36 for the $^2\Sigma_u^+$ wave function for H_2^- is energy-optimized when ζ'' = 0.74. The energy is −0.827 81 au. When $R = \infty$, the energy is −0.846 45 for ζ' = 1.0 and ζ'' = 0.74.

An earlier VB study[43] of H_2^-, which suggested that the ground state for this anion has $^2\Sigma_g^+$ symmetry, has been shown to be fallacious.[39,44] The reason for this is that optimization of the exponent for the midbond AO which accommodates the third electron of the configuration designated as Ψ(H_2,e) in ref 43 leads to ionization of the anion to form H_2.

Calculations for H_2^- with 1s AO for H, and 1s and 2pσ AOs for H^-

In Table 2, the results of some VB calculations for H_2^-, with 2pσ AOs included for the H^-, are also reported. The 2p AO exponent for the $(1s)^1(2p)^1$ configuration of H^- has an energy-optimized value of zero. An estimate of 0.304 297 for the 2p AO exponent was calculated for the closed-shell $(2p)^2$ configuration from the energy minimization of $\xi^2 - \xi + 0.391406\xi$. The four additional Lewis structures that have been included in the VB calculations (Table 2) arise when the a′ or b′ electron of each of the (a′a‴)b_0 and (b′b‴)a_0 configurations (a‴ = $2p_A$, b‴ = $2p_B$, with $\langle 2p_A|2p_B\rangle > 0$) is delocalized into either the $\psi'_{a'b_0} = a' + K'b_0$ MO or the $\psi'_{b'a_0} = b' + K'a_0$ MO. (Delocalization of the a‴ = 2p electron generates no additional Lewis structures). The resulting wave function is given by eqs 40 and 41,

$$\Psi_I(a',a''',b',b''') = \Psi_I(a'''b_0\psi'_{a'b_0}) + \Psi_I(a'b_0\psi_{a'''b_0}) - \Psi_I(b'''a_0\psi'_{b'a_0}) - \Psi_I(b'a_0\psi_{b'''a_0}) \quad (40)$$

$$= 3\{|a'''^{\alpha}b_0^{\alpha}a'^{\beta}| + |a'^{\alpha}b_0^{\alpha}a'''^{\beta}| - |b'''^{\alpha}a_0^{\alpha}b'^{\beta}| - |b'^{\alpha}a_0^{\alpha}b'''^{\beta}| + K'(|a'''^{\alpha}b_0^{\alpha}b_0^{\beta}| + |b'''^{\alpha}a_0^{\alpha}a_0^{\beta}|) + K'''(|a'^{\alpha}b_0^{\alpha}b_0^{\beta}| - |b'^{\alpha}a_0^{\alpha}a_0^{\beta}|)\} \quad (41)$$

and interacts with the $\Psi_I(a',a'',b',b'')$ of eq 26 to give the CI wave function of eq 42.

$$\Psi_I(CI) = \Psi_I(a',a'',b',b'') + \rho\Psi_I(a',a'',b',b''') \quad (42)$$

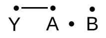
$$= C_1[\psi_1\{(a'a'')b_0\} - \psi_1\{(b'b'')a_0\}] + C_2[\psi_2\{a'(b_0b_0)\} - \psi_2\{b'(a_0a_0)\}] + C_3[\psi_3\{a''(b_0b_0)\} - \psi_3\{b''(a_0a_0)\}] \quad (43)$$

$$C_4[\psi_4\{(a'a''')b_0\} - \psi_4\{(b'b''')a_0\}] + C_5[\psi_5\{a'''(b_0b_0)\} - \psi_5\{b'''(a_0a_0)\}]$$

A minimum energy of −1.019 630 au for eq 41 occurs for R_e = 4.95 au. The resulting values for the polarity parameters and CI coefficient ρ are k' = 0.0253, k'' = 0.0855, ρ = 0.1528, and K' = 0.3349 when $K''' = k''$.

Increased-Valence Structures

On many occasions,[12,14−25,33,34,41,42] increased-valence structures of the type 12 have been obtained by spin-pairing the



(12)

antibonding electron of the AB three-electron bond configuration $|\psi_{ab}^{\alpha}\psi_{ab}^{\beta}\psi^*{}_{ab}^{\alpha}|$ with the unpaired electron of a Y atom, when the latter electron occupies an AO (y) that overlaps with ψ^*_{ab}. The resulting $S = 0$ spin wave function is given by eq 44.

$$\psi(\overset{\bullet\!\!-\!\!-\!\!-\!\!\bullet}{\text{Y}\quad\text{A}}\cdot\dot{\text{B}}) = |\psi_{ab}^{\alpha}\psi_{ab}^{\beta}\psi^*{}_{ab}^{\alpha}y^{\beta}| - |\psi_{ab}^{\alpha}\psi_{ab}^{\beta}\psi^*{}_{ab}^{\beta}y^{\alpha}| \quad (44)$$

$$= -(1 + kk^*)(|a^{\alpha}\psi_{ab}^{\beta}b^{\alpha}y^{\beta}| - |\psi_{ab}^{\alpha}a^{\beta}b^{\beta}y^{\alpha}|) \quad (45)$$

To obtain a double-ζ formulation for eq 45, it is necessary to replace the three-electron bond components of the Slater determinants in eq 45 by the three-electron bond formulation of eq 28. Eight rather than two Slater determinants will then contribute to Ψ_{12}, each of which may be expressed in terms of either VB or MO configurations.

Conclusions

The establishment of equivalences between the VB and MO descriptions of the three-electron bond when more than two AOs are used to accommodate the electrons has required the inclusion in the VB resonance scheme of additional AO configurations for VB structures of types 2 and 3. Use of either of these equivalent formulations for the three-electron bond configuration of H_2^- does not lead to ionization of the third electron of this anion at normal internuclear separations. In contrast, this ionization occurs when canonical MOs are used to accommodate the electrons, and the orbital exponent for the antibonding electron is energy-optimized.

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