Generalized Valence Bond Description of Bonding in Low-Lying States of Molecules

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Some of the most important present-day concepts concerning the states and geometries of molecules have come from simple considerations of *molecular orbitals*. Examples include the orbital correlation diagrams used by Mulliken[2] and Walsh[3] to explain the electronic structure of diatomic and polyatomic molecules and by Hoffmann and Woodward[4] to develop selection rules for chemical reactions.

In this Account we present an alternative approach for discussing the states of molecules using wave functions generalized from the *valence-bond* (VB) form. In this generalized valence bond (GVB) description we examine the *atomic* orbitals of the various atoms rather than *molecular* orbitals (MO). We find that simple GVB considerations lead to correct semiquantitative predictions of the geometry and ordering of the excited states of simple hydrocarbon and fluorocarbon radicals. Moreover, the GVB description leads to useful predictions of the ordering and geometries of the excited states of ozone, a system whose states were only poorly understood from previous experimental and MO considerations.

First we will review some basic ideas about wave functions. Consider the H_2 molecule. In the molecular orbital (MO) description there is one molecular orbital containing two electrons (one electron with each spin). In the Hartree–Fock (HF) method this orbital is optimized to give the best such wave function, leading to the orbital in Figure 1a. Note that the orbital is symmetric and remains so as the molecule is pulled apart. Since both electrons are in the same orbital,[5] the HF wave function for large R (internuclear distance) has the form in (1) (where χ_l

$$\Psi^{HF} = \psi(1)\psi(2) = [\chi_l(1) + \chi_r(1)][\chi_l(2) + \chi_r(2)]$$

$$= (\chi_l\chi_l + \chi_r\chi_r) + (\chi_l\chi_r + \chi_r\chi_l) \qquad (1)$$

and χ_r are orbitals centered on the left and right nuclei, respectively, and normalization is ignored). From (1) we find a 50% probability of *both* electrons

being near the *same* nucleus. But if the atoms are, say, a foot apart, there should be essentially *zero* probability of the electrons being together. Thus the HF wave function is a very poor approximation to the true wave function for large R. This difficulty arises essentially because the HF wave function has *one* doubly occupied orbital for all R whereas at $R = \infty$ the "molecule" should utilize two singly occupied orbitals that do not overlap (are orthogonal).

An alternative approach is to use the VB wave function (eq 2)[5] which (by construction) leads to the

$$\Psi^{VB} = (\chi_l\chi_r + \chi_r\chi_l) \qquad (2)$$

proper wave function for $R = \infty$. However, this wave function does poorly for small R, as indicated in Figure 2. The changes in the atomic orbitals brought about by molecular formation are just too large to ignore.

Thus neither the HF nor VB approaches lead to satisfactory descriptions for all R of interest. In order to get around these problems, we use the VB *form* of the wave function (eq 3),[5] so that the wave function

$$\Psi^{GVB} = (\phi_l\phi_r + \phi_r\phi_l) \qquad (3)$$

is appropriate at large R, but we solve for the orbitals self-consistently at each R just as in the HF method. This combines the good attributes of both HF and VB and leads to a wave function that both behaves properly as the atoms are separated and is accurate for small R (better than HF). This approach is called the *generalized valence bond* (GVB) method[6,7] and differs from the Hartree–Fock method in that we now have two orbitals, one for each electron, rather than one orbital per electron pair. Thus the GVB wave function is the self-consistent generalization of the VB wave function just as the HF wave

(1) (a) This paper is based on a lecture presented (by W. A. G.) at the 27th Annual Symposium on Molecular Structure and Spectroscopy, The Ohio State University, Columbus, Ohio, June 14, 1972. (b) Contribution No. 4622.

(2) R. S. Mulliken, *Phys. Rev.*, **32**, 213 (1928); *Rev. Mod. Phys.*, **4**, 1 (1932); F. Hund, *Z. Physik*, **51**, 759 (1928); **63**, 719 (1936).

(3) A. D. Walsh, *J. Chem. Soc.*, 2260, 2266 (1953).

(4) R. Hoffmann and R. B. Woodward, *J. Amer. Chem. Soc.*, **87**, 2046, 4388, 4389 (1965); R. B. Woodward and R. Hoffmann, *J. Amer. Chem. Soc.*, **87**, 399, 2511 (1965); *Angew. Chem., Int. Ed. Engl.*, **8**, 781 (1969).

(5) In (1), (2), and (3) only the spatial part of each wave function is shown; the spin part is $(\alpha\beta - \beta\alpha)$ in each case. In all orbital products the first orbital contains electron 1, the second electron 2, etc. [*e.g.*, $\chi_l\chi_r = \chi_l(1)\chi_r(2)$].

(6) More detailed discussions are given in (a) W. A. Goddard III, *Phys. Rev.*, **157**, 81 (1967); (b) W. A. Goddard III and R. C. Ladner, *J. Amer. Chem. Soc.*, **93**, 6750 (1971); (c) W. J. Hunt, P. J. Hay, and W. A. Goddard III, *J. Chem. Phys.*, **57**, 738 (1972).

(7) R. C. Ladner and W. A. Goddard, III, *J. Chem. Phys.* **51**, 1073 (1969).

Figure 1. The Hartree–Fock and GVB orbitals of H_2.

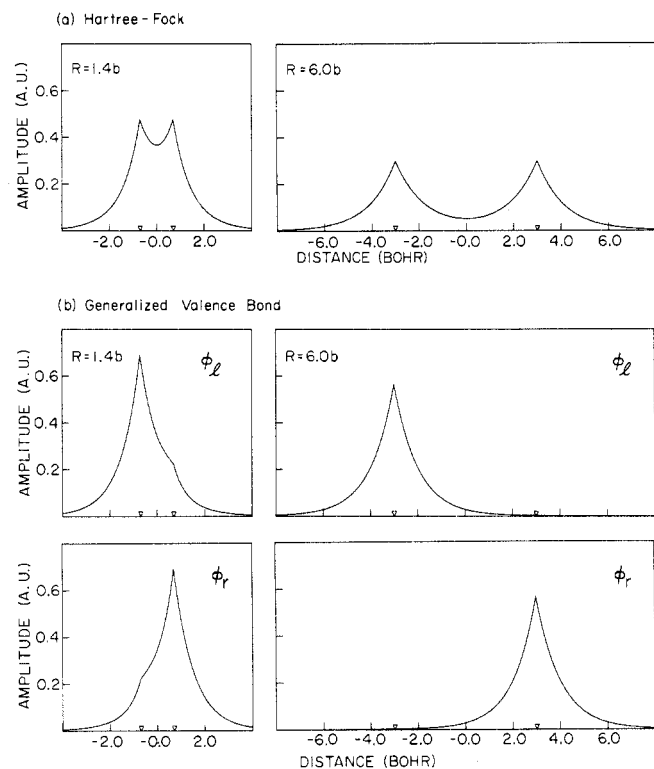**Figure 2.** The MO, VB, HF, GVB, and exact energies for H_2. The MO and VB wave functions are special cases of the HF and GVB wave functions in which χ_1 and χ_r in (1) and (2) are taken as atomic orbitals.

function is the self-consistent generalization of the simple MO wave function.

The resulting GVB orbitals[6a] for H_2 are also shown in Figure 1b. Comparing the HF and GVB wave functions at R_e, we see that the GVB orbitals localize (one more on the left, the other more on the right) so as to increase the average electron–electron separation, thereby decreasing the energy. As R increases, the GVB orbitals become more and more localized, eventually becoming atomic hydrogen 1s orbitals. The GVB energies for H_2 are shown in Figure 2. Near R_e the GVB energy is about half way between the HF value and experiment, and as R increases the GVB energy and wave function approach the correct limits.

For more than two electrons the GVB method involves a similar procedure. As above, we take the VB form of the wave function and solve for all orbitals self-consistently.[6,7]

We will now examine the GVB description of several molecules. In each case we report the results of *ab initio* calculations; however, our emphasis will be upon developing concepts and ways of thinking about the molecules so that one can predict the major features of these wave functions *without* doing calculations. First we consider the GVB description of some representative atoms.

The GVB Description of Atoms

For carbon the usual orbital description is as symbolized by $(1s)^2(2s)^2(2p)^2$, with doubly occupied 1s and 2s orbitals and two singly occupied 2p orbitals. The GVB description allows a different orbital for every electron. This leads to only minor changes (unimportant herein) in the two 1s orbitals and the two 2p orbitals; however, significant changes occur in the orbitals corresponding to the 2s pair. The two GVB
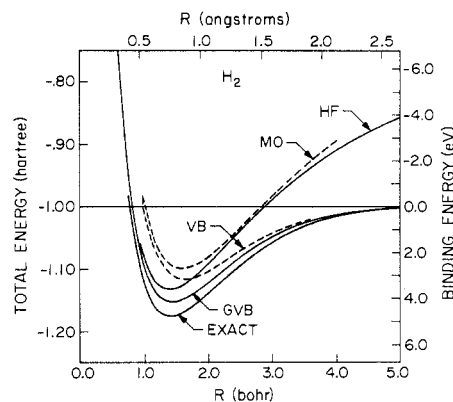
"2s" orbitals distort so as to increase the average distance between electrons. The resulting orbitals are shown in Figure 3a, where they are denoted as s_x and $s_{\bar{x}}$. These orbitals have the form of sp hybrids (the amount of p character is 17%) and will be referred to as *lobe orbitals* (not to be confused with the lobe of a p orbital). We did not *force* these orbitals to have such shapes: rather, the variational principle was applied, leading to the optimum orbitals shown in Figure 3a. Thus in the *ground state* of C atom the "2s" valence orbitals hybridize in this way in order to reduce the energy of the system.

The Hartree–Fock description of F is $(1s)^2(2s)^2(2p_x)^2(2p_y)^2(2p_z)$; that is, all orbitals are doubly occupied except for one 2p orbital. In the GVB description each pair splits into two highly overlapping orbitals ($S \sim 0.9$), both of which behave in a similar way to the doubly occupied Hartree–Fock orbital when F forms a bond. In our discussions we will ignore such splittings and will simply consider such a pair of highly overlapping orbitals as a single orbital that is doubly occupied. The resulting orbitals are shown in Figure 3b.

A similar result is found for the ground states of O and N atoms. In none of these cases does the 2s pair split in the way that it does in C (and also in Be and B). The reason is that for N, O, and F there are occupied p orbitals in each direction. Splitting the 2s pair into one of these directions (say x) as for C would lead to the s_x and $s_{\bar{x}}$ orbitals, both of which would overlap the occupied p_x orbital. Because of the Pauli principle we cannot have three highly overlapping orbitals, and hence the F $s_x,s_{\bar{x}}$ orbitals cannot have the form found for C.

A Brief Review of the Principles of Chemical Bonding

Before considering the wave functions of molecules, we will review briefly some of the conditions important for bonding.[8] The orbitals of the atoms are optimum at $R = \infty$, and any distortions (as upon molecular formation) will raise the atomic energies. Since atomic excitation energies are comparable in size to molecular bonding energies, we would expect

(8) See, for example, C. W. Wilson, Jr., and W. A. Goddard III, *Chem. Phys. Lett.*, **5**, 45 (1970); *Theor. Chim. Acta*, **26**, 195, 211 (1972).
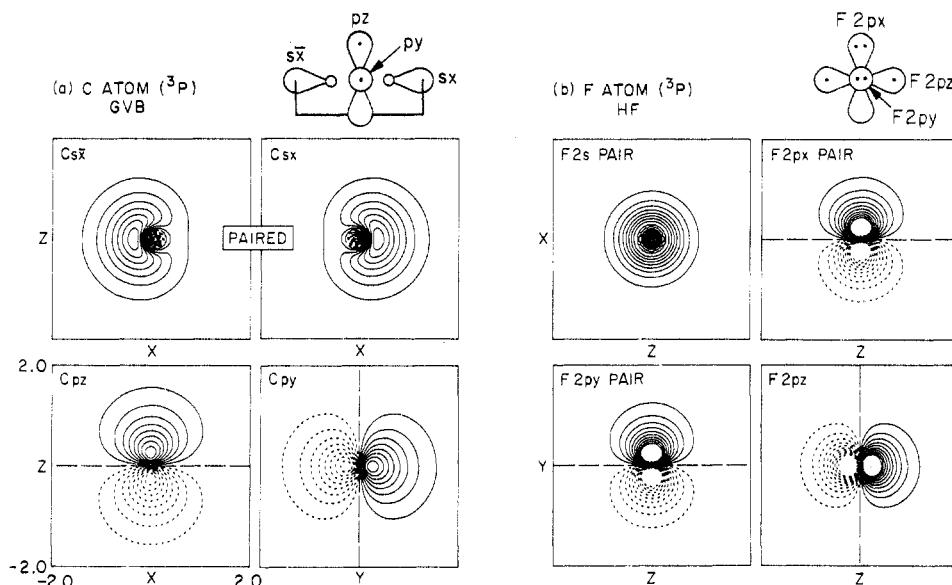
Figure 3. (a) The GVB valence orbitals for carbon (^{3}P). A schematic representation of the GVB orbitals is included at the top. Each orbital contains one electron. The p orbitals are represented by a normal two-lobed shape if in the plane and a circle if perpendicular to the plane. Each lobe orbital (s_x and $s_{\bar{x}}$) is denoted by a single lobe with a small circle at one end. The line connecting these orbitals indicates that they are singlet coupled. The dots in the p orbitals indicate unpaired orbitals which are coupled into a triplet state here. The contour plots show the calculated self-consistent GVB valence orbitals of carbon (^{3}P). Long dashes indicate zero amplitude and solid lines and short dashes indicate positive and negative amplitudes, respectively. The increment between contours is 0.05 au. (b) The HF valence orbitals of F(^{2}P).
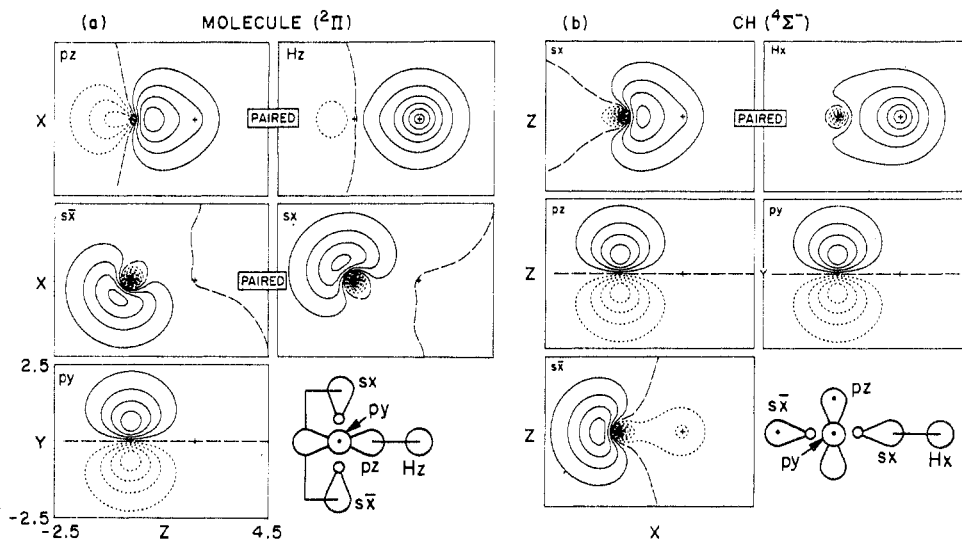
Figure 4. The GVB valence orbitals of the $^2\Pi$ and $^4\Sigma^-$ states of CH. The schematic representation shows the coupling of the atomic carbon and hydrogen orbitals without allowing for self-consistent adjustments upon molecule formation. A line indicates that singly occupied orbitals on two centers are coupled into a bonding pair; the dots indicate unpaired orbitals coupled to high spin. The contour increment for the calculated orbitals is 0.1 au.

the low-lying states of molecules to be those in which the wave function near each atom is atomic-like in character. For this reason we will examine bond formation in terms of the atomic GVB orbitals. The low-lying excited states will then be obtained by considering excitation of the atomic orbitals not involved in bonds.

If the atoms are placed so that two (singly occupied) orbitals overlap substantially, a low energy (favoring bonding) is obtained if the orbitals are coupled into a singlet pair (that is, a chemical bond is formed), and a high energy is obtained if they are coupled into a triplet pair. Because of the Pauli principle no more than two electrons can be simultaneously coupled into singlet pairs with each other, and hence normal bonds involve two electrons. If orbitals of two different (singlet) pairs have high overlaps, they lead to repulsive (energy raising) interactions (this again arises from the Pauli principle); thus orbitals of different pairs should have small overlaps and will generally readjust so as to become orthogonal. (Such readjustments will often lead to a new nodal plane in an orbital; in this case the orbital is said to be antibonding.)

The above considerations imply that in order to form a strong covalent bond between atoms A and B, we require that (1) a singly occupied orbital ϕ_a on A and a singly occupied orbital ϕ_b on B be such that they will overlap greatly when A and B are brought together and (2) the orbitals of the bond must be nearly orthogonal to the other orbitals of the molecule.
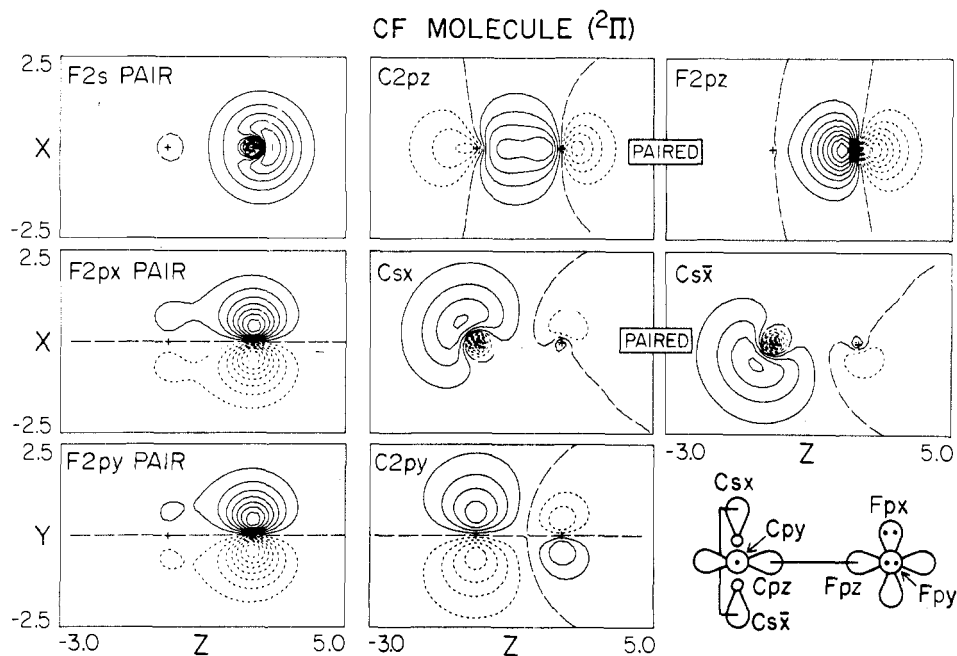
Figure 5. The GVB valence orbitals of the $^2\Pi$ state of CF. In the schematic representation an orbital with two dots indicates a doubly occupied orbital. The contour increment is 0.1 au.

The GVB Description of Hydrocarbons and Fluorocarbons

Starting with the GVB description of C, H, and F, we will now examine the wave functions to be expected for some simple hydrocarbons and fluorocarbons.[9]

First we add an H to C to form CH. To form a strong bond we must combine the orbital on the H atom with an orbital on the C so that these two orbitals have a high overlap with each other while the H orbital has a small overlap with all other orbitals of the molecule. Pairing the H orbital with a p orbital on the C leads to a doublet state ($^2\Pi$) of CH (Figure 4a), which should be strongly bound.

In addition, there is another way of bonding C and H. The orbitals of the lobe pair (the "2s" pair) are polarized in opposite directions; thus we expect that the H can bond effectively to one of these lobe orbitals since the H orbital would still have small overlap with the other lobe orbital and the C 2p orbitals.[10] Since the other three orbitals are unpaired, and orthogonal, this leads to a quartet state ($^4\Sigma^-$) (Figure 4b). (That a set of orthogonal orbitals favors the high-spin state is usually referred to as Hund's rule: it arises from the form of the two-electron exchange interactions.)

The self-consistent GVB orbitals for these states of CH are shown in Figure 4, where the orbitals are denoted by the names of the corresponding orbitals of the separated atoms. As the H bonds to the C p_z orbital to form the $^2\Pi$ state, the H orbital overlaps the lobe orbitals. Because of the Pauli principle this leads to repulsive interactions,[11] and as a result the lobe pair bends back out of the way as shown in Figure 4a (the angle of the lobe orbital to the CH axis is calculated to be 128°). At the same time the C $2p_z$ orbital distorts (hybridizes) in such a way as to stay orthogonal to the lobe pair. In the $^4\Sigma^-$ state (Figure 4b) we see that the GVB orbitals for the molecule are similar to the atomic orbitals even though the orbitals of the molecule are coupled differently than for the separated atoms.

The above considerations suggest that the $^2\Pi$ and $^4\Sigma^-$ states should have comparable binding energies. The $^4\Sigma^-$ state is not known experimentally, but the $^2\Pi$ state is well established as the ground state. Theoretical calculations[12] show the $^4\Sigma^-$ state to be only about 0.5 eV above the $^2\Pi$ state.

Next we want to compare the bonding in CH to that in CF. Both H and F atoms have only one orbital available for bonding (*i.e.*, singly occupied orbitals), and thus we expect many similarities between CH and CF. The qualitative description for the $^2\Pi$ state of CF is given in Figure 5. Just as for CH we obtain strongly bound $^2\Pi$ and $^4\Sigma^-$ states. However, a significant difference is that for CF the $p\pi$ orbitals on the C now overlap doubly occupied $p\pi$ orbitals on the F. This leads to additional repulsive interactions. In the $^2\Pi$ state the lobe pairs of the C also overlap a F $p\pi$ pair which should lead to additional repulsive interactions. However, the lobe orbitals bend back as for CH, and as a result have such a small overlap with the F $p\pi$ pair that they acquire little antibonding character (see Figure 5). Thus there is *one* bad interaction for $^2\Pi$ and *two* for $^4\Sigma^-$, and we expect the $^2\Pi$ state to be much more strongly bound than the $^4\Sigma^-$ state.

The self-consistent GVB orbitals[10b] of CF ($^2\Pi$) are

(9) For a more detailed description, see (a) P. J. Hay, W. J. Hunt, and W. A. Goddard III, *J. Amer. Chem. Soc.*, **94**, 8492 (1972); (b) W. J. Hunt, W. A. Goddard III, and P. J. Hay, to be published. (c) F. Bobrowicz and W. A. Goddard III, *Chem. Phys. Lett.*, to be published.

(10) See, for example, W. A. Goddard III and R. J. Blint, *Chem. Phys. Lett.*, **14**, 616 (1972); R. J. Blint and W. A. Goddard III, *Chem. Phys.*, in press.

(11) Because the wave function must be antisymmetrized, the presence of a doubly occupied orbital ϕ_a on one center requires that an orbital ϕ_b on another center be orthogonalized to ϕ_a. This then raises the energy of ϕ_b.

(12) Hay, Hunt, and Goddard[9a] report 0.36 eV based on GVB-CI calculations of the $^2\Pi$ and $^4\Sigma^-$ states; G. C. Lie, J. Hinze, and B. Liu [*J. Chem. Phys.*, **57**, 625 (1972)] estimate 0.6 ± 0.1 eV based on extensive CI calculations on the $^4\Sigma^-$ state and the experimental D_e of the $^2\Pi$ state.
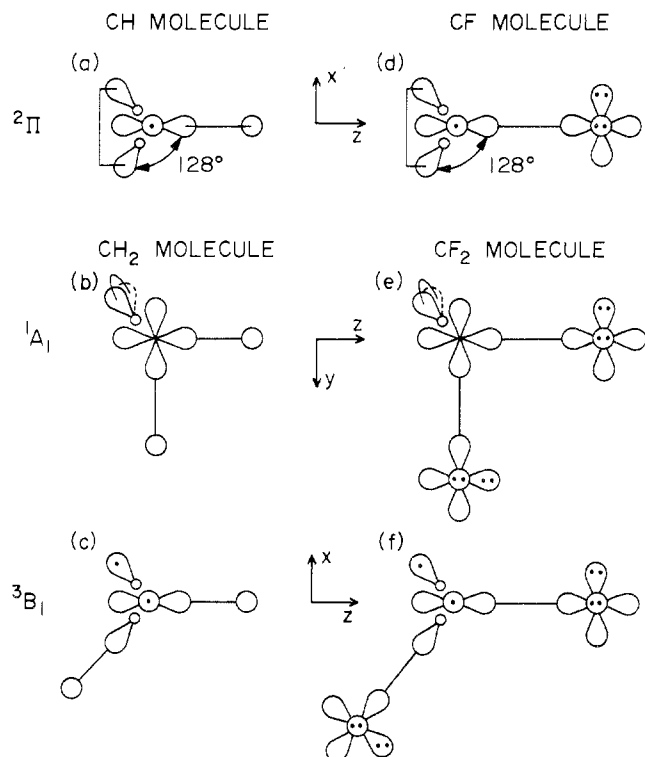
CH MOLECULE   CF MOLECULE

(a)

$^2\Pi$

128°

(d)

128°

CH$_2$ MOLECULE   CF$_2$ MOLECULE

(b)

$^1A_1$

(e)

(c)

$^3B_1$

(f)

Figure 6. Schematic representations of the GVB wave functions of CH$_2$ and CF$_2$.

shown in Figure 5 where again the orbitals are denoted by the names of the corresponding atomic orbitals. Consider first the two orbitals of the σ bond (C $2p_z$ and F $2p_z$ in Figure 5). The F orbital starts off as an F p_z orbital and hardly changes upon bond formation. The other one starts off as a C p_z orbital but is sucked over by the F to become about equally associated with each atom. Such behavior is rather typical for a bond with high ionic character.[13] The lobe pair (C s_x and C s_x) bends back to ~128° just as for CH. The F 2s pair, if it did not change, would overlap the new bonding orbital, and in order to reduce the resulting bad interactions, this orbital distorts away from the C. Both of the F $p\pi$ pairs delocalize somewhat onto the C (this might be referred to as back-bonding). The C $p\pi_y$ orbital becomes orthogonal to the F $p\pi_y$ pair, leading to an additional nodal plane and a higher kinetic energy for the C $p\pi_y$ orbital. Such an orbital is referred to as antibonding.

Because of the additional C π orbital and the resulting additional antibonding interaction, we expect the $^4\Sigma^-$ state of CF to be much higher than the $^2\Pi$ state. There is no experimental evidence for this $^4\Sigma^-$ state, and the ground state is generally believed to be $^2\Pi$. Theoretical calculations put the $^4\Sigma^-$ state at around 2.8[14] to 2.9[10b] eV above the $^2\Pi$ state.

Now consider forming CH$_2$ and CF$_2$ from CH and CF (Figure 6). Starting with the $^2\Pi$ state of CH (Figure 6a), the second H atom can be bonded to the $p\pi$ orbital in CH to obtain the singlet state ($^1A_1$) of CH$_2$ (Figure 6b). In the first approximation the bond angle would be 90°, but the new bond overlaps the

old one and both bonding pairs distort so as to decrease this overlap, leading to an increase in the bond angle (to 103°). For CH we recall that a strong bond could also be obtained by bonding the H atom to a lobe orbital of the C atom. Doing the same for CH + H leads to another state of CH$_2$ having two unpaired orbitals, as shown in Figure 6c. This is a triplet state ($^3B_1$) with an expected bond angle of ~128°. As the new bond forms, it overlaps the old one, which should (as above) lead to small changes in the bond angle.[15] The best recent experimental values[16] are 136° ± 10° and the best theoretical values (by Bender, Schaefer, and coworkers[17]) lead to 135°. Indeed the theoretical calculations[18] indicate that the $^3B_1$ state is lower than the $^1A_1$ state by 0.5 eV (experimental estimates of this quantity vary from 0.1 to 1.0 eV).

Carrying out the same analysis for CF + F leads to similar results (see Figure 6d–f). The major difference is that bonding an F atom to a lobe orbital is much worse than bonding it to a p orbital, as discussed in conjunction with CF. Thus we expect the $^3B_1$ state to be ~2.5 eV higher than the $^1A_1$ state.[19] The bond angles should be about 128° and approximately 105°, respectively. The triplet state has not been observed, but the corresponding singlet state ($^1B_1$) is experimentally known[20] to be 5 eV above the ground state with a bond angle of 122°; the ground state ($^1A_1$) is known experimentally to have a bond angle of 105°.[19]

Adding another H to CH$_2$, one might expect a strong bond to result from coupling of the new H orbital with either of the singly occupied orbitals of CH$_2$ ($^3B_1$). However, bonding the new H orbital to the π orbital of CH$_2$ leads to much higher overlap with the other bonding pairs than if the new H orbital is bonded to the (planar) lobe orbital of CH$_2$. As a result bonding to the planar orbital is favored, leading to planar CH$_3$ (as observed experimentally). Adding an F to CF$_2$ we expect pyramidal CF$_3$ (as observed experimentally). Adding a fourth atom leads to tetrahedral CH$_4$ and CF$_4$. As the fourth H is added to CH$_3$, the new orbitals are initially not orthogonal to the orbitals of the other three bonds, resulting in repulsive interactions; the other bond orbitals distort in order to reduce these repulsive interactions and as a result these three bonds bend back from the newly forming one, leading to a tetrahedral structure.

From the above discussions we see that the tetravalent character of carbon is manifest in the GVB

(13) For example, see W. E. Palke and W. A. Goddard III, *J. Chem. Phys.*, **50**, 4524 (1969).
(14) W. P. White, T. H. Dunning, R. M. Pitzer, and W. Mathews, to be published.

(15) In Figure 6 we show the two bonds of the triplet state, as inequivalent, one arising from bonding to the p orbital and one from bonding to the s_x orbital. However, as the second bond forms, the orbitals in this bond are no longer orthogonal to those of the first bond. As a result the orbitals of both bonds distort a bit, resulting in equivalent bonds. Even so, the carbon part of these bonds has the character of the average of Cp and C lobe orbitals.
(16) E. Wassermann, W. A. Yager, and V. Kuck, *J. Amer. Chem. Soc.*, **92**, 7491 (1970); G. Herzberg and J. W. C. Johns, *J. Chem. Phys.*, **54**, 2276 (1971).
(17) S. V. O'Neil, H. F. Schaefer III, and C. F. Bender, *J. Chem. Phys.*, **55**, 162 (1971); C. F. Bender, H. F. Schaefer III, D. R. Franceschetti, and L. C. Allen, *J. Amer. Chem. Soc.*, **94**, 6888 (1972).
(18) P. J. Hay, W. J. Hunt, and W. A. Goddard III, *Chem. Phys. Lett.*, **13**, 30 (1972).
(19) This is also consistent with the results of limited configuration interaction (CI) calculations by J. F. Harrison, *J. Amer. Chem. Soc.*, **93**, 4112 (1971).
(20) W. Mathews, *J. Chem. Phys.*, **45**, 1068 (1966).

orbitals of the *ground state* of carbon *atom*. There are four spatially separated orbitals associated with the atom, each of which can be involved in a different bond. Moreover, the geometries and symmetries of the low-lying states of CH_n and CF_n (including the radicals) can be understood on the basis of simple considerations of the *atomic* GVB orbitals with proper inclusion of the effects arising from the Pauli principle. This GVB model is derived directly from rigorous quantum mechanical considerations and hence can be considered as the theoretical foundation for many of the concepts normally used in the description of chemical bonding (*e.g.*, localized orbitals, hybridization, etc.).

The GVB Description of Ozone

Our next illustration of the GVB analysis of electronic structure will be directed toward the states of O_3, a molecule isoelectronic with CF_2. We will find that these two isoelectronic systems have quite different electronic structures.

Consider first an O atom, which has four electrons in three p orbitals so that one p orbital is doubly occupied while the other two are singly occupied (as indicated in the earlier discussion). Taking two such atoms we couple two of the singly occupied p orbitals to form a σ bond. As shown in Figure 7a, there are two ways to combine the O $p\pi$ orbitals.

In case A we combine a singly occupied $p\pi_x$ orbital on the left atom with a doubly occupied $p\pi_x$ orbital of the right atom and a doubly occupied $p\pi_y$ orbital on the left atom with a singly occupied $p\pi_y$ on the right atom (see A in Figure 7a). The singly occupied π_x orbital on the left O atom must acquire antibonding character to become orthogonal to the pair of occupied π_x orbitals on the right. In addition, this doubly occupied $p\pi_x$ pair on the right O atom can effectively reduce its electron–electron interactions by delocalizing onto the left O atom, just as was true for the F $p\pi$ orbitals in CF. Thus with a second (left) O atom present, we expect the right O $p\pi$ pair to delocalize onto the second center (called back-bonding in CF). In O_2 this effect should be very strong since the centers are equivalent. This effect is reinforced by the antibonding character of the singly occupied $p\pi_x$ orbital on the left which leads to a decrease in the shielding of the left nucleus. The net effect of the interactions involving these three $p\pi_x$ O electrons is bonding (probably by about 30 kcal). Exactly the same situation prevails for the three O $p\pi_y$ electrons (so that the total π bonding is about 60 kcal).

In case B the two singly occupied $p\pi_x$ orbitals are coupled into a π bond, but there is now a significant overlap between the doubly occupied π_y pairs of the two oxygen atoms. As a result each doubly occupied π_y pair must readjust to get orthogonal to the other π_y pair, and hence all four of these orbitals acquire antibonding character. Because of these bad pair–pair repulsions in case B, we expect case A to be more stable.

Since there are two singly occupied π orbitals in A, we can form both a singlet state and a triplet state. The singly occupied orbitals are orthogonal, so that the triplet state is lower in energy (due to the exchange interaction, just as in Hund's rule). This is
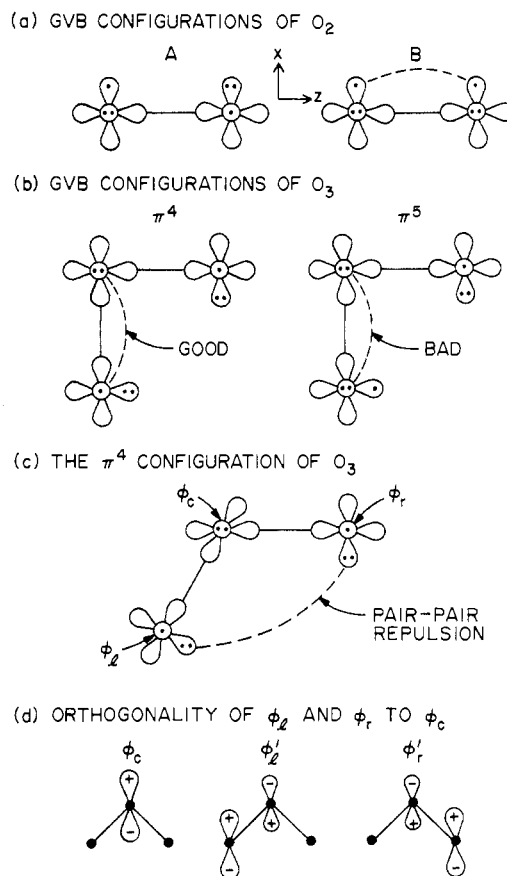

Figure 7. (a) The bonding GVB configurations of O_2. (b) The bonding GVB configuration of ozone. The upper two O atoms represent the original O_2 molecule to which the lower O atom is added, resulting in the two configurations shown. (c) The π^4 configuration of ozone. (d) Orthogonality effects for the π orbitals of ozone. Orbitals $\phi_{l'}$ and $\phi_{r'}$ result from orthogonalizing atomic orbitals ϕ_l and ϕ_r to ϕ_c.

the GVB explanation[21] of the triplet ground state of O_2.

Now we bring in a third O to form O_3 as in Figure 7b (here the lower O atom is taken as the new one). Combining singly occupied orbitals into a σ bond, we can form two configurations (π^4 and π^5) depending on the occupation of the π orbitals of the new O. (In this section we use the normal convention of letting π indicate orbitals antisymmetric with respect to the molecular plane; thus the $p\pi_y$ orbitals of O_2 become π orbitals of O_3, but the $p\pi_x$ orbitals of O_2 are now called σ orbitals of O_3.) The significant difference between these two configurations is to be found in the π interactions (marked good and bad in Figure 7b). In the π^5 case there is a π pair–π pair repulsion, just as for case B of O_2 (Figure 7a), whereas in the π^4 case the corresponding interactions are of the more favorable π pair–π electron type, as in case A of O_2 (Figure 7a). Thus the π^4 case should be the ground configuration of ozone.

In Figure 7c we consider this π^4 case more carefully. There are two singly occupied orbitals (ϕ_l and ϕ_r); hence we obtain a singlet state (S) and a triplet

(21) The correct prediction of the triplet ground state of O_2 by R. S. Mulliken [*Phys. Rev.* **32**, 213 (1928)] is properly considered as a major early success of the MO approach. It is often stated that the VB approach leads to the incorrect prediction of a singlet ground state for O_2. However, we see from the discussion in the text that proper inclusion of the Pauli principle in the VB analysis leads to the correct prediction of a triplet ground state.
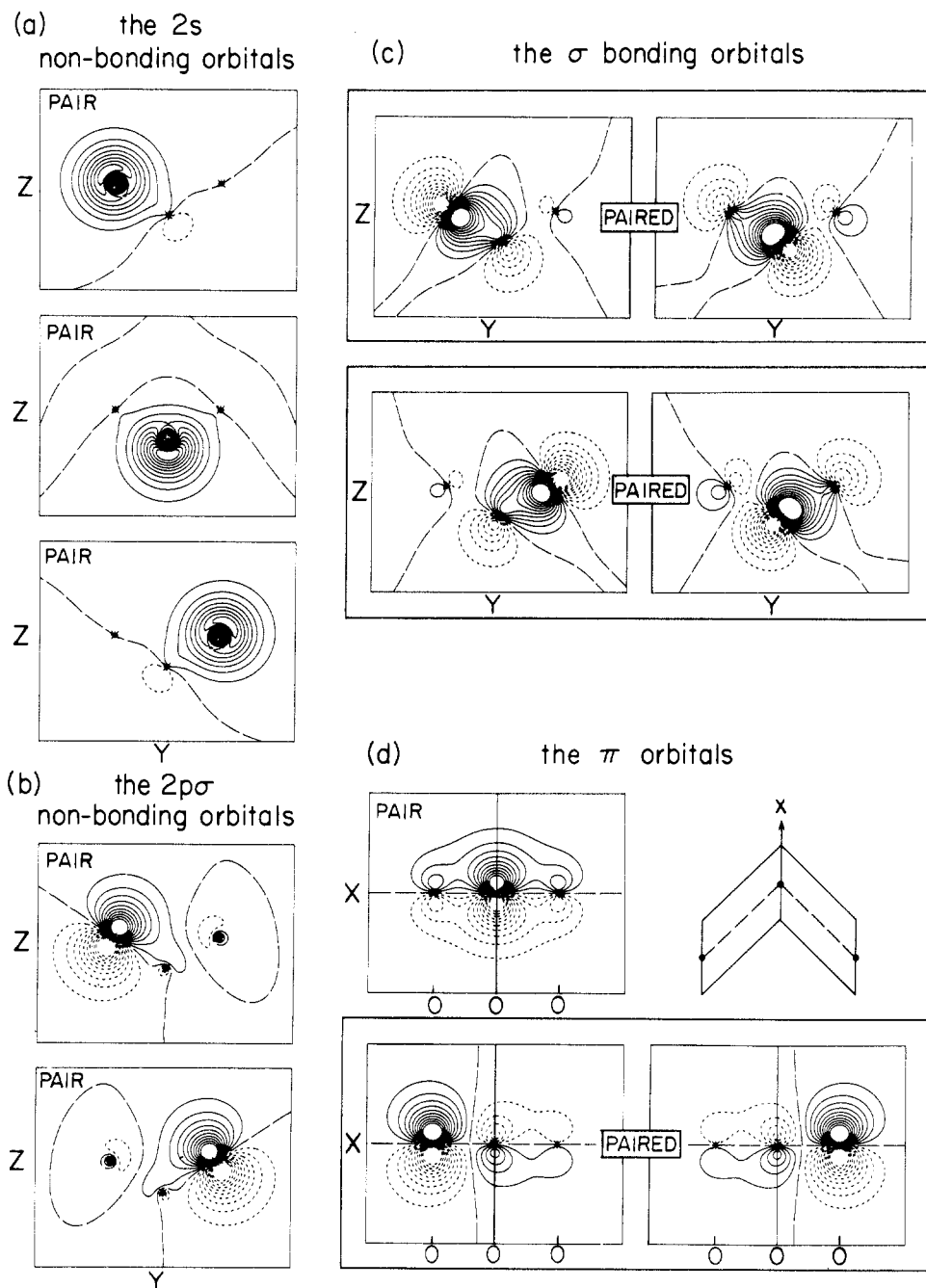
OZONE ($^1A_1$)

(a)   the 2s non-bonding orbitals

(b)   the 2pσ non-bonding orbitals

(c)   the σ bonding orbitals

(d)   the π orbitals

Figure 8. The calculated GVB orbitals of ozone ($^1A_1$ state). These orbitals are coupled as in Figure 7c. The contour increment is 0.05 au.

state (T). Since these orbitals overlap, the singlet state is expected to be lower. (This case is analogous to that of H plus H at large R (2 to 4 Å) where the orbital overlap is small but leads to the S state below the T state.) Even so, two orbitals this far apart ($\sim$4.2 Å) would normally have small overlap ($\sim$0.03 Å), and hence one might expect only a small separation between the S and T states. However there is a significant new feature in the π^4 configuration of ozone (as compared to the case of H_2 at large R). Namely, each of the singly occupied orbitals (ϕ_1 and ϕ_r in Figure 7c) has a repulsive (antibonding) interaction with the doubly occupied π pair (ϕ_c) on the central oxygen. This has two major effects. (i) Each singly occupied π orbital readjusts to become orthogonal[11] to the central pair of π orbitals ϕ_c as in-

dicated in Figure 7d, where the adjusted orbitals are labeled as ϕ_1' and ϕ_r'. This in turn leads to a much higher overlap (S = 0.10) between the readjusted singly occupied orbitals, ϕ_1' and ϕ_r'. (ii) The central pair of orbitals ϕ_c delocalizes onto the outer O atoms, just as in case A of O_2. This in turn leads to greater antibonding character of ϕ_1' and ϕ_r' and greater overlaps (the overlap $\langle \phi_1' | \phi_r' \rangle$ for the self-consistent GVB orbitals is 0.28).

As a result of (i) and (ii) the singlet state (S) is much lower (0.7 eV) than the triplet state (T). Thus the singly occupied orbitals ϕ_1 and ϕ_r are strongly coupled through an intervening doubly occupied orbital pair (ϕ_c), an interaction resulting basically from the Pauli principle. This type of coupling is also responsible for the magnetic coupling in solids usual-
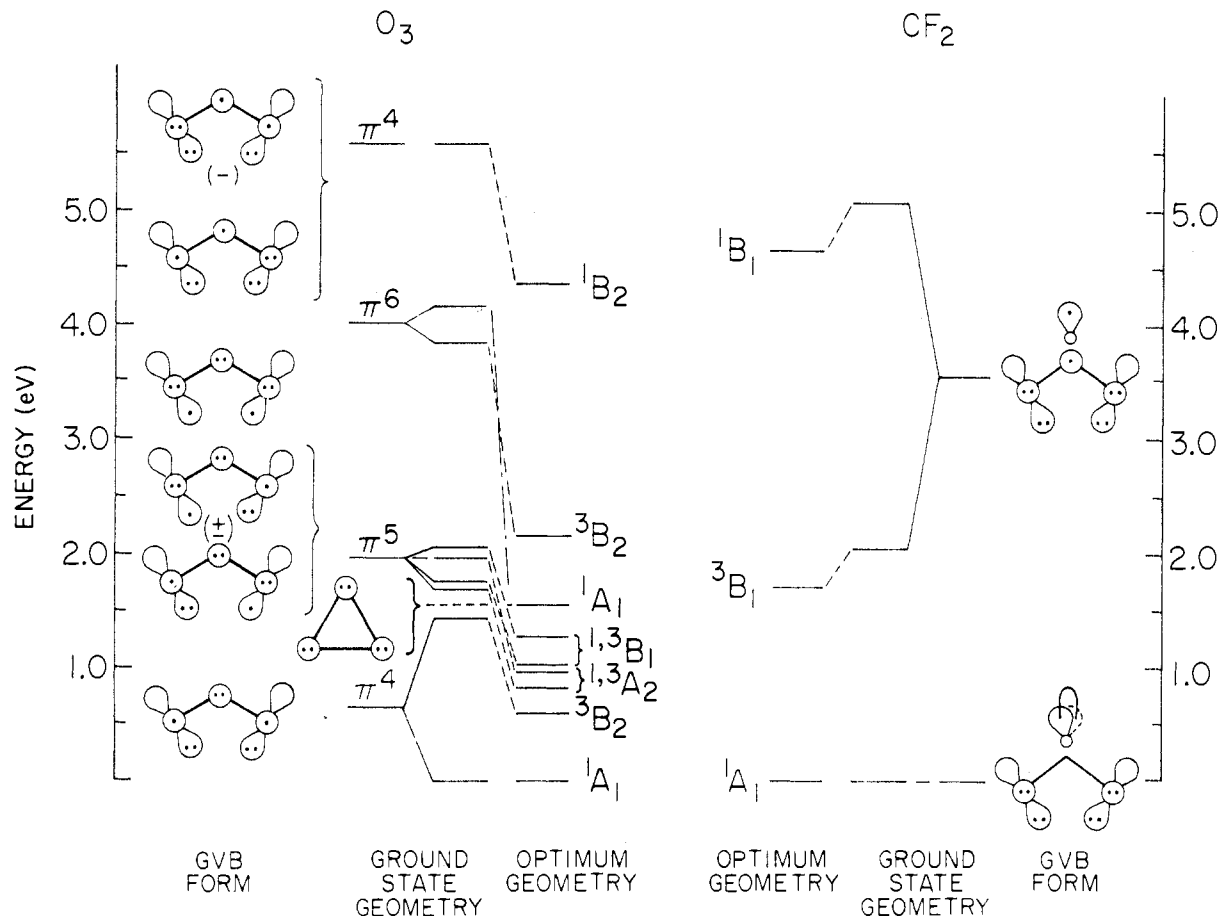
Figure 9. Comparison of the excited states of CF_2 and O_3. The energies shown are based upon the theoretical calculations. The GVB configurations for the various states are included at the left and right. In two cases for ozone (π^5 and the ionic π^4 case), there are two equivalent GVB configurations which are combined to yield the total wave function.

ly referred to as superexchange[22] and is furthermore responsible for the coupling of remote orbitals in diazines discovered by Hoffmann and called through-bond coupling.[23] It may also be the dominant feature in the bonding of hypervalent compounds (*e.g.*, ClF_3, ClF_5, XeF_2, SF_4, etc.). The self-consistent GVB π orbitals[24] for O_3 are shown in Figure 8d.

Finally we consider the manifold of excited states of O_3. Starting with the ground state π^4 configuration (lowest configuration on the left of Figure 9) and exciting an electron from a doubly occupied O p orbital in the plane to the singly occupied O p orbital perpendicular to the plane leads to two equivalent π^5 configurations (as in Figure 7b), each of which has a bad π pair–π pair interaction, increasing the energy by ~1.5 eV. This leads to two singlet and two triplet states [$^{3,1}A_2$,$^{3,1}B_1$], as in Figure 9, separated by only a few tenths of an electron volt.

A similar additional excitation on the opposite terminal atom leads to the π^6 configuration of Figure 9; this gives rise to new $^1A_1$ and $^3B_2$ states at ~4 eV (if we retain the ground-state geometry). In the new $^1A_1$ state (denoted as 2^1A_1 to distinguish it from the ground state) the two singly occupied orbitals can bond. This bonding interaction will decrease the

bond angle and the optimum geometry for this state has a bond angle of 60° (the ring state),[25,26] leading to an energy of only 1.5 eV[24,26] above the ground state.

If the ozone orbitals involved in the above transition were pure atomic orbitals, these transitions would all be dipole forbidden. The orbitals distort somewhat from their atomic character, but the transitions remain weak ($f \sim 10^{-4}$ for the allowed $\pi^4 \rightarrow \pi^5$ case). In order to find a strong transition we must examine charge-transfer excitations. The most important one involves a transition from the doubly occupied π pair of the central O to one of the singly occupied orbitals of the terminal O (see Figure 9). This leads to two excited states, $^1B_2$ and $^1A_1$ (this is the third $^1A_1$, *i.e.*, 3^1A_1), and the transition from the ground state to either should be strong ($f \sim 0.1$). The $^1B_2$ state is responsible for the strong Hartley band[27] (peak at 5 eV) and the higher 3^1A_1 state is probably associated with the absorption bands around 6.5 eV.

The above conclusions about the electronic structure of ozone arise quite naturally from the GVB considerations, and in fact all the qualitative features were predicted in this way before the *ab initio*

(22) P. W. Anderson, *Solid State Phys.*, **14**, 99 (1963); see also P. J. Hay and W. A. Goddard III, to be published.

(23) R. Hoffmann, *Accounts Chem. Res.*, **4**, 1 (1971).

(24) W. A. Goddard, T. H. Dunning, and P. J. Hay, submitted for publication in *J. Amer. Chem. Soc.*

(25) R. Hoffmann (private communication); S. D. Peyerimhoff and R. J. Buenker, *J. Chem. Phys.*, **47**, 1953 (1967), and E. F. Hayes, G. V. Pfeiffer, *J. Amer. Chem. Soc.*, **90**, 4773 (1968), have also suggested that ozone might have a metastable ring form.

(26) P. J. Hay and W. A. Goddard III, *Chem. Phys. Lett.*, **14**, 46 (1972).

calculations. This system is an example of a case where neither VB nor MO considerations[27,28] were able to lead to good predictions of the electronic structure. (Using the ground-state geometry, the HF method predicts that the ground state of O_3 is the $^3B_2(\pi^4)$ state and places the $^1A_1\pi^4$ state as the third electronic state, 2.2 eV *above* the lowest triplet state.[24]) In addition, the experimental situation was also sufficiently complicated[27] that the nature and location of most of the electronic states were not established before the GVB considerations.[26]

The GVB descriptions of the excited states of O_3 and CF_2 are summarized in Figure 9. We see that the differences between the two molecules are great, none of the states corresponding very closely. On the other hand, in the MO description one would use the same Walsh diagram[2,27] for describing both molecules, leading one to expect a similar spectrum for each. In fact, earlier MO analyses[28] had suggested that the state at 5 eV in CF_2 is of $^1B_2$ symmetry, just as for O_3. However, Mathews[20] showed that this state is $^1B_1$. Similar MO analyses[3,28] of O_3 did not predict the low-lying $^3B_2$ state, nor the $^{3,1}A_2$ states, nor the 2^1A_1 and 2^3B_2 states. This illustrates a particular advantage of the GVB view in that it emphasizes the local atomic character of the orbitals and hence accounts for the *chemical* effects (that is, the difference between F and O and between C and O) upon the electronic structure.

Summary

Herein we have considered a few representative molecular systems in order to indicate how simple generalized valence bond considerations can lead to useful qualitative predictions concerning the geometries and states of polyatomic molecules.

The basic approach is to start with the orbitals of the atoms and to examine how these orbitals can be combined to form bonding states of molecules. This contrasts sharply with the MO approach in which one starts with a molecular framework, forms molecular orbitals, and then occupies these orbitals with electrons.

The GVB approach differs from the usual VB considerations in that, rather than using the HF representation of the atom, we also treat the atom in a VB manner. For some atoms (*e.g.*, H, O, and F) this does not lead to significant changes, but for others (*e.g.*, Be, B, and C) it does. In fact, it is because we allowed a VB description of the atom that the ground state of carbon atom exhibits *four* orbitals appropriate for bonding. This contrasts with the usual VB rationalization of the tetravalence of car-bon, which is attributed to the carbon in the molecule having the sp³ configuration appropriate for certain excited states of C atom.

A second major difference between the GVB and VB views is that the GVB orbitals are allowed to distort under the influence of the other orbitals of the system rather than taken as (fixed) atomic orbitals. This allows us to consider just the one basic set of GVB atomic orbitals (for each atom) and yet to account for various molecular effects (pair-pair repulsion, through-bond coupling, etc.) through consideration of the distortions of these orbitals induced by the molecular environment. In the usual VB description, effects similar to those obtained by allowing molecular distortions of the GVB orbitals can only be included by introducing extra VB structure diagrams (as in C—F, C⁺F⁻, C=F⁺), significantly complicating both the computation and interpretation of the wave function. Allowing for the SCF adjustment of the atomic orbitals takes these effects into account in an effective and efficient manner.

An important feature of the GVB qualitative description is that it is derived from an accurate method (the GVB method) for quantitative calculations. Thus for systems which are not understood, we can (often) carry out quantitative calculations which can be analyzed in terms of simple qualitative concepts that can in turn generate a more complete understanding of the electronic structure (and reactions[29]) of molecules. Thus for O_3 and CF_2 the qualitative GVB predictions were made *before* the detailed calculations and led to the correct ordering of the ground and excited states. However, analysis of the detailed shapes of the orbitals from the GVB calculations led to additional insights, and the confirmation of the correctness of the interpretation gave us the confidence to make predictions on even more complicated systems. (In contrast, earlier molecular orbital considerations had led to rather different and incorrect predictions.)

The objective in developing such qualitative models is to enable us to make predictions on systems far too large for rigorous calculations. Ultimately one would hope to be able to predict not only bonding, geometries, and energies of the ground and excited states of molecules but also the energetics and mechanisms of the reactions of both the ground and excited states of molecules.

(27) G. Herzberg, "Electronic Spectra of Polyatomic Molecules," Van Nostrand, New York, N. Y., 1966.
(28) R. S. Mulliken, *Can. J. Chem.*, **36**, 10 (1958).

(29) W. A. Goddard III, *J. Amer. Chem. Soc.*, **94**, 793 (1972).