

# Wavefunctions for "4-Electron, 3-Centre" Bonding Units

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The simplest type of triatomic electron-excess system is one which involves four electrons distributed amongst three overlapping atomic orbitals on three adjacent atoms. If Y, A and B are the three atoms, and Y and B are symmetrically equivalent atoms, wavefunctions for the following types of

valence formulae are constructed and compared: (i) delocalized molecular orbital  $\overset{\pi}{\text{Y}} \text{---} \text{A} \text{---} \text{B}$ , (ii) standard valence-bond  $\ddot{\text{Y}} \text{---} \text{A} \text{---} \text{B} \leftrightarrow \text{Y} \text{---} \text{A} \text{---} \ddot{\text{B}}$ , (iii) non-paired spatial orbital  $\dot{\text{Y}} \cdot \text{A} \cdot \dot{\text{B}}$ , (iv) increased-valence  $\text{Y} \text{---} \text{A} \cdot \dot{\text{B}} \leftrightarrow \dot{\text{Y}} \cdot \text{A} \text{---} \text{B}$ , and (v)  $\text{Y} \text{---} \text{A} \text{---} \text{B}$  with 2-centre non-orthogonal bond-orbitals, each of which is doubly occupied.

Where appropriate, a different spatial orbital is used for each of the bonding electrons in (ii)-(v). When 2-centre bond-orbitals are used as wavefunctions for both the one-electron bonds and the two-electron bonds of (iv), the resulting "increased-valence" wave-function with three different bond-orbital parameters is equivalent to the complete configuration interaction wave-function.

For (i)-(v), energies are calculated for the four  $\pi$ -electrons of  $\text{HCO}_2^-$ ,  $\text{NO}_2^-$  and  $\text{C}_3\text{H}_3^-$ , and also for the four bonding  $\sigma$ -electrons of  $\text{XeF}_2$ . For each of these systems, the non-paired spatial orbital and increased-valence wave-functions generate low energies. The importance of the "long bond"

canonical structure  $\text{Y} \text{---} \ddot{\text{A}} \text{---} \text{B}$  is discussed.

In valence theory for triatomic systems, it is extremely common to find "4-electron, 3-centre" bonding units. These bonding units (which are examples of "electron-excess" or "hypervalent" bonding units) consist of four electrons distributed amongst three overlapping atomic orbitals, which are centred on three

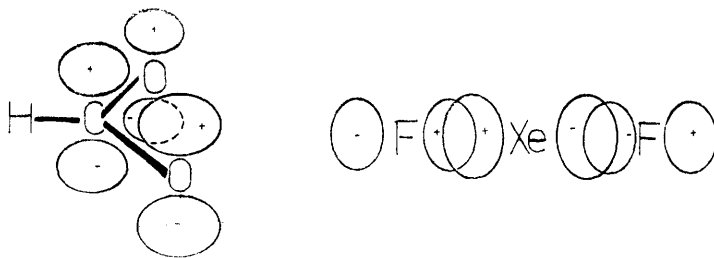


FIG. 1.—Atomic orbitals for 3-centre  $\pi$ - and  $\sigma$ -bonding of  $\text{HCO}_2^-$  and  $\text{XeF}_2$ .

atoms.<sup>1-12, 22</sup> Two familiar examples are four  $\sigma$ -electrons occupying three overlapping  $p\sigma$  atomic orbitals of  $\text{XeF}_2$ , and four  $\pi$ -electrons occupying three overlapping  $p\pi$  atomic orbitals of  $\text{HCO}_2^-$ ; the atomic orbitals are shown in fig. 1. Very often, polyatomic molecules can be partitioned into one or more sets of "4-electron, 3-centre" bonding units.<sup>11</sup> In this paper, we shall compare different types of valence formulae and wavefunctions for symmetrical bonding units of this type.

## TYPES OF WAVEFUNCTIONS AND VALENCE FORMULAE

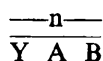
For triatomic "4-electron 3-centre" bonding units, several simple types of valence formulae and wavefunctions may be used to represent the electron distributions. The most familiar of these are

- (i) Delocalized 3-centre molecular orbital (mo) and
- (ii) Standard valence-bond resonance (vb).

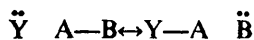
Recently, two other representations have been developed, namely

- (iii) Non-paired spatial orbital<sup>13</sup> (npso) and
- (iv) Increased-valence<sup>11, 22</sup> (iv).

If Y, A and B are the three atoms, and Y and B are symmetrically equivalent atoms, the valence formulae for (i)-(iv) are those of (I), (IIa)→(IIb), (III) and (IVa)→(IVb) respectively. In (I), n is a node for a non-bonding molecular orbital.



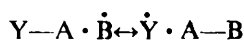
(I)



(IIa) (IIb)



(III)

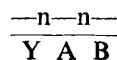


(IVa)

(IVb)



(V)



(VI)

It is also possible to use a valence formula of type (V), with two 2-electron 2-centre bonds. The (non-orthogonal) orbitals for these bonds are called either localized molecular orbitals, or 2-centre bond orbitals. A simple form of the wavefunction for (V) can be shown to be equivalent<sup>6,8,10,11b,11c</sup> to the molecular orbital wavefunction for (I). We shall refer to the wavefunctions for (V) as bond-orbital (bo) wavefunctions.\*

In fig. 2, we have displayed these different types of valence formulae for XeF<sub>2</sub>. Elsewhere,<sup>11a, b</sup> similar formulae have been displayed for HCO<sub>2</sub><sup>-</sup> and O<sub>3</sub>.

The purpose of this paper is to provide some relationships and comparisons which exist between certain wavefunctions for (I)-(V). In some previous papers,<sup>11b, 15-22</sup> comparisons were made using one variational parameter in each of the valence-bond, molecular orbital and non-paired spatial orbital wavefunctions. Here, we shall be concerned primarily with wavefunctions that involve two and sometimes three variational parameters. To illustrate our discussion, we have calculated these wavefunctions and their energies for the four  $\pi$ -electrons of C<sub>3</sub>H<sub>5</sub><sup>-</sup>, NO<sub>2</sub><sup>-</sup> and HCO<sub>2</sub><sup>-</sup> and four  $p\sigma$  electrons of XeF<sub>2</sub>, using Hamiltonian and overlap matrix elements given by other workers. Since completing this work, Duke<sup>23</sup> has reported the results of some two-parameter non-paired spatial orbital studies for C<sub>3</sub>H<sub>5</sub><sup>-</sup> and NO<sub>2</sub><sup>-</sup>. He has used the same matrix elements, but he has examined different properties from those which we report here.

\* In (IV) and (V), it has been deduced<sup>11b</sup> that the YA and AB electron-pair bonds have bond-orders (or bond-numbers) which are less than those for the valence-bond formulae of (II). Therefore we have used thin bond lines to represent these bonds in valence formulae.<sup>11, 22</sup>

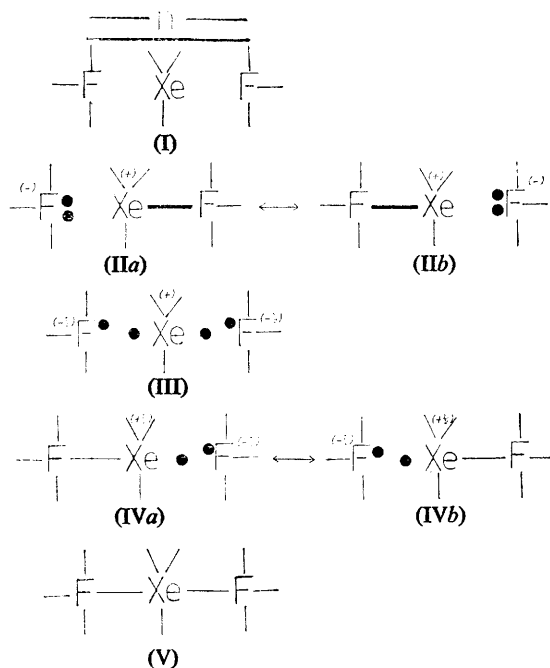


FIG. 2.—Delocalized molecular orbital (I), simple valence-bond (II), non-paired spatial orbital (III), increased-valence (IV) and bond-orbital (V) valence formulae for  $\text{XeF}_2$ . Formal charges for (II)–(IV) are those which pertain if it is assumed that bonding electrons are shared equally by pairs of atoms.

## CONSTRUCTION OF WAVEFUNCTIONS

We shall designate the normalized atomic orbitals centred on atoms Y, A and B as  $y$ ,  $a$  and  $b$ , and we shall assume also that the overlap integrals  $S(y, a)$  and  $S(a, b)$  are each larger than zero in magnitude. In fig. 1, the atomic orbitals are orientated so that this overlap relationship pertains. For the valence structures (I)–(V), we may construct the following wavefunctions from these atomic orbitals.

### (I) DELOCALIZED MOLECULAR ORBITAL

#### (i) SIMPLE MOLECULAR ORBITAL

The YA and AB bonding, non-bonding and antibonding molecular orbitals are given by (1), in which  $k_1$  and  $k_3$  are constants related through (2) by the requirement that  $\phi_1$  and  $\phi_3$  be orthogonal.

$$\phi_1 = y + k_1 a + b, \quad \phi_2 = y - b, \quad \phi_3 = y - k_3 a + b \quad (1)$$

$$2 - k_1 k_3 + 2(k_1 - k_3)S(y, a) + 2S(y, b) = 0. \quad (2)$$

The molecular orbital configuration of lowest energy may be expressed as (3), and this is the simplest wavefunction for the valence formula (I).

$$\Psi_{\text{mo},1}(k_1) = |\phi_1 \bar{\phi}_1 \phi_2 \bar{\phi}_2| \quad (3)$$

$$= 1/\sqrt{4!} \begin{vmatrix} \phi_1(1)\alpha(1) & \phi_1(2)\alpha(2) & \phi_1(3)\alpha(3) & \phi_1(4)\alpha(4) \\ \phi_1(1)\beta(1) & \phi_1(2)\beta(2) & \phi_1(3)\beta(3) & \phi_1(4)\beta(4) \\ \phi_2(1)\alpha(1) & \phi_2(2)\alpha(2) & \phi_2(3)\alpha(3) & \phi_2(4)\alpha(4) \\ \phi_2(1)\beta(1) & \phi_2(2)\beta(2) & \phi_2(3)\beta(3) & \phi_2(4)\beta(4) \end{vmatrix}$$

When  $\phi_1$  and  $\phi_2$  are normalized,  $\Psi_{\text{mo},1}(k_1)$  of (3) is normalized.

## (ii) ALTERNANT MOLECULAR ORBITAL

By using different spatial molecular orbitals for different electron spins, we may obtain a two-parameter molecular orbital wavefunction. To do this, linear combinations of  $\phi_1$  and  $\phi_3$  may be constructed. (The symmetry of  $\phi_2$  prevents it from combining effectively with either  $\phi_1$  or  $\phi_3$ ). The four-electron wave function that results, namely (4), is an alternant molecular orbital (amo) wavefunction.<sup>24</sup> In (4),  $\phi'_1$  and  $\phi''_1$  are molecular orbitals which are given by (5).

$$\Psi_{\text{amo}}(k'_1, k''_1) = |\phi'_1 \bar{\phi}_1 \phi_2 \bar{\phi}_2| + |\phi''_1 \bar{\phi}_1 \phi_2 \bar{\phi}_2| \quad (4)$$

$$\phi'_1 = y + k'_1 a + b, \quad \phi''_1 = y + k''_1 a + b. \quad (5)$$

## (iii) MOLECULAR ORBITAL CONFIGURATION INTERACTION

The doubly excited configurations of (6) and (7) may also be constructed from the molecular orbitals of (1), and configuration interaction (ci) may then be invoked by forming linear combinations of these configurations with  $\Psi_{\text{mo},1}$  of (3). To obtain a two-parameter variational function for comparison with similar variational functions pertaining to valence formulae (II)-(V), we shall restrict our attention here to the linear combination of (8) with variational parameters  $k_1$  and  $\mu$ .  $\Psi_{\text{mo},3}$  of (7) has a higher energy than have  $\Psi_{\text{mo},1}$  and  $\Psi_{\text{mo},2}$  and therefore it should combine less effectively with  $\Psi_{\text{mo},1}$  than does  $\Psi_{\text{mo},2}$ . The molecular orbital valence formula for  $\Psi_{\text{mo},2}$  is (VI), in which the antibonding orbital  $\phi_3$  has generated two nodes. (When the molecular orbitals for  $\Psi_{\text{mo},1}$  are self-consistent, the singlet-spin configuration arising from a  $\phi_1 \rightarrow \phi_3$  excitation will not interact with  $\Psi_{\text{mo},1}$ .)

$$\Psi_{\text{mo},2} = |\phi_1 \bar{\phi}_1 \phi_3 \bar{\phi}_3| \quad (6)$$

$$\Psi_{\text{mo},3} = |\phi_2 \bar{\phi}_2 \phi_3 \bar{\phi}_3| \quad (7)$$

$$\Psi_{\text{ci}}(k_1, \mu) = \Psi_{\text{mo},1} + \mu \Psi_{\text{mo},2}. \quad (8)$$

## (II) STANDARD VALENCE BOND

For the two-electron bonds of the valence-bond formulae of (II), and also for the increased-valence formulae of (IV), we may use either Heitler-London (HL) or two-centre bond-orbital (bo) wavefunctions. In this section, we shall describe the bond-orbital functions. These are also the types of wavefunctions that will be used for the one-electron bonds of (III) and (IV). For the valence-bond formulae (IIa) and (IIb), we shall use different bond-orbitals for different electron spins, namely those of (9) and (10) respectively. The resulting wavefunction for the resonance of (IIa)  $\leftrightarrow$  (IIb) is given by (11). This function has spin quantum numbers  $S$  and  $S_z$  equal to zero, i.e., it represents a singlet spin state.

$$\phi_{\text{R}} = b + la, \quad \phi'_{\text{R}} = b + l'a \quad (9)$$

$$\phi_{\text{L}} = y + la, \quad \phi'_{\text{L}} = y + l'a \quad (10)$$

$$\begin{aligned} \Psi_{\text{vbbo}}(l, l') &= \Psi(\text{IIa}) + \Psi(\text{IIb}) \\ &= |y\bar{y}\phi'_{\text{R}}\bar{\phi}_{\text{R}}| + |y\bar{y}\phi_{\text{R}}\bar{\phi}_{\text{R}}| + |\phi_{\text{L}}\bar{\phi}_{\text{L}}b\bar{b}| + |\phi'_{\text{L}}\bar{\phi}_{\text{L}}b\bar{b}|. \end{aligned} \quad (11)$$

## (III) NON-PAIRED SPATIAL ORBITAL

For the non-paired spatial formula (III), the bond-orbitals for the one-electron bonds are those of (12) and (13).

$$\phi_{\text{L}} = y + la, \quad \phi''_{\text{R}} = b + l''a \quad (12)$$

$$\phi'_{\text{L}} = y + l'a, \quad \phi_{\text{R}} = b + la. \quad (13)$$

Our designation of bond parameters as  $l$  and  $l''$  in (12) and (13) differs from those of (9) and (10). This is because we wish to distinguish those electrons which are simultaneously in different moieties of the molecule, as in (III), from those electrons which are in the same moiety, as in (IIa) or (IIb). The singlet wavefunction for (III) is (14), in which electrons occupying adjacent spatial orbitals have opposed spins. This is the simplest singlet wavefunction but more elaborate functions are possible.<sup>15-20</sup> In our discussions of valence formulae (IV) and (V) below, we shall use the same type of spin function which pertains to (14) when four electrons occupy different spatial orbitals.

$$\Psi_{\text{nps}}(l, l'') = |y\bar{\phi}_L\phi_R''\bar{b}| + |\bar{y}\phi_L\bar{\phi}_R b| + |y\bar{\phi}_L''\phi_R\bar{b}| + |\bar{y}\phi_L''\bar{\phi}_R b|. \quad (14)$$

#### (IV) INCREASED-VALENCE

##### (i) INCREASED-VALENCE BOND-ORBITAL

When non-orthogonal bond-orbitals are used as wavefunctions for both the one-electron bonds and the two-electron bonds of (IV), we require three bond-parameters which we designate as  $l$ ,  $l'$  and  $l''$ . For (IVa) and (IVb), the bond-orbitals are given by (15) and (16) respectively.

$$\phi_L = y + la, \quad \phi'_L = y + l'a, \quad \phi''_R = b + l''a \quad (15)$$

$$\phi''_L = y + l''a, \quad \phi'_R = b + l'a, \quad \phi_R = b + la. \quad (16)$$

We shall also assume that the two electrons occupying  $\phi'_L$  and  $\phi''_R$  of (15) have the same spins, and that the spin of  $\phi_L$  is opposed to those of  $\phi'_L$  and  $\phi''_R$ . Similarly, the spins of  $\phi'_L$  and  $\phi'_R$  of (16) are opposed to that of  $\phi_R$ . The resulting bond-orbital wavefunction for (IV) is given by (17)

$$\Psi_{\text{ivbo}}(l, l', l'') = |\phi'_L\bar{\phi}_L\phi_R''\bar{b}| + |\bar{\phi}'_L\phi_L\bar{\phi}_R b| + |y\bar{\phi}'_L\phi_R\bar{\phi}_R| + |\bar{y}\phi'_L\bar{\phi}_R\phi_R|. \quad (17)$$

##### (ii) INCREASED-VALENCE HEITLER-LONDON

The Heitler-London wavefunction for (IV) has been reported previously,<sup>11b</sup> and it is given by (18), in which the  $\phi_R$  and  $\phi_L$  of (9) and (10) accommodate the single electron of the AB bond of (IVa) and the single electron of the YA bond of (IVb)

$$\Psi_{\text{ivHL}}(l) = |y\bar{a}\phi_R\bar{b}| + |\bar{y}a\bar{\phi}_R b| + |y\bar{\phi}_L a\bar{b}| + |\bar{y}\phi_L \bar{a}b|. \quad (18)$$

#### (V) DOUBLY-OCCUPIED BOND ORBITALS

Valence formula (V) has two two-electron bonds. Using the non-orthogonal bond orbitals  $\phi_L$ ,  $\phi'_L$ ,  $\phi_R$  and  $\phi'_R$  of (9) and (10), we may construct two bond-orbital wavefunctions for (V) which we shall designate as  $\Psi_{\text{bo,A}}(l, l')$  and  $\Psi_{\text{bo,B}}(l, l')$ . These wavefunctions differ in the types of spin distributions that are used. In (19) for  $\Psi_{\text{bo,A}}(l, l')$ , electrons having the same spins have the same bond parameter  $l$  or  $l'$ , whereas in (20) for  $\Psi_{\text{bo,B}}(l, l')$ , electrons with opposed spins in different moieties have the same bond parameter.

$$\Psi_{\text{bo,A}}(l, l') = |\phi_L\bar{\phi}'_L\phi_R\bar{\phi}'_R| + |\bar{\phi}_L\phi'_L\bar{\phi}_R\phi'_R| \quad (19)$$

$$\Psi_{\text{bo,B}}(l, l') = |\phi_L\bar{\phi}'_L\phi'_R\bar{\phi}_R| + |\bar{\phi}_L\phi'_L\bar{\phi}'_R\phi_R|. \quad (20)$$

For (V), a bond-orbital function with four variational parameters may also be constructed, but one of the parameters is redundant.

## EXPANSIONS IN TERMS OF WAVEFUNCTIONS FOR CANONICAL STRUCTURES

In earlier papers,<sup>11b, 15-21</sup> wavefunctions for (I)-(V) have been expressed in terms of canonical structure functions which are given by the  $\psi_i$  of (21)-(24).  $\psi_1$  and  $\psi_2$  are the Heitler-London functions for the valence-bond formulae of (IIa)↔(IIb) and (IIc) respectively;  $\psi_3$  and  $\psi_4$  are wavefunctions for the ionic structures of (IId) and (IIe)↔(IIf).

$$\psi_1 = |y\bar{y}a\bar{b}| + |y\bar{y}b\bar{a}| + |b\bar{b}a\bar{y}| + |b\bar{b}y\bar{a}| \quad (21)$$

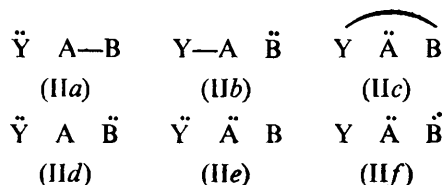
$$\psi_2 = |a\bar{a}y\bar{b}| + |a\bar{a}b\bar{y}| \quad (22)$$

$$\psi_3 = |y\bar{y}b\bar{b}| \quad (23)$$

$$\psi_4 = |y\bar{y}a\bar{a}| + |a\bar{a}b\bar{b}|. \quad (24)$$

The expansions of (3), (4), (6), (11), (14), (17), (18), (19) and (20) in terms of these are reported in table 1. We may also construct a "best" linear combination of the  $\psi_i$ , and this is the configuration interaction function of (25).

$$\Psi_{ci}(C_1, C_2, C_3, C_4) = C_1\psi_1 + C_2\psi_2 + C_3\psi_3 + C_4\psi_4 \quad (25)$$

TABLE 1.—EXPANSIONS IN TERMS OF  $\psi_i$  BASIS FUNCTIONS

		$\psi_1$	$\psi_2$	$\psi_3$	$\psi_4$
$\Psi_{mo,1}(k_1)$	(3)	$2k_1$	$k_1^2$	4	$k_1^2$
$\Psi_{amo}(k'_1, k''_1)$	(4)	$k'_1 + k''_1$	$k'_1 k''_1$	4	$k'_1 k''_1$
$\Psi_{mo,2}(k_1)$	(6)	0	$-(k_1 - k_3)^2$	0	$(k_1 - k_3)^2$
$\Psi_{vbo}(l, l')$	(11)	$l + l'$	0	4	$2l'l$
$\Psi_{nps}(l, l'')$	(14)	$l + l''$	$2l''l$	4	0
$\Psi_{ivbo}(l, l', l'')$	(17)	$l + l' + l''$	$2l''l$	4	$2l'l$
$\Psi_{ivHL}(l)$	(18)	1	$2l$	0	0
$\Psi_{bo,A}(l, l')$	(19)	$l + l'$	$l^2 + l'^2$	2	$2l'l$
$\Psi_{bo,B}(l, l')$	(20)	$l + l'$	$2l'l$	2	$2l'l$
$\Psi_{ci}(C_1, C_2, C_3, C_4)$	(25)	$C_1$	$C_2$	$C_3$	$C_4$

The number in parenthesis after each function refers to its definition in the text.

## RELATIONSHIPS BETWEEN WAVEFUNCTIONS

On examination of table 1, the following relationships may be found to occur between the various functions for the valence formulae of (I)-(V).

$$(i) \quad \Psi_{ivbo}(l, l', l'') = (4/C_3)\Psi_{ci}(C_1, C_2, C_3, C_4).$$

This equality arises because the parameters  $l$ ,  $l'$  and  $l''$  may be expressed in terms of the coefficients  $C_1$ ,  $C_2$ ,  $C_3$  and  $C_4$ , as in (26)-(28).

$$l = \{2C_1 \pm \sqrt{4C_1^2 - 2C_3(C_2 + C_4)}\} / C_3 \quad (26)$$

$$l' = 2C_4 / C_3 l \quad (27)$$

$$l'' = 2C_2 / C_3 l. \quad (28)$$

We therefore obtain two sets of  $l$ ,  $l'$  and  $l''$  parameters according to the choice of sign in (26).

- (ii)  $\Psi_{ivbo}(l, l', 0) = \Psi_{vbbo}(l, l')$
- (iii)  $\Psi_{ivbo}(l, 0, l'') = \Psi_{npso}(l, l'')$
- (iv)  $\Psi_{ivbo}(l+l', 2l'l/(l+l'), (l^2+l'^2)/(l+l')) = 2\Psi_{bo,A}(l, l')$
- (v)  $\Psi_{ivbo}(2l, l', l') = 2\Psi_{bo,B}(l, l') = \Psi_{amo}(2l, 2l')$
- (vi)  $\Psi_{ivbo}(k_1, \frac{1}{2}k_1, \frac{1}{2}k_1) = \Psi_{mo,1}(k_1) = 2\Psi_{bo,A}(\frac{1}{2}k_1, \frac{1}{2}k_1) = 2\Psi_{bo,B}(\frac{1}{2}k_1, \frac{1}{2}k_1)$
- (vii)  $\Psi_{ivbo}(\infty, 0, l) = \Psi_{ivHL}(l)$
- (viii)  $\Psi_{npso}(\infty, l) = \Psi_{ivHL}(l)$
- (ix)  $\Psi_{mo,1}(k_1) = \frac{1}{2}\{\Psi_{vbbo}(k_1, k_1) + \Psi_{npso}(k_1, k_1)\}$
- (x)  $\Psi_{mo,2}(k_1) = \frac{1}{2}\{(k_1 - k_3)^2/k_1^2\}\{\Psi_{vbbo}(k_1, k_1) - \Psi_{npso}(k_1, k_1)\}$
- (xi)  $\Psi_{moci}(k_1, \mu) = \Psi_{mo,1}(k_1) + \mu\Psi_{mo,2}(k_1) = \frac{1}{2}[\Psi_{npso}(k_1, k_1) + \Psi_{vbbo}(k_1, k_1) + \{\mu(k_1 - k_3)^2/k_1^2\}\{\Psi_{vbbo}(k_1, k_1) - \Psi_{npso}(k_1, k_1)\}]$ .

On substituting  $\mu(k_1 - k_3)^2 = \kappa k_1^2$ , we may write  $\Psi_{moci}(k_1, \mu)$  as

$$\begin{aligned}\Psi_{moci}(k_1, \kappa) &= \frac{1}{2}(1 - \kappa)\Psi_{npso}(k_1, k_1) + \frac{1}{2}(1 + \kappa)\Psi_{vbbo}(k_1, k_1) \\ &= 2\Psi_{bo,A}(\frac{1}{2}k_1(1 + \sqrt{-\kappa}), \frac{1}{2}k_1(1 - \sqrt{-\kappa})).\end{aligned}$$

This relationship is formally similar to one which pertains between molecular-orbital and valence-bond wavefunctions for the hydrogen molecule, namely that configuration interaction involving the bonding and antibonding configurations  $|\sigma 1s \sigma 1s|$  and  $|\sigma^* 1s \sigma^* 1s|$  (with  $\sigma 1s = 1s_a + 1s_b$ ,  $\sigma^* 1s = 1s_a - 1s_b$ , and  $1s_a$  and  $1s_b$  are hydrogen atom  $1s$  atomic orbitals) is equivalent to resonance between the covalent and ionic functions,  $|1s_a 1s_b| + |1s_b 1s_a|$  and  $|1s_a 1\bar{s}_a| + |1s_b 1\bar{s}_b|$ . For  $N_2O_4$ , molecular orbital-configuration interaction and covalent-ionic valence-bond wavefunctions have also been related.<sup>25</sup>

## CALCULATIONS

For the four  $\sigma$ -electrons of xenon difluoride, and for the four  $\pi$ -electrons of the allyl anion, nitrite and formate, we have calculated the various wave-functions of table 1, using the Hamiltonian and overlap matrix elements obtained by other workers.<sup>17, 15, 20, 19</sup> The "best" functions, and some of the single parameter functions have been reported previously,<sup>11b, 15, 17, 19, 20</sup> but we have repeated the calculations and include them here for the purpose of comparison with the other functions.

In table 2, we give the energies (in eV relative to that of the "best" function) of

TABLE 2.—ENERGIES OF THE BASIS FUNCTIONS  $\psi_1, \psi_2, \psi_3, \psi_4$

	XeF <sub>2</sub>	C <sub>3</sub> H <sub>3</sub> <sup>-</sup>	NO <sub>2</sub> <sup>-</sup>	HCO <sub>2</sub> <sup>-</sup>
$\psi_1$	10.3860	1.9361	4.9266	5.1618
$\psi_2$	1.1184	4.7461	5.6066	5.1203
$\psi_3$	24.4537	8.8969	16.7178	16.7727
$\psi_4$	25.1448	16.0399	23.2101	22.5567

Energies (in eV) in this table and in table 4 are expressed relative to those of  $\Psi_{ci}(\text{best})$ .

the canonical basis functions,  $\psi_i$ . In fig. 3, we have indicated each type of canonical structure, together with their formal charges, for  $\text{XeF}_2$  and  $\text{NO}_2^-$ . The canonical structures for  $\text{HCO}_2^-$  and  $\text{C}_3\text{H}_5^-$  are similar to those of  $\text{NO}_2^-$ , with CH replacing the nitrogen atom in both cases, and also for  $\text{C}_3\text{H}_5^-$ , a  $\text{CH}_2$  replacing each oxygen atom.

Table 3(i) contains the eigenvectors ( $C_i$ ) for the "best" functions. When the  $\psi_i$  of (21)–(24) are normalized, the eigenvectors are transformed to those reported in table 3(ii).

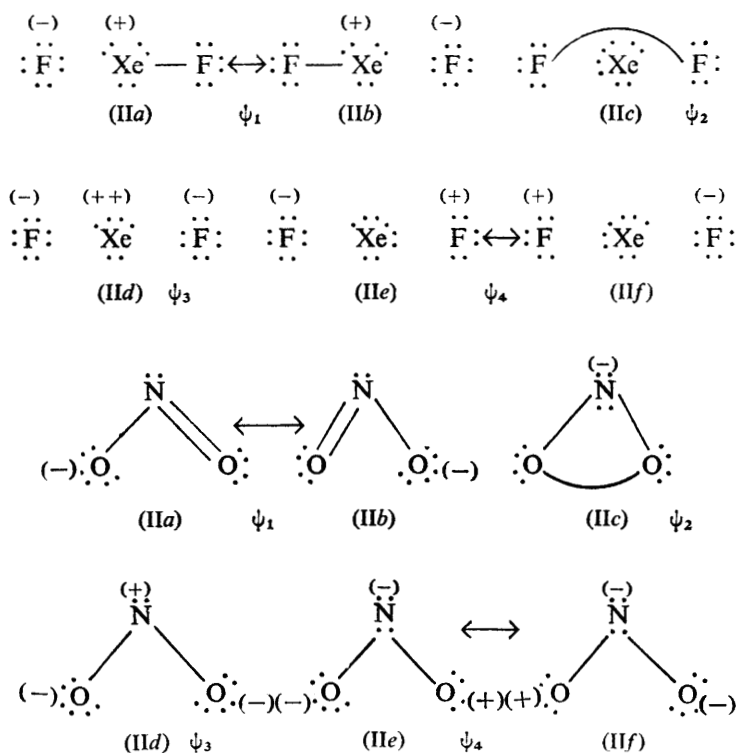


FIG. 3.—Canonical structures for  $\text{XeF}_2$  and  $\text{NO}_2^-$ .

TABLE 3.—EIGENVECTORS FOR "BEST"  $\Psi_{ci}$

(i)  $\psi_i$  not normalized, as in (21), (22), (23) and (24)

	$\text{XeF}_2$	$\text{C}_3\text{H}_5^-$	$\text{NO}_2^-$	$\text{HCO}_2^-$
$C_1$	0.1310	0.3184	0.3057	0.2733
$C_2$	0.6385	0.3041	0.3914	0.4148
$C_3$	0.0972	0.1954	0.1850	0.1675
$C_4$	0.0353	0.0448	0.0701	0.0780

(ii)  $\psi_i$  of (21), (22), (23) and (24) normalized

	$\text{XeF}_2$	$\text{C}_3\text{H}_5^-$	$\text{NO}_2^-$	$\text{HCO}_2^-$
$C_1$	0.2687	0.6632	0.6249	0.5679
$C_2$	0.8796	0.4012	0.5376	0.5608
$C_3$	0.0972	0.1951	0.1850	0.1675
$C_4$	0.0487	0.0591	0.0963	0.1054



The energies (in eV relative to those of the "best" functions) and the overlaps of the functions of table 1 with the "best" functions are given in tables 4 and 5 respectively. The bond parameters of these functions are reported in tables 6, 7 and 8.

In tables 4, 5 and 7, there are three increased-valence bond-orbital functions, each of which has two variation parameters. These are (i)  $\Psi_{ivbo,A}(l, l', l)$  with  $l'' = l$  in (17); (ii)  $\Psi_{ivbo,B}(l, l', l'')$  with  $l'' = l'$  in (17) (this function becomes the alternant molecular orbital function of (4) if we put  $l = k'_1$  and  $2l' = k''_1$ ); (iii)  $\Psi_{ivbo,C}(l, l, l'')$  with  $l' = l$  in (17).

TABLE 4.—ENERGIES OF WAVEFUNCTIONS FOR VALENCE FORMULAE (I)–(V)

		XeF <sub>2</sub>	C <sub>3</sub> H <sub>5</sub> <sup>−</sup>	NO <sub>2</sub> <sup>−</sup>	HCO <sub>2</sub> <sup>−</sup>
$\Psi_{vbbo}$	(1)	11.082 69	3.010 82	5.922 96	5.817 28
$\Psi_{vbbo}$	(2)	8.075 15	1.200 44	2.981 18	3.367 92
$\Psi_{mo,1}$	(1)	5.761 45	1.067 77	2.042 26	1.906 08
$\Psi_{ivbo}$	(1)	5.711 24	0.993 66	1.908 57	1.815 71
$\Psi_{bo,B} \equiv \Psi_{amo} \equiv \Psi_{ivbo,B}$	(2)	5.636 89	0.611 87	1.386 04	1.527 17
$\Psi_{ivHL}$	(1)	0.291 74	0.469 94	0.878 44	0.809 01
$\Psi_{npso}$	(1)	0.094 70	0.407 80	0.592 34	0.476 04
$\Psi_{npso}$	(2)	0.060 23	0.057 64	0.224 84	0.265 71
$\Psi_{bo,A}$	(2)	0.043 47	0.232 73	0.245 60	0.109 46
$\Psi_{ivbo,A}$	(2)	0.043 55	0.229 03	0.240 47	0.106 29
$\Psi_{ivbo,C}$	(2)	0.190 11	0.002 66	0.000 01	0.005 39
$\Psi_{ci}(\text{best})$	(3)	0	0	0	0

The numbers in parenthesis in this table and in table 5, give the number of variational parameters with respect to which the energies have been minimized.

TABLE 5.—OVERLAPS OF WAVEFUNCTIONS FOR VALENCE FORMULAE (I)–(V) WITH  $\Psi_{ci}(\text{best})$ 

		XeF <sub>2</sub>	C <sub>3</sub> H <sub>5</sub> <sup>−</sup>	NO <sub>2</sub> <sup>−</sup>	HCO <sub>2</sub> <sup>−</sup>
$\Psi_{vbbo}$	(1)	0.454 58	0.851 10	0.769 92	0.775 10
$\Psi_{vbbo}$	(2)	0.510 17	0.924 77	0.849 26	0.840 35
$\Psi_{mo,1}$	(1)	0.771 85	0.962 21	0.941 56	0.943 39
$\Psi_{ivbo}$	(1)	0.768 26	0.963 67	0.942 83	0.943 89
$\Psi_{bo,B} \equiv \Psi_{amo} \equiv \Psi_{ivbo,B}$	(2)	0.755 77	0.967 94	0.943 19	0.942 47
$\Psi_{ivHL}$	(1)	0.993 37	0.983 17	0.977 36	0.981 38
$\Psi_{npso}$	(1)	0.998 40	0.984 62	0.983 74	0.988 35
$\Psi_{npso}$	(2)	0.998 80	0.998 50	0.995 47	0.994 77
$\Psi_{bo,A}$	(2)	0.999 42	0.992 71	0.994 51	0.997 82
$\Psi_{ivbo,A}$	(2)	0.999 37	0.992 90	0.994 66	0.997 91
$\Psi_{ivbo,C}$	(2)	0.996 57	0.999 88	1.000 00	0.999 93
$\Psi_{ci}(\text{best})$	(3)	1.000 02	1.000 02	0.999 99	1.000 00

TABLE 6.—BOND PARAMETERS FOR SINGLE PARAMETER FUNCTIONS

		XeF <sub>2</sub>	C <sub>3</sub> H <sub>5</sub> <sup>−</sup>	NO <sub>2</sub> <sup>−</sup>	HCO <sub>2</sub> <sup>−</sup>
$\Psi_{vbbo}$	$l$	1.0564	0.8967	0.9834	1.0143
$\Psi_{mo}$	$k_1$	2.0762	1.4770	1.6468	1.7733
$\Psi_{ivbo}$	$l$	1.4727	1.0452	1.1674	1.2600
$\Psi_{ivHL}$	$l$	2.6024	0.4622	0.6887	0.7720
$\Psi_{npso}$	$l$	4.3827	1.5991	1.8686	2.0010

Table 9 contains the eigenvectors for the "best" functions <sup>16, 18</sup> for O<sub>3</sub> and H<sub>3</sub><sup>−</sup>. From these, we have calculated the bond parameters for the three-parameter  $\Psi_{ivbo}$  which are reported in table 10.

TABLE 7.—BOND PARAMETERS FOR TWO-PARAMETER FUNCTIONS

		XeF <sub>2</sub>	C <sub>3</sub> H <sub>5</sub> <sup>-</sup>	NO <sub>2</sub> <sup>-</sup>	HCO <sub>2</sub> <sup>-</sup>
$\Psi_{vbbo}$	$l$	5.3238	6.2806	5.6373	5.7507
	$l'$	0.1045	0.0602	0.1196	0.1330
$\Psi_{bo,B} \equiv \Psi_{amo} \equiv \Psi_{ivbo,B}$	$k'_1$	4.5268	5.8304	5.6079	5.4878
	$k''_1$	1.0045	0.3892	0.5459	0.6669
$\Psi_{moci}$	$k_1$	4.6146	1.7490	2.0281	2.2135
	$\mu$	-0.6783	-0.2169	-0.2750	-0.2933
$(1-\kappa)\Psi_{npso} + (1+\kappa)\Psi_{vbbo}$	$k_1$	4.6144	1.7490	2.0281	2.2135
	$\kappa$	-0.9024	-0.6661	-0.6733	-0.6653
$\Psi_{bo,A}$	$l$	4.4992	1.5883	1.8460	2.0094
	$l'$	0.1156	0.1607	0.1820	0.2041
$\Psi_{ivbo,A}$	$l$	4.5016	1.5953	1.8544	2.0208
	$l'$	0.2308	0.3265	0.3677	0.4096
$\Psi_{npso}$	$l$	3.6457†	6.1852	5.9223	5.7989
	$l''$	3.6457†	0.5041	0.7236	0.8620
$\Psi_{ivbo,C}$	$l$	2.7648	0.6115	0.8697	1.0240
	$l''$	41.2304	5.0207	4.8620	5.1078

† For XeF<sub>2</sub>, the npso parameters are complex conjugates, with  $l = 2.7502 + 2.3932i$  and  $l'' = 2.7502 - 2.3932i$ . Their moduli are reported.

TABLE 8.—BOND PARAMETERS FOR THREE-PARAMETER FUNCTION,  $\Psi_{ivbo}(l, l', l'')$ 

		XeF <sub>2</sub>	C <sub>3</sub> H <sub>5</sub> <sup>-</sup>	NO <sub>2</sub> <sup>-</sup>	HCO <sub>2</sub> <sup>-</sup>
(a)	$l$	3.7244†	5.9160	5.7396	5.4464
	$l'$	0.1953†	0.0776	0.1321	0.1709
	$l''$	3.5291†	0.5263	0.7372	0.9092
(b)	$l$	3.7244†	0.6038	0.8692	1.0801
	$l'$	0.1953†	0.7599	0.8720	0.8617
	$l''$	3.5291†	5.1562	4.8676	4.5849

(a) +  $\sqrt{\phantom{x}}$  in (26), (b) -  $\sqrt{\phantom{x}}$  in (26); † for XeF<sub>2</sub>, the parameters of (a) and (b) are complex conjugates. They are (a)  $l = 2.6958 + 2.5698i$ ,  $l' = 0.1413 - 0.1347i$ ,  $l'' = 2.5545 - 2.4351i$ ; (b)  $l = 2.6958 - 2.5698i$ ,  $l' = 0.1413 + 0.1347i$ ,  $l'' = 2.5545 + 2.4351i$ .

TABLE 9.—EIGENVECTORS FOR  $\Psi_{ci}(\text{best})$  OF O<sub>3</sub> AND H<sub>3</sub><sup>-</sup>

	O <sub>3</sub> (S)	O <sub>3</sub> (H)	H <sub>3</sub> <sup>-</sup> ( $z = 1$ )	H <sub>3</sub> <sup>-</sup> ( $z = 0.9$ )
$C_1$	0.3508	0.3501	0.7838	0.8121
$C_2$	0.3898	0.3876	0.4677	0.4834
$C_3$	0.1235	0.1313	0.4069	0.3136
$C_4$	0.0282	0.0322	0.0413	0.0922

(S) Penetration integrals calculated using Slater 2s a.o. (H) Penetration integrals calculated using hydrogenic 2s a.o.

It should be noted here that the matrix elements for XeF<sub>2</sub> were constructed using fluorine 2p $\sigma$  and xenon 5p $\sigma$  Slater atomic orbitals ( $r^{n-1} \cos \theta \cdot \exp(-\alpha r)$ ) in the Slater determinants for the  $\psi_i$ . Because these orbitals are not orthogonal to certain core orbitals (in particular, 5p $\sigma$  is not orthogonal to the inner-shell p $\sigma$  orbitals of xenon), the  $\psi_i$  do not satisfy the requirement for a true variational calculation. However, the general similarity of the results of our calculations for XeF<sub>2</sub> with those for the other systems leads us to conjecture that the error involved in this non-orthogonality is not so great that it will invalidate the qualitative aspects of the results. It is for this reason that we report them, although we are aware that the quantitative details need

to be revised in order that the variation theorem can be applied correctly. We also expect that improved techniques for calculating the basic integrals will alter the relative magnitudes of the matrix elements for the  $\pi$ -electron systems, as will inclusion of the core electrons in the construction of the  $\psi_i$ . However, we consider that the matrix elements used in this paper are satisfactory to demonstrate comparisons between the different types of wavefunctions. This is because our general conclusions concerning

TABLE 10.—BOND PARAMETERS FOR THREE PARAMETER FUNCTIONS OF  $\Psi_{\text{ivbo}}(l, l', l'')$   $\text{O}_3$ , AND  $\text{H}_3^-$

		$\text{O}_3(\text{S})$	$\text{O}_3(\text{H})$	$\text{H}_3^-(z = 1)$	$\text{H}_3^-(z = 0.9)$
(a)	$l$	10.7311	10.0280	7.3654	9.9910
	$l'$	0.0426	0.0489	0.0276	0.0588
	$l''$	0.5882	0.5888	0.3121	0.3086
(b)	$l$	0.6308	0.6377	0.3397	0.3674
	$l'$	0.7240	0.7692	0.5976	0.6004
	$l''$	10.0072	9.2588	6.7678	8.3906

(S) Penetration integrals calculated using Slater  $2s$  a.o.s. (H) Penetration integrals calculated using hydrogenic  $2s$  a.o.

the degree of goodness of the wavefunctions of table 1, depend on the nature of the linear combinations reported in that table. These conclusions also depend on the use of simple qualitative concepts—in particular, the electroneutrality principle, numbers of covalent bonds and the extent of electron charge correlation—and the  $\psi_i$  which have been calculated to be important in the “best” wavefunctions are just those which we would deduce by application of these concepts.\*

## DISCUSSION

### (a) “BEST” CONFIGURATION INTERACTION FUNCTIONS

We shall examine the properties of the basis functions  $\psi_i$  and the  $\Psi_{\text{ci}}$  of table 2. Similar considerations have been described elsewhere for other systems. (For some studies of  $\text{N}_3^-$ ,  $\text{CO}_2$ ,  $\text{NO}_2^+$  and  $\text{N}_2\text{O}$ , each having eight  $\pi$ -electrons,<sup>22</sup> and also for  $\text{N}_2\text{O}_4$  with ten mobile  $\sigma$ -electrons<sup>21, 25</sup> the method of calculation was different. Zero differential overlap was assumed, and certain atomic integrals were evaluated empirically. However, the conclusions were similar to those that are reported here).

The results of table 2 indicate that the canonical structures of low energy are those which carry small atomic formal charges. For the anions, these are the structures whose wavefunctions are  $\psi_1$  and  $\psi_2$ , each of which carries a formal negative charge on one atom. The  $\psi_2$  of  $\text{XeF}_2$  carries zero formal charges on all three atoms, and its energy is much lower than that of the other functions. In all cases, as the magnitudes of the formal charges increase, the energies of the  $\psi_i$  increase.

Catton and Mitchell<sup>12</sup> have reported the results of valence-bond studies for  $\text{XeF}_2$ . They have considered the  $\psi_1$  and  $\psi_3$  of fig. 3, and wavefunctions for  $\text{F—Xe—F}$  and  $\text{F}^{(-)}\text{Xe}^{(+)}\text{—F} \leftrightarrow \text{F—Xe}^{(+)}\text{F}^{(-)}$  each of the latter three structures utilizing xenon  $pd$  hybrid orbitals for bonding. Catton and Mitchell have found that  $\text{F—Xe—F}$  is the most stable structure. As a consequence of the discussion in the previous paragraph, we think that it would be of some interest to compare their energies with that of the “best” linear combination of  $\psi_1$ – $\psi_4$ .

As well as having small formal charges,  $\psi_1$  and  $\psi_2$  have better electron separation than do  $\psi_3$  and  $\psi_4$ , and therefore less electronic repulsion energy. The electrons

\* We thank a referee for bringing to our attention, the problems discussed in this paragraph.

that singly occupy atomic orbitals in  $\psi_1$  and  $\psi_2$ , are available for covalent bonding, and this bonding will give extra stability to the structure if the unpaired electrons occupy atomic orbitals on adjacent atoms, as is the case for  $\psi_1$ . However, the formation of covalent bonds is not always an energetically favourable process, especially if it is accompanied by the creation of a formal charge separation, which may require considerable energy. The energies for  $\psi_1$  and  $\psi_2$  of  $\text{XeF}_2$  show this, and the results of some calculations<sup>22</sup> for  $\text{CF}_2$  also indicate that small formal charges can sometimes be more important than is the number of covalent bonds or the extent of electron charge correlation in determining the stability of a canonical structure of a triatomic (or polyatomic) molecule.

For  $\text{HCO}_2^-$ ,  $\psi_2$  is calculated to have a lower energy than has  $\psi_1$ . We would have expected  $\psi_1$  to be more stable because (i) it localizes the formal negative charge on the oxygen atoms rather than on the carbon atom, and (ii) it has shorter  $\pi$ -bonds. For similar reasons,  $\psi_1$  of isoelectronic  $\text{NO}_2^-$  is more stable than  $\psi_2$ .

For all systems, the coefficients of  $\psi_1$  and  $\psi_2$  in table 3 are largest in the  $\Psi_{\text{ci}}$ . The coefficients for the normalized  $\psi_i$  show this very clearly. These large coefficients reflect the low energies of  $\psi_1$  and  $\psi_2$ , but the importance of  $\psi_1$  is also partially a consequence of the large magnitudes for all of the off-diagonal Hamiltonian matrix elements that involve this function (see, for example, table 6 of ref. (19)).

#### (b) ONE-PARAMETER FUNCTIONS

The energies of table 4, and the overlaps of table 5 show that  $\Psi_{\text{npso}}$  is the best one-parameter function for all systems studied. Some reasons for the low energies of  $\Psi_{\text{npso}}$  have been described elsewhere, and the expression for it in table 1 indicates that this is because it includes those  $\psi_i$  with small formal charge separation, here  $\psi_1$  and  $\psi_2$ , and excludes the high-energy function  $\psi_4$ . The same is true for  $\Psi_{\text{ivhl}}$ , but because it is a more restricted function than  $\Psi_{\text{npso}}$  ( $\Psi_{\text{ivhl}}$  excludes  $\psi_3$ ) its energy is a little higher than that of  $\Psi_{\text{npso}}$ .  $\Psi_{\text{vbbo}}$  excludes the low-energy function  $\psi_2$ , and therefore it is always of high energy.

Both  $\Psi_{\text{mo}}$  and  $\Psi_{\text{ivbo}}$  have very similar wave-functions and energies, (see also ref. (11b)) and each involves a linear combination of all four  $\psi_i$ . However, their energies are much higher than either  $\Psi_{\text{ivhl}}$  or  $\Psi_{\text{npso}}$ . This is because they give large coefficients to the high-energy wave-functions  $\psi_3$  and  $\psi_4$ , which carry large formal charge separations.

#### (c) TWO-PARAMETER FUNCTIONS

The equality between  $\Psi_{\text{moci}}$ ,  $(1-\kappa)\Psi_{\text{npso}} + (1+\kappa)\Psi_{\text{vbbo}}$  and  $\Psi_{\text{bo,A}}$  is demonstrated by the bond parameters of table 7 generating the energy for  $\Psi_{\text{bo,A}}$  of table 4. For all systems studied, the energies for these functions are very low, as are those for the two-parameter  $\Psi_{\text{npso}}$ . Obviously this is not unexpected, because the single parameter  $\Psi_{\text{npso}}$  is a special case of these functions, and it is also of low energy.

$\Psi_{\text{amo}}$ , which is equivalent to  $\psi_{\text{bo,B}}$  and  $\Psi_{\text{ivbo,B}}$  in energy, does not generate a low energy. This is because it gives equal weight to the functions  $\psi_2$  and  $\psi_4$  in the expansion of table 1, and therefore does not reflect the relative importance of these functions in the  $\Psi_{\text{ci}}$  of table 2, where in all cases,  $C_2 > C_4$ . By contrast, this inequality pertains to both  $\Psi_{\text{bo,A}}$  and  $\Psi_{\text{npso}}$ . For  $\Psi_{\text{bo,A}}$ ,  $l^2 + l'^2 > 2l'l$ , whereas for  $\Psi_{\text{npso}}$ , the coefficient of  $\psi_4$  is zero.

Of the two-parameter functions that have been studied,  $\Psi_{\text{vbbo}}$  always has the highest energy. This is chiefly because of the neglect of  $\psi_2$ , which, as we have already pointed out, is so important in the "best" function  $\Psi_{\text{ci}}$ . Simple resonance descrip-

tions of molecules will never imply a very low energy if contributions from canonical structures having both long bonds and small or zero formal charges are omitted.

For  $\text{XeF}_2$ , there is no valence-bond function, either of bond-orbital or Heitler–London type, which has an energy as low as that for  $\psi_2$  alone. This latter function involves a long-bond between the fluorine atoms instead of between the xenon and one of the fluorine atoms. Therefore, for this molecule, our results suggest that the simple valence-bond description is unstable relative to the three atoms at the same internuclear separation. This valence-bond instability does not occur for the three anions.

For each three-parameter  $\Psi_{\text{ivbo}}$  of table 8, there are two sets of parameters, (a) and (b). The  $l$ ,  $l'$  and  $l''$  of (a) are generally different in magnitude. The  $l$  and  $l'$  are similar to those for  $\Psi_{\text{vbbo}}$  in table 7, but the  $l''$  is usually appreciable in magnitude, not zero as they are for  $\Psi_{\text{vbbo}}$ . On the other hand, the  $l'$  for (a) in table 8 are small, and the values for  $l$  and  $l''$  are very similar to those for  $\Psi_{\text{npso}}$  in table 7 (for which  $l'$  is zero). These considerations indicate further why  $\Psi_{\text{npso}}$  is a good function, whereas  $\Psi_{\text{vbbo}}$  is not.

For the increased-valence functions  $\Psi_{\text{ivbo,A}}$  and  $\Psi_{\text{ivbo,C}}$  of table 1, the coefficients of  $\psi_2$  and  $\psi_4$  are not equal. Except for  $\text{XeF}_2$ , the latter function ( $\Psi_{\text{ivbo,C}}$ ) generates a lower energy than does any other two parameter function. By examining the  $l$ ,  $l'$  and  $l''$  parameters of (b) in table 8, we can see why this is so. For  $\text{C}_3\text{H}_5^-$ ,  $\text{NO}_2^-$  and  $\text{HCO}_2^-$ , the  $l$  and  $l'$  of (b) are nearly equal, and so requiring them to be equal (as in  $\Psi_{\text{ivbo,C}}$ ), will not alter the energy very much. For  $\text{XeF}_2$ , the magnitudes of  $l$  and  $l'$  in table 8 are very different, and so the energy of  $\Psi_{\text{ivbo,C}}$  is rather higher than the energy of the “best” function.

Although we have not calculated them, we may make predictions about the energies of the  $\Psi_{\text{ivbo,C}}$  for some other systems. The “best”  $\Psi_{\text{ci}}$  have been reported elsewhere<sup>16, 18</sup> for the four  $\pi$ -electrons of  $\text{O}_3$ , and for the four bonding  $\sigma$ -electrons of  $\text{H}_3^-$ , and these are given in table 9. From these functions, the parameters  $l$ ,  $l'$ , and  $l''$  have been calculated, and these are reported in table 10. For  $\text{O}_3$ , but not for  $\text{H}_3^-$ ,  $l$  and  $l'$  are approximately equal, and therefore the  $\Psi_{\text{ivbo,C}}$  should generate a very low energy for  $\text{O}_3$ .

The  $\Psi_{\text{ivbo,C}}$  has an advantage over the  $\Psi_{\text{npso}}$  one- and two-parameter functions in that it has two instead of four singly occupied orbitals. Therefore its spin eigenfunction is simpler. For four-electron systems, this is perhaps not important, but for systems such as  $\text{CO}_2$ ,  $\text{N}_3^-$  and  $\text{NO}_2^+$  with eight  $\pi$ -electrons, important non-paired spatial orbital formulae have eight electrons in different spatial orbitals. The construction of spin eigenfunctions for eight unpaired electrons is very complicated, but for  $\Psi_{\text{ivbo,C}}$ , the appropriate spin eigenfunction for the four unpaired electrons is easy to construct.

As can be seen in tables 4 and 5,  $\Psi_{\text{ivbo,A}}$  generates energies and overlaps that are very close to those of  $\Psi_{\text{bo,A}}$  (which, as we have discussed above, is equivalent to both  $\Psi_{\text{moc1}}$  and to  $\frac{1}{2}(1-\kappa)\Psi_{\text{npso}} + \frac{1}{2}(1+\kappa)\Psi_{\text{vbbo}}$ ). This is not surprising since we have

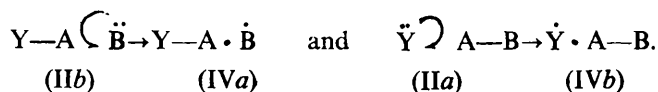
$$\Psi_{\text{ivbo,A}}(l, l', l) = (2l+l')\psi_1 + 2l^2\psi_2 + 4\psi_3 + 2l'l\psi_4 \quad (29)$$

and

$$2\Psi_{\text{bo,A}}(l, \frac{1}{2}l') = (2l+l')\psi_1 + (2l^2 + \frac{1}{2}l'^2)\psi_2 + 4\psi_3 + 2l'l\psi_4 \quad (30)$$

that is, the wavefunctions differ only in the coefficient of  $\psi_2$ . For the systems studied,  $l'$  is usually small relative to  $l$ , and hence the similarity of the functions is explained. This similarity is carried over to their bond parameters which are reported in table 7.

One of us has shown<sup>11</sup> that increased-valence formulae (IVa) and (IVb) can be generated very easily from the standard valence-bond formulae (IIa) and (IIb). Perhaps the simplest (but *not* the only) way to do this is to delocalize a non-bonding electron into a bonding orbital, as in<sup>11c-11f, 22</sup>



This type of delocalization stabilizes the standard valence-bond structures by allowing them to participate in resonance with the long-bond structure.

## CONCLUSIONS

For a number of symmetrical electron-excess systems, we have provided evidence

that the long-bond valence structure  $\text{Y} \overset{\curvearrowright}{\text{A}} \text{B}$  can participate appreciably in resonance with the standard valence-bond structures  $\text{Y}-\text{A} \cdot \dot{\text{B}}$  and  $\ddot{\text{Y}} \text{A}-\text{B}$ . A similar conclusion has also been obtained from semiempirical studies<sup>22</sup> of  $\text{N}_3^-$ ,  $\text{N}_2\text{O}$ ,  $\text{CO}_2$ ,  $\text{NO}_2^+$  and<sup>25</sup>  $\text{N}_2\text{O}_4$ , and from non-empirical valence-bond calculations<sup>26</sup> for systems which have one or more non-symmetrical bonding units such as  $\text{FNO}_2$ ,  $\text{FO}_2$  and  $\text{CH}_2\text{N}_2$ . This type of resonance-stabilization seems to be of particular importance for 1,3-dipolar molecules and ions, but it can also be important for systems such as  $\text{H}_3^-$ ,  $\text{HCO}_2^-$ ,  $\text{NO}_2^-$  and  $\text{C}_3\text{H}_5^-$  with other types of formal charge arrangements.

Both the increased-valence and the non-paired spatial orbital structures summarize resonance between the standard and the long-bond valence structures. Therefore, for the purpose of providing simple localized representations of electronic structure, they should be preferred to using the standard valence-bond structures alone. Numerous examples of chemical insights which may be obtained by constructing increased-valence and non-paired spatial orbital formulae have been discussed elsewhere.<sup>11, 13</sup> It is our opinion that these new valence formulae should constitute an important component of elementary valence theory.

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