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Four-Electron Three-Center Bonding: One-Electron and Concerted Two-Electron Delocalizations into Bonding and Antibonding Molecular Orbitals

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For a four-electron three-center bonding unit that arises from the interaction between an atomic electron donor $\ddot{\mathrm{Y}}$ and a diatomic electron acceptor A:B, it is deduced that some concerted delocalization of the two lone-pair electrons of $\ddot{\mathrm{Y}}$ into the antibonding molecular orbital of A:B is equivalent to the concerted delocalization of these electrons into a Y−A bonding molecular orbital. For neutral intermolecular electron donors and acceptors that involve a four-electron three-center bonding unit, second-order perturbation theory is used to deduce a condition for which concerted delocalization of the two $\ddot{\mathrm{Y}}$ electrons into the Y−A bonding molecular orbital may generate a higher energy than does a one-electron delocalization into this molecular orbital. The theory is illustrated via the results of STO-6G valence-bond studies for the hydrogen-bonding interactions that arise for an idealized HF dimer.

Introduction

With a minimal basis set, a four-electron three-center bonding unit involves four electrons distributed among three overlapping atomic orbitals (AOs),[1−4] designated as y, a, and b, which are located around three atomic centers, designated as Y, A, and B. One type of Lewis valence-bond (VB) representation for this type of bonding unit involves resonance between the Lewis structures **1** and **2**, each of which has an electron-pair bond and a lone pair of electrons. When the wavefunction for the electron-pair bond of either of these structures is formulated in terms of a doubly-occupied two-center bonding molecular orbital (MO), the localized MO (LMO) structural wavefunctions for these VB structures are then given by eqs 1 and 2, respectively, in which

1

2

$$\psi_{\mathbf{1}} = |\mathrm{y}^{\alpha}\mathrm{y}^{\beta}\psi_{\mathrm{ab}}{}^{\alpha}\psi_{\mathrm{ab}}{}^{\beta}| \tag{1}$$

$$\psi_{\mathbf{2}} = |\mathrm{b}^{\alpha}\mathrm{b}^{\beta}\psi_{\mathrm{ay}}{}^{\alpha}\psi_{\mathrm{ay}}{}^{\beta}| \tag{2}$$

α and β are the $m_s = +{}^1/_2$ and $m_s = -{}^1/_2$ spin wavefunctions, $\psi_{\mathrm{ab}} = \mathrm{a} + k\mathrm{b}$ and $\psi_{\mathrm{ay}} = \mathrm{a} + \kappa\mathrm{y}$ are A−B and Y−A bonding MOs, and k and κ are variationally-controlled polarity parameters.

When intra- and intermolecular donor−acceptor interactions (with designations such as n-type electron-donor sacrificial aσ^* electron-acceptor[5] and secondary interactions,[6] the anomeric effect,[7] and negative hyperconjugation[8]) are considered, one form of approximate MO theory that is often used to describe the three-center bonding involves some delocalization of the lone pair of electrons on a donor atom into a vacant diatomic antibonding MO of an acceptor molecule.[9,10] For example for structure **1**, the relevant antibonding MO is $\psi^*_{\mathrm{ab}} = k^*\mathrm{a} - \mathrm{b}$, with $k^* = (k + S_{\mathrm{ab}})/(1 + kS_{\mathrm{ab}})$ and $S_{\mathrm{ab}} \equiv \langle \mathrm{a}|\mathrm{b}\rangle$, in order that ψ^*_{ab} and ψ_{ab} be orthogonal. Focusing attention on this structure, some delocalization of the y electrons into ψ^*_{ab} gives the MO configuration of eqs 3−5, in which λ determines variationally

$$\begin{aligned}\Psi_{\mathbf{1}}(\mathrm{MO}) &= |(\mathrm{y} + \lambda\psi^*_{\mathrm{ab}})^{\alpha}(\mathrm{y} + \lambda\psi^*_{\mathrm{ab}})^{\beta}\psi_{\mathrm{ab}}{}^{\alpha}\psi_{\mathrm{ab}}{}^{\beta}| && (3)\\ &\equiv |\mathrm{y}^{\alpha}\mathrm{y}^{\beta}\psi_{\mathrm{ab}}{}^{\alpha}\psi_{\mathrm{ab}}{}^{\beta}| + \lambda\{|\mathrm{y}^{\alpha}\psi^*_{\mathrm{ab}}{}^{\beta}\psi_{\mathrm{ab}}{}^{\alpha}\psi_{\mathrm{ab}}{}^{\beta}| + \\ &\quad |\psi^*_{\mathrm{ab}}{}^{\alpha}\mathrm{y}^{\beta}\psi_{\mathrm{ab}}{}^{\alpha}\psi_{\mathrm{ab}}{}^{\beta}|\} + \lambda^2|\psi^*_{\mathrm{ab}}{}^{\alpha}\psi^*_{\mathrm{ab}}{}^{\beta}\psi_{\mathrm{ab}}{}^{\alpha}\psi_{\mathrm{ab}}{}^{\beta}| && (4)\\ &\equiv \psi_{\mathrm{I}} + \lambda\psi_{\mathrm{II}} + \lambda^2\psi_{\mathrm{III}} && (5)\end{aligned}$$

the extent of delocalization and $\psi_{\mathrm{I}} \equiv \psi_{\mathbf{1}}$. The purpose of this paper is to demonstrate that (i) some delocalization of the y electrons of structure **1** into the antibonding MO ψ^*_{ab} according to eq 3 is equivalent to delocalization of these electrons into the Y−A *bonding* MO $\psi_{\mathrm{ya}} = \mathrm{y} + l\mathrm{a}$, as indicated in **3** → **4**,

3 **4**

and (ii) delocalization of one y electron of structure **1** into the Y−A bonding MO $\psi_{\mathrm{ya}} = y + la$, as in **5** → **6**, may generate a lower energy than does the concerted two-electron delocalization

5 **6**

of **3** → **4**. The theory will be illustrated via an STO-6G VB study of model hydrogen-bonding interactions between two HF molecules. (By concerted it is meant that the two electrons occupy the same orbital at any stage along the reaction cooordinate.)

Delocalization of Donor Electrons into Bonding and Antibonding LMOs

The wavefunction for structure **4** is given by eqs 6 and 7.

When the identities $|\psi^*_{\mathrm{ab}}{}^{\alpha}\psi_{\mathrm{ab}}{}^{\alpha}| = (kk^* + 1)|\mathrm{a}^{\alpha}\mathrm{b}^{\alpha}|$ and $|\psi^*_{\mathrm{ab}}{}^{\beta}\psi_{\mathrm{ab}}{}^{\beta}| = (kk^* + 1)|\mathrm{a}^{\beta}\mathrm{b}^{\beta}|$ are introduced into eq 4, we obtain eq 8 which corresponds to eq 9, where $\psi_{\mathbf{7}}$ and $\psi_{\mathbf{8}}$ are the

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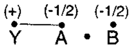
$$\psi_{\mathbf{4}} = |\psi_{ya}{}^{\alpha}\psi_{ya}{}^{\beta}\psi_{ab}{}^{\alpha}\psi_{ab}{}^{\beta}| \tag{6}$$

$$\equiv |y^{\alpha}y^{\beta}\psi_{ab}{}^{\alpha}\psi_{ab}{}^{\beta}| + l\{|y^{\alpha}a^{\beta}\psi_{ab}{}^{\alpha}\psi_{ab}{}^{\beta}| + |a^{\alpha}y^{\beta}\psi_{ab}{}^{\alpha}\psi_{ab}{}^{\beta}|\} + l^2|a^{\alpha}a^{\beta}\psi_{ab}{}^{\alpha}\psi_{ab}{}^{\beta}| \tag{7}$$

$$\Psi_{\mathbf{1}}(\mathrm{MO}) = |y^{\alpha}y^{\beta}\psi_{ab}{}^{\alpha}\psi_{ab}{}^{\beta}| + (kk^* + 1)\lambda\{|y^{\alpha}a^{\beta}\psi_{ab}{}^{\alpha}b^{\beta}| + |a^{\alpha}y^{\beta}b^{\alpha}\psi_{ab}{}^{\beta}|\} + (kk^* + 1)^2\lambda^2 l a^{\alpha}a^{\beta}b^{\alpha}b^{\beta}| \tag{8}$$

$$\equiv \psi_{\mathbf{1}} + (kk^* + 1)\lambda\psi_{\mathbf{7}} + (kk^* + 1)^2\lambda^2\psi_{\mathbf{8}} \tag{9}$$

wavefunctions for VB structures **7** and **8** respectively. Structure



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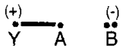
8

7, with a Heitler−London type wavefunction ($|y^{\alpha}\psi^*{}_{ab}{}^{\beta}| + |\psi^*{}_{ab}{}^{\alpha}y^{\beta}| \equiv k^*(|y^{\alpha}a^{\beta}| + |a^{\alpha}y^{\beta}|) - (|y^{\alpha}b^{\beta}| + |b^{\alpha}y^{\beta}|)$ for the (fractional) Y−A and Y−B bonds, is an example of a Heitler−London increased-valence structure.[2,3] This type of VB structure, with a Pauling "three-electron bond"[2,3,11] as a diatomic component, is equivalent to resonance between the canonical Lewis structures **9** and **10**,



9

10

in which the y and a AOs and the y and b AOs are used respectively to accommodate the electrons that form the Y−A and Y−B electron-pair bonds. Structure **10**, involves a "long" or formal Y−B bond and is an example of a singlet-diradical or Dewar-type canonical Lewis structure.[2,3] The properties of these types of VB structures have been described extensively in refs 2 and 3 and are not needed here.

When the identities $|a^{\alpha}\psi_{ab}{}^{\alpha}| = k|a^{\alpha}b^{\alpha}|$ and $|a^{\beta}\psi_{ab}{}^{\beta}| = k|a^{\beta}b^{\beta}|$ are introduced into eq 7, we obtain eq 10.

$$\psi_{\mathbf{4}} = \psi_{\mathbf{1}} + kl\psi_{\mathbf{7}} + k^2l^2\psi_{\mathbf{8}} \tag{10}$$

The $\Psi_{\mathbf{1}}$(MO) and $\psi_{\mathbf{4}}$ of eqs 9 and 10 are equivalent when $\lambda = kl/(kk^* + 1)$. When this equivalence occurs, the identity is established that some delocalization of the Y electrons into the antibonding A−B MO of VB structure **1** is equivalent to delocalization of the Y electrons into the bonding Y−A MO.

VB structures **7** and **8** arise from the delocalization of either one or two Y electrons of structure **1** into the antibonding A−B MO. As indicated in the Introduction, when one Y-electron of structure **1** is delocalized into the Y−A bonding MO $\psi_{ya} = y + la$, VB structure **6** is obtained. Its $S = 0$ spin wavefunction is given by eq 11, which is equivalent to the linear combinations

$$\psi_{\mathbf{6}} = |y^{\alpha}\psi_{ya}{}^{\beta}\psi_{ab}{}^{\alpha}\psi_{ab}{}^{\beta}| + |\psi_{ya}{}^{\alpha}y^{\beta}\psi_{ab}{}^{\alpha}\psi_{ab}{}^{\beta}| \tag{11}$$

$$= |y^{\alpha}y^{\beta}\psi_{ab}{}^{\alpha}\psi_{ab}{}^{\beta}| + kl\{|y^{\alpha}a^{\beta}\psi_{ab}{}^{\alpha}b^{\beta}| + |a^{\alpha}y^{\beta}b^{\alpha}\psi_{ab}{}^{\beta}|\} \tag{12}$$

$$\equiv \psi_{\mathbf{1}} + kl\psi_{\mathbf{7}} \equiv \psi_{\mathrm{I}} + \{kl/(kk^* + 1)\}\psi_{\mathrm{II}} \tag{13}$$

of eqs 12 and 13. When the Wiberg-type[12] definition of atomic valence is used, it has been demonstrated[2d,3k] that the valence of A cannot exceed unity in VB structure **4**, but it may have a maximum value of 1.21 in VB structure **6**. For this reason, and others, VB structure **6** is an example of a LMO increased-valence structure.

One-Electron Delocalizations vs Concerted Two-Electron Delocalizations

In the subsequent treatment, we will use normalized forms ($\Psi_{\mathrm{I}} = N_{\mathrm{I}}\psi_{\mathrm{I}}$, $\Psi_{\mathrm{II}} = N_{\mathrm{II}}\psi_{\mathrm{II}}$ and $\Psi_{\mathrm{III}} = N_{\mathrm{III}}\psi_{\mathrm{III}}$) of the ψ_{I}, ψ_{II}, and ψ_{III} of eqs 5 and 13. Expressions for the normalizing constants N_{I}, N_{II}, and N_{III} are provided in the Appendix. Equations 5 and 13 may then be written as

$$\psi_{\mathbf{4}} = \Psi_{\mathrm{I}} + \mu\Psi_{\mathrm{II}} + \rho\mu^2\Psi_{\mathrm{III}} \tag{14}$$

$$\equiv \Psi_{\mathrm{I}} + (\mu/N)N(\Psi_{\mathrm{II}} + \rho\mu\Psi_{\mathrm{III}}) \tag{15}$$

$$\psi_{\mathbf{6}} = \Psi_{\mathrm{I}} + \nu\Psi_{\mathrm{II}} \tag{16}$$

in which $\mu = (N_1/N_7)kl/(kk^* + 1) = (N_{\mathrm{I}}/N_{\mathrm{II}})\lambda$, $\rho = N_{\mathrm{II}}{}^2/(N_{\mathrm{I}}N_{\mathrm{III}})$, and $N_{\mathbf{1}}$, $N_{\mathbf{7}}$, and N ($\equiv 1/\sqrt{(1 + \rho\mu S_{\mathrm{II,III}} + \rho^2\mu^2)}$) are the normalizing constants for $\psi_{\mathbf{1}}$, $\psi_{\mathbf{7}}$, and $\Psi_{\mathrm{II}} + \rho\mu\Psi_{\mathrm{III}}$, respectively.

For the same value of the polarity parameter k for the A−B σ bond in each of the VB structures, we now give consideration to the second-order perturbation[13] estimates of the energies for structures **4** and **6** relative to structure **1**. These energies are given by eqs 17 and 18, respectively, in which $T_{\mathrm{I,II}} = H_{\mathrm{I,II}} - S_{\mathrm{I,II}}E_{\mathrm{I}}$, $A_{\mathrm{I,II}} = E_{\mathrm{II}} - E_{\mathrm{I}}$, and $S_{\mathrm{I,II}} = \langle\Psi_{\mathrm{I}}|\Psi_{\mathrm{II}}\rangle$, etc.

$$\Delta E_{\mathbf{4}} \approx -(T_{\mathrm{I,II}} + \rho\mu T_{\mathrm{I,III}})^2/(A_{\mathrm{I,II}} + 2\rho\mu T_{\mathrm{II,III}} + \rho^2\mu^2 A_{\mathrm{I,III}}) \tag{17}$$

$$\Delta E_{\mathbf{6}} \approx -T_{\mathrm{I,II}}{}^2/A_{\mathrm{I,II}} \tag{18}$$

It may be deduced that each of $S_{\mathrm{I,II}}$, $S_{\mathrm{II,III}}$, $T_{\mathrm{I,II}}$, and $T_{\mathrm{II,III}}$ is primarily $\sqrt{2}S_{y\psi^*}$ dependent, whereas $S_{\mathrm{I,III}}$ and $T_{\mathrm{I,III}}$ are primarily $S_{y\psi^*}{}^2$ dependent. Therefore $S_{\mathrm{I,III}} \ll S_{\mathrm{I,II}}$ and $|T_{\mathrm{I,III}}| \ll |T_{\mathrm{I,II}}|$. Consequently, $S_{\mathrm{I,III}}$ and $T_{\mathrm{I,III}}$ will be omitted from the subsequent development, and the results of the calculations described below show that inclusion of these terms has only a small effect on the energy of structure **4**. When this is done, $\Delta E_{\mathbf{4}}$ is given by eq 19, for which the corresponding first-order estimate of μ is

$$\Delta E_{\mathbf{4}} \approx -(T_{\mathrm{I,II}})^2/(A_{\mathrm{I,II}} + 2\rho\mu T_{\mathrm{II,III}} + \rho^2\mu^2 A_{\mathrm{I,III}}) \tag{19}$$

given by eq 20. According to their definitions, each of ρ and μ must have a value that is greater than zero. For neutral donor

$$\mu \approx -T_{\mathrm{I,II}}/(A_{\mathrm{I,II}} + 2\rho\mu T_{\mathrm{II,III}} + \rho^2\mu^2 A_{\mathrm{I,III}}) \tag{20}$$

and acceptor molecules, $A_{\mathrm{I,III}} > A_{\mathrm{I,II}} > 0$. By comparison of eq 19 with eq 18, it is seen that $E_{\mathbf{4}} > E_{\mathbf{6}}$ when the requirement of eq 21 is satisfied. The results of calculations described below

$$A_{\mathrm{I,III}} > -2T_{\mathrm{II,III}}/\rho\mu \tag{21}$$

for the HF dimer give values for $T_{\mathrm{I,II}}$ and $T_{\mathrm{II,III}}$ that are respectively negative and positive in sign. When $T_{\mathrm{I,II}} < 0$ and $T_{\mathrm{II,III}} > 0$, eq 21 indicates that the energy of structure **4** will always lie above the energy for structure **6**; i.e., the one-electron delocalization process of **5** → **6** will always generate a lower energy than the concerted two-electron delocalization of **3** → **4**.

Should $T_{\mathrm{I,II}}$ and $T_{\mathrm{II,III}}$ both have the same sign (negative), then it would be less easy to deduce the nature of the primary

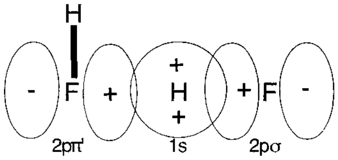
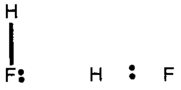


Figure 1. AOs for HF...HF four-electron 3-center bonding unit.

condition that is needed in order for eq 21 to be satisfied, and therefore attention will not be given to this situation here.

Illustrative Calculations: Donor−Acceptor Interactions between Two HF Molecules

To illustrate aspects of the theory, we report the results of some STO-6G VB calculations for the (gas-phase) interaction between two HF molecules when they are oriented as indicated in Figure 1. Roso's ab-initio VB program[3o,14] was used to perform the calculations. The y, a, and b AOs for the primary four-electron three-center bonding unit are respectively a fluorine lone-pair 2pπ' AO of the donor HF molecule and the hydrogen 1s and fluorine 2pσ AO of the acceptor HF molecule. These AOs are displayed in Figure 1. The a and b AOs are used to form the A−B bonding MO $\psi_{ab} = a + kb$. The VB structures **11**−**13** correspond to VB structures **1**, **7**, and **8**, respectively,



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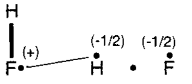

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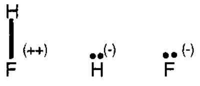


13

with wavefunctions given by eqs 22−24. In these wavefunc-

$$\Psi_{11} = |\mathrm{Core}\ y^{\alpha} y^{\beta} \psi_{ab}{}^{\alpha} \psi_{ab}{}^{\beta}| \tag{22}$$

$$\Psi_{12} = (|\mathrm{Core}\ y^{\alpha} \psi^*{}_{ab}{}^{\beta} \psi_{ab}{}^{\alpha} \psi_{ab}{}^{\beta}| + |\mathrm{Core}\ \psi^*{}_{ab}{}^{\alpha} y^{\beta} \psi_{ab}{}^{\alpha} \psi_{ab}{}^{\beta}|)/(kk^* + 1) \tag{23}$$

$$\Psi_{13} = |\mathrm{Core}\ \psi^*{}_{ab}{}^{\alpha} \psi^*{}_{ab}{}^{\beta} \psi_{ab}{}^{\alpha} \psi_{ab}{}^{\beta}|/(kk^* + 1)^2 \tag{24}$$

tions, the core configuration is given by eq 25. The bond lengths for each HF monomer were fixed at 0.92 Å, Slater orbital

$$\mathrm{Core} = \{(1s_F)^2(2s_F)^2(1s_H + k'2p\sigma_F)^2(2p\pi_F)^2\}_{\mathrm{Donor}}\{(1s_F)^2(2s_F)^2(2p\pi_F)^2(2p\pi'_F)^2\}_{\mathrm{Acceptor}} \tag{25}$$

exponents for $F^{-0.5}$ were used together with a H-atom exponent of 1.2. A value of 1.29 was determined variationally for the H−F polarity parameter, $k = k'$, for a free monomer. Calculations for the dimer were then performed by varying the intermolecular F-H bond distance r(F...H), with both k and k' assigned the monomer value of 1.29. Better energies will be obtained by allowing for independent variation of k and k' with distance, but the energies reported for $k = k' = 1.29$ are good enough to illustrate those aspects of delocalization theory with which we are concerned.

TABLE 1: Variational Energies (au) for 1 ↔ 7 ↔ 8, 1 ↔ 7, and 1

r(F...H)/Å	**1 ↔ 7 ↔ 8**	**1 ↔ 7**	**1**
1.4	−198.968 708	−198.968 694	−198.937 499
1.6	−198.976 779	−198.976 776	−198.957 329
1.8	−198.977 776	−198.977 775	−198.966 835
2.0	−198.976 812	−198.976 812	−198.971 073
∞	−198.973 392	−198.973 392	−198.973 392

The Amovilli−McWeeny VB study[15] of the HF dimer uses better AO basis sets, and a larger number of canonical Lewis VB structures. For their study, the primary minimum energy occurs when ⟨FHF = 168°, ⟨HFF = 116° and r(F...F) = 2.76 Å. For the present calculations, the two angles have been idealized to 180° and 90°, respectively, in order that nonhybrid AOs may be used to simplify slightly the calculations. It should be stressed that the purpose of the present study is to use the HF dimer to make comparisons between one-electron and two-electron delocalization processes, *not* to examine quantitatively the nature of the hydrogen-bonding interactions.

Energies for several values of r(F...H) are reported in Table 1. For these distances, the minimum energy occurs when r(F...H) = 1.80 Å, to give r(F...F) = 2.72 Å. Corrections for possible basis set superposition errors have not been included. The associated dissociation energy (D_e) for the F...H hydrogen bond is 11.5 kJ mol^{-1}. These results are in qualitative accord with the estimates of 2.76 Å and 20.2 kJ mol^{-1} for r(F...F) and D_e provided in ref 15. The matrix elements for r(F...H) = 1.8 Å (Table 2) are used for the subsequent discussion.

The energies reported in Table 3 for r(F...H) = 1.8 Å show that the lowest-energy linear combination of Ψ_I and Ψ_{II} (to give the ψ_6 of eq 16 is almost identical to the best linear combination of Ψ_I, Ψ_{II}, and Ψ_{III} and that the $\psi_4 \equiv \Psi_1$(MO) of eq 15 lies above the ψ_6 of eq 16. The latter result is obtained from either the accurate calculations or the approximate calculations via eqs 17−19. It is also seen that the $S_{I,III}$ and $T_{I,III}$ matrix elements have small magnitudes and that their omission from eq 17 has only a small effect on the value of ΔE_4. Estimates for $E_4 - E_6$ are 0.32 kJ mol^{-1} (no approximations), 0.35 kJ mol^{-1} (eqs 17 and 18) and 0.68 kJ mol^{-1} (eqs 18 and 19).

It may be noted that the Amovilli−McWeeny study excludes the F−F "long-bond" Lewis structure of type **10**, which contributes to the VB scheme considered here through the inclusion of $\psi_7 = k\psi_9 + \psi_{10}$. (The type **9** Lewis structure is included in the Amovilli−McWeeny study.) To demonstrate the effect of excluding structure **10** in the present study, we have set ψ_7 equal to ψ_9 in the calculations for r(F...H) = 1.80 Å. The resulting dissociation energy is reduced from 11.5 to 0.3 kJ mol^{-1}. However if we set ψ_7 equal to ψ_{10}, a negative dissociation energy of −2.7 kJ mol^{-1} is obtained.

In ref 15, the charge transfer contribution to the dissociation energy of 20.2 kJ mol^{-1} is 3.6 kJ mol^{-1}. Inspection of Table 1 shows that, for the present type of calculation, charge transfer (via the inclusion of structure **7** in particular) is solely responsible for the stabilization of the dimer relative to the HF monomers as dissociation products.

More Complete Descriptions of Four-Electron Three-Center Bonding Units

A more complete MO description of the four-electron three-center bonding is obtained via linearly combining Ψ_1(MO) of

TABLE 2: Hamiltonian (au), Overlap, and $T_{i,j} = H_{i,j} - S_{i,j}E_I$ (au) Matrix Elements for r(F...H) = 1.80 Å ($A_{I,II} = H_{II,II} - H_{I,I}$, etc.)

$H_{I,I}$	−229.637 819	$S_{I,I} = S_{II,II} = S_{III,III} = 1.0$	$A_{I,II} = 0.812\ 205\ 078$
$H_{I,II}$	−31.521 806 67	$S_{I,II} = S_{II,III}$ 0.136 847 36	$A_{I,III} = 2.780\ 872\ 859$
$H_{I,III}$	−2.180 112 483	$S_{I,III} = 0.009\ 452\ 158$	$T_{I,II} = -0.096\ 390\ 933$
$H_{II,II}$	−228.825 613 9	$S_{y\psi} = 0.055\ 025\ 06$	$T_{II,III} = +0.084\ 109\ 367$
$H_{II,III}$	−31.335 716 61	$S_{y\psi*} = 0.081\ 939\ 02$	$T_{I,III} = -0.009\ 539\ 473$
$H_{III,III}$	−226.857 446 1	$S_{ab} = 0.344\ 187\ 38$	$E_{nuclear} = +30.670\ 983\ 7$

TABLE 3: Energies (au) for Structures 1, 4, and 6 at r(F...H) = 1.80 Å

	no approximations	2nd-order perturbation
$E_{\mathbf{I}}$	−198.966 835	−198.966 835
$E_{\mathbf{6}}$	−198.977 775 ($\nu = 0.1153$)	−198.978 274 ($\nu = 0.1187^{c}$)
$E_{\mathbf{4}} = E_1$(MO)	−198.977 654 ($\mu = 0.1122$)	−198.978 015[a] ($\mu = 0.1160^{d}$)
$E_{\mathbf{4}} = E_1$(MO)		−198.978 141[b] ($\mu = 0.1166^{e}$)

[a] $T_{I,III}$ omitted. [b] $T_{I,III}$ included. [c] $\nu = -T_{I,II}/A_{I,II}$. [d] From eq 20 via Newton's method. [e] As for footnote d, but with $T_{I,II}$ replaced by $T_{I,II} + \rho\mu T_{I,III}$.

eq 3 with the Ψ_2(MO) of eq 26 in which $\psi_{ay} = a + \kappa y$ and

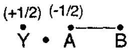
$$\Psi_2(\mathrm{MO}) = |(b + \lambda'\psi^*_{ay})^{\alpha}(b + \lambda'\psi^*_{ay})^{\beta}\psi_{ay}{}^{\alpha}\psi_{ay}{}^{\beta}| \qquad (26)$$

$$\equiv |b^{\alpha}b^{\beta}\psi_{ay}{}^{\alpha}\psi_{ay}{}^{\beta}| + \lambda'\{|b^{\alpha}\psi^*_{ay}{}^{\beta}\psi_{ay}{}^{\alpha}\psi_{ay}{}^{\beta}| + |\psi^*_{ay}{}^{\alpha}b^{\beta}\psi_{ay}{}^{\alpha}\psi_{ay}{}^{\beta}|\} + \lambda'^2|\psi^*_{ay}{}^{\alpha}\psi^*_{ay}{}^{\beta}\psi_{ay}{}^{\alpha}\psi_{ay}{}^{\beta}| \qquad (27)$$

$$= |b^{\alpha}b^{\beta}\psi_{ay}{}^{\alpha}\psi_{ay}{}^{\beta}| + (\kappa\kappa^* + 1)\lambda'\{|b^{\alpha}a^{\beta}\psi_{ay}{}^{\alpha}y^{\beta}| + |a^{\alpha}b^{\beta}y^{\alpha}\psi_{ay}{}^{\beta}|\} + (\kappa\kappa^* + 1)^2\lambda'^2|a^{\alpha}a^{\beta}y^{\alpha}y^{\beta}| \qquad (28)$$

$$\equiv \psi_{\mathbf{2}} + (\kappa\kappa^* + 1)\lambda'\psi_{\mathbf{14}} + (\kappa\kappa^* + 1)^2\lambda'^2\psi_{\mathbf{15}} \qquad (29)$$

$\psi^*_{ay} = \kappa^*a - y$.



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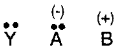

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When $\lambda' = \kappa\gamma/(\kappa\kappa^* + 1)$, Ψ_2(MO) is equivalent to the wavefunction $\psi_{\mathbf{16}}$ of eq 30 for VB structure **16**, with $\psi_{ba} = b + \gamma a$.

$$\psi_{\mathbf{16}} = |\psi_{ba}{}^{\alpha}\psi_{ba}{}^{\beta}\psi_{ay}{}^{\alpha}\psi_{ay}{}^{\beta}| \qquad (30)$$

$$\equiv |b^{\alpha}b^{\beta}\psi_{ay}{}^{\alpha}\psi_{ay}{}^{\beta}| + \gamma\{|b^{\alpha}a^{\beta}\psi_{ay}{}^{\alpha}\psi_{ay}{}^{\beta}| + |a^{\alpha}b^{\beta}\psi_{ay}{}^{\alpha}\psi_{ay}{}^{\beta}|\} + \gamma^2|a^{\alpha}a^{\beta}\psi_{ay}{}^{\alpha}\psi_{ay}{}^{\beta}| \qquad (31)$$

$$\equiv \psi_{\mathbf{2}} + \kappa\gamma\psi_{\mathbf{14}} + \kappa^2\gamma^2\psi_{\mathbf{15}} \qquad (32)$$

$$\psi_{\mathbf{17}} = |b^{\alpha}\psi_{ba}{}^{\beta}\psi_{ay}{}^{\alpha}\psi_{ay}{}^{\beta}| + |\psi_{ba}{}^{\alpha}b^{\beta}\psi_{ay}{}^{\alpha}\psi_{ay}{}^{\beta}| \qquad (33)$$

$$= |b^{\alpha}b^{\beta}\psi_{ay}{}^{\alpha}\psi_{ay}{}^{\beta}| + \kappa\gamma\{|b^{\alpha}a^{\beta}\psi_{ay}{}^{\alpha}y^{\beta}| + |a^{\alpha}b^{\beta}y^{\alpha}\psi_{ay}{}^{\beta}|\} \qquad (34)$$

$$\equiv \psi_{\mathbf{2}} + \kappa\gamma\psi_{\mathbf{14}} \qquad (35)$$

The latter VB structure may be generated from the Lewis structure **2** by delocalizing the B electrons into the B−A bonding MO ψ_{ba}, as indicated.

2 **16**

The increased-valence structure **17** may also be constructed from the Lewis structure **2** via the delocalization of a B electron of the latter structure into the B−A bonding MO ψ_{ba}. The wavefunction for structure **17** is then given by eq 33.

2 **17**

At each stage along the reaction coordinate, the wavefunction for a reacting four-electron three-center bonding unit is given approximately by either eq 36 or 37.

$$\Psi(\mathrm{MO}) = C_1(\mathrm{MO})\Psi_1(\mathrm{MO}) + C_2(\mathrm{MO})\Psi_2(\mathrm{MO}) \equiv C_{\mathbf{4}}\Psi_{\mathbf{4}} + C_{\mathbf{16}}\Psi_{\mathbf{16}} \qquad (36)$$

$$\Psi(\text{increased−valence}) = C_{\mathbf{6}}\Psi_{\mathbf{6}} + C_{\mathbf{17}}\Psi_{\mathbf{17}} \qquad (37)$$

With the y, a, and b AO basis set, "exact" wavefunctions for a four-electron three-center bonding unit are obtained by replacing the (fractional[2,3]) electron-pair bond wavefunctions for $(\psi_{ab})^2$ in structures **4** and **6**, and for $(\psi_{ay})^2$ in structures **16** and **17**, by Coulson−Fischer[16] type wavefunctions for $(\psi'_{ab})^1(\psi''_{ab})^1$ and $(\psi'_{ay})^1(\psi''_{ay})^1$, respectively. Further details for $C_{\mathbf{6}}\Psi_{\mathbf{6}} + C_{\mathbf{17}}\Psi_{\mathbf{17}}$ are provided in refs 2b−e, 3e,g,h,k, and 17 together with its use to show how electron reorganization may occur via one-electron delocalizations for gas-phase S_N2 reactions. The considerations presented here, together with those provided in ref 3k, indicate that the one-electron delocalization representation via $C_{\mathbf{6}}\Psi_{\mathbf{6}} + C_{\mathbf{17}}\Psi_{\mathbf{17}}$ should be preferred to the concerted electron-pair delocalization representation via $C_{\mathbf{4}}\Psi_{\mathbf{4}} + C_{\mathbf{16}}\Psi_{\mathbf{16}}$.

Conclusions

The theory described here suggests that for a four-electron three-center bonding unit that involves an electron donor $\ddot{Y}$ and an electron acceptor A:B, the delocalization of one $\ddot{Y}$-electron into a Y−A bonding MO may generate a lower energy than does either a concerted two-electron delocalization into the bonding Y−A MO or the corresponding concerted two-electron delocalization into the antibonding A−B MO. When this is the case, the primary description of the charge-transfer component of the donor−acceptor interaction involves the formation of a one-electron bond between the donor and the acceptor. The conclusion has relevance for descriptions of both intra- and intermolecular donor−acceptor interactions; examples include the anomeric effect and hydrogen bonding, and the formation of reactant-like and product-like complexes near the commencement and conclusion of gas-phase nucleophilic substitution reactions.[2b−e,3g,h,k,17] Application to the so-called pentavalent nitrogen atom is in progress.[18]

I am indebted to and thank Dr. W. Roso for providing me with his ab initio valence-bond program and Dr. F. L. Skrezenek for installing it.

Appendix: Normalization Constants for ψ_I, ψ_{II}, and ψ_{III}

With $\psi \equiv \psi_{ab} = a + kb$, $\psi^* \equiv \psi^*_{ab} = k^*a - b$, and $k^* = (k + S_{ab})/(1 + kS_{ab})$, it may be deduced that

$$S_{\psi\psi} = k^2 + 2kS_{\mathrm{ab}} + 1,$$
$$S_{\psi^*\psi^*} = (1 - S_{\mathrm{ab}}{}^2)S_{\psi\psi}/(1 + kS_{\mathrm{ab}})^2,$$
$$S_{\mathrm{y}\psi} = S_{\mathrm{ya}} + kS_{\mathrm{yb}}, \qquad S_{\mathrm{y}\psi^*} = k^*S_{\mathrm{ya}} - S_{\mathrm{yb}},$$
$$N_{\mathrm{I}} = 1/(S_{\psi\psi} - S_{\mathrm{y}\psi}{}^2),$$
$$N_{\mathrm{II}}{}^2 = 0.5/\{S_{\psi\psi}(S_{\psi^*\psi^*}{}^2 - S_{\psi^*\psi^*}S_{\mathrm{y}\psi}{}^2 + S_{\psi\psi}S_{\mathrm{y}\psi^*}{}^2)\},$$
$$N_{\mathrm{III}} = 1/(S_{\psi\psi}S_{\psi^*\psi^*})$$

In Table 2, the values for $S_{\mathrm{y}\psi}$ and $S_{\mathrm{y}\psi^*}$ are for normalized ψ and ψ^*.

Note Added in Proof. References listed in the present paper have relevance for some content of three recent publications.

(a) A review titled "Valence Bond Diagrams and Chemical Reactivity" (Shaik, S.; Shurki, A. *Angew. Chem., Int. Ed. Engl.* **1999**, *38*, 586) discusses nucleophilic substitution reactions. In refs 2b−e, 3g,h,k, and 17 here, increased-valence structures of types **6** and **17** are used to provide a VB representation for electronic reorganization needed to convert reactants into products for reactions of this class. The VB symbolism for the Pauling "three-electron bond" used by Shaik and Shurki (and another symbolism used by F. M. Bickelhaupt, A. Diefenbach, S. P. de Visser, and M. M. Nibbering (*J. Phys. Chem. A* **1998**, *102*, 9549)) differs from that used in refs 2a−e, 3a−q, 11, 14a−c, and 17 here.

(b) A theoretical study of electronic structure of CH_2N_2 (Papakondylis, A.; Mavridis, A. *J. Phys. Chem. A* **1999**, *103*, 1255) displays zwitterionic and singlet biradical VB structures. The resonance between these structures is equivalent to the use of increased-valence structures [cf. refs 2a (section 22-4) and 3d,o here; see also ref 3i and Harcourt and Little (*J. Am. Chem. Soc.* **1984**, *106*, 41) for further VB discussion of this molecule. As discussed in refs 2d and 3q here for isoelectronic $N_2O \rightarrow N_2 + O^*$, the presence of singlet biradical character of CH_2N_2 may change the nature of the C−N bond-breaking process from polar to nonpolar; for explicit reference to $CH_2N_2 \rightarrow N_2 + CH_2^*$, see also: Harcourt, R. D. *J. Mol. Struct.* (*Theochem*) **1995**, *342*, 51.

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