

Self-Consistent Procedures for Generalized Valence Bond Wavefunctions. Applications H_3 , BH , H_2O , C_2H_6 , and O_2 *

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Methods of efficiently optimizing the orbitals of generalized valence bond (GVB) wavefunctions are discussed and applied to LiH , BH , H_3 , H_2O , C_2H_6 , and O_2 . The strong orthogonality and perfect pairing restrictions are tested for the $X^1\Sigma^+$ state of LiH , the $X^1\Sigma^+$, $a^3\Pi$, and $A^1\Pi$ states of BH , and the $H_2 + D \rightleftharpoons H + HD$ exchange reaction. The orbitals of H_2O and C_2H_6 naturally localize into OH , CH , and CC bonding pairs. The nonbonding orbitals of H_2O are approximately tetrahedral but this description is only 2 kcal lower than the optimum description in terms of σ and π lone-pair functions. The calculated rotational barrier for C_2H_6 is 3.1 kcal, in good agreement with the experimental value (2.9 kcal). The description of the O_2 molecule in the GVB approach is presented and the results of carrying out CI calculations using the GVB orbitals are discussed. The GVB orbitals are found to be a good basis set for configuration interaction calculations. The general features of GVB orbitals in other molecules are summarized.

I. INTRODUCTION

The electronic structure of molecules is usually described in terms of either the molecular orbital (MO) or valence bond (VB) models. In particular, the single-configuration MO (or Hartree-Fock) wavefunction has proved extremely useful in computing properties of ground and excited state molecules. Configuration interaction studies have shown that for typical molecules near the equilibrium geometry the Hartree-Fock wavefunction is by far the most important configuration in the "exact" wavefunction. Conceptually, such advances as Walsh diagrams¹ for predicting molecular geometries and the Woodward-Hoffmann rules² for predicting chemical reactions have their origins in molecular orbital theory.

There are, however, at least two serious drawbacks to the Hartree-Fock model:

(1) Molecular orbitals do not usually dissociate correctly, so that one cannot describe bond-breaking processes within this model.

(2) Molecular orbitals have the full symmetry of the molecule and bear little resemblance to the expected shapes of bond orbitals and lone-pair orbitals.³

Our objective here is to discuss an improved SCF method which is tractable and yet removes these serious deficiencies of MO theory. The emphasis will not be on getting 100% of the correlation energy. Rather the aim will be to obtain a generally useful orbital representation for describing molecular bonding and chemical reactions.

II. THE WAVEFUNCTIONS

A. Basic Approach

The Hartree-Fock (HF) wavefunction for (a closed shell) singlet state has the form

$$\alpha(\phi_1\alpha\phi_1\beta\phi_2\alpha\phi_2\beta\cdots\phi_n\alpha\phi_n\beta), \quad (1)$$

with each orbital appearing twice (doubly occupied). This double occupation of the orbitals leads to some of the deficiencies of the HF procedure, and several approaches, the spin coupling optimized GI(SOGI) method,^{4a} the spin-optimized SCF (SO SCF) method,^{4b} and the best radial natural orbitals (BRNO) method,^{4c} have been proposed in which the pair

$$\phi_i\alpha\phi_i\beta$$

is replaced by

$$\phi_{ia}\alpha\phi_{ib}\beta$$

to yield the wavefunction

$$\alpha(\phi_{1a}\phi_{1b}\phi_{2a}\phi_{2b}\cdots\chi), \quad (2)$$

where χ is allowed to be a general N -electron spin function and where χ and the orbitals ϕ_i are solved for self-consistency. This approach leads to the proper description of bond breaking⁵ and leads directly to localized bonding and nonbonding orbitals (*vide infra*).

One reason for the simplicity of Hartree-Fock calculations is that the orbitals of (1) can be taken as orthogonal. Unfortunately this is not the case for wavefunctions of the form (2) (where χ is a general N -electron spin function). This lack of orthogonality leads to significant computational problems for large systems and greatly restricts the usefulness of such approaches. We would like to retain the conceptual usefulness of wavefunctions of the form (2) and yet simplify the calculations so that reasonably large molecules can be considered. Most of the basic restrictions and approaches to be used have been suggested elsewhere,^{6,7} but are summarized here to clarify our later discussions:

(i) The spin function χ is taken to be

$$\chi_{VB} = [\alpha(1)\beta(2) - \beta(1)\alpha(2)] \\ \times [\alpha(3)\beta(4) - \beta(3)\alpha(4)] \cdots,$$

where for a state of spin S the last $2S$ spins are α . This

spin function is the one used in GI⁸ and simple valence bond⁹ wavefunctions. With restriction (i) the wavefunction (2) can be rewritten as

$$\alpha[(\phi_{1a}\phi_{1b} + \phi_{1b}\phi_{1a})(\phi_{2a}\phi_{2b} + \phi_{2b}\phi_{2a}) \cdots \times (\phi_{na}\phi_{nb} + \phi_{nb}\phi_{na})\alpha\beta\alpha\beta \cdots \alpha\beta], \quad (3)$$

where each term in parentheses is said to be singlet paired.

(ii) The various orbitals are required to be orthogonal to each other unless they are singlet paired, i.e.,

$$\langle \phi_{ia} | \phi_{ib} \rangle \neq 0, \\ \langle \phi_i | \phi_j \rangle = 0 \quad \text{otherwise.}$$

This restriction has often been used for wavefunctions and is known as the *strong orthogonality*¹⁰ or separated-pair^{11,12} restriction.

(iii) The orbitals of (3) are solved for self consistency. The wavefunction (3) has the form of a simple valence bond (VB) function, the difference being that in (3) the orbitals are solved for self-consistency rather than being taken as (hybridized) atomic orbitals as in VB. For this reason we refer to the wavefunction (3) as the *generalized valence bond* (GVB) wavefunction.

Wavefunction (3) is a special case of the strongly orthogonal geminal¹² wavefunction

$$\alpha[\Omega_1(1, 2)\Omega_2(3, 4) \cdots \chi_{\text{VB}}], \quad (4)$$

where each geminal Ω_i can be expanded in terms of natural orbitals,¹³

$$\Omega_i(1, 2) = \sum_{j=1}^P C_{ji}\phi_{ji}(1)\phi_{ji}(2). \quad (5)$$

The ideas of representing electron pairs in this form were originally formulated by Hurley, Lennard-Jones, and Pople⁶ (HLJP), who discussed the strong orthogonality restriction as well as the representation of pair functions in both the natural orbital (5) and generalized valence bond (3) forms.

In terms of natural orbitals,¹³ each pair function of (3) has the form

$$\phi_{ia}(1)\phi_{ib}(2) + \phi_{ib}(1)\phi_{ia}(2) = C_{1i}\phi_{1i}(1)\phi_{1i}(2) \\ + C_{2i}\phi_{2i}(1)\phi_{2i}(2), \quad (6)$$

that is, only two natural orbitals are used for each pair function.¹⁴ Substituting (6) into (3) we find that the expansion of (3) in terms of those natural orbitals contains only terms of closed shell form. As discussed below this leads to great simplification in the calculations.

There are many cases in which we will want to keep some pairs doubly occupied rather than allowing them to be split. In such cases we take

$$C_{1i} = 1 \quad \text{and} \quad C_{2i} = 0$$

in (6). In addition, for nonsinglet states of spin S we will usually take the last $2S$ orbitals to be unpaired and with the same spin.

B. The Equations

As has been shown by HLJP and Kutzelnigg,⁷ the dependence of the energy in (3) upon the orbitals of pair i has the form

$$E = E_{(i)} + f_{1i}\langle \phi_{1i} | (2h_{\text{eff}} + J_{1i}) | \phi_{1i} \rangle \\ + f_{2i}\langle \phi_{2i} | (2h_{\text{eff}} + J_{2i}) | \phi_{2i} \rangle + C_{1i}C_{2i}\langle \phi_{1i} | K_{2i} | \phi_{1i} \rangle, \quad (7)$$

where $E_{(i)}$ is independent of the orbitals in pair i ,

$$h_{\text{eff}} = h + \sum_{j \neq 1i, 2i} f_j(2J_j - K_j)$$

and

$$f_k = 1 \quad \text{for a double occupied orbital} \\ = \frac{1}{2} \quad \text{for an open-shell singly occupied orbital} \\ = C_k^2 \quad \text{for a natural orbital of a split pair as in (6).}$$

Here h_{eff} is analogous to the usual Hartree-Fock one-electron Hamiltonian except that it contains no terms due to either orbital of pair i . For a nonsinglet state of spin S there will be $2S$ orbitals corresponding to the unpaired spins; these orbitals are referred to as open-shell orbitals ($f_k = \frac{1}{2}$). Any number of the pairs can be double occupied ($f_k = 1$).

Separating from E_i the terms involving the other pairs, we obtain the general expansion

$$E = \sum_k f_k h_k + \sum_{k,l} (a_{kl}J_{kl} + b_{kl}K_{kl}), \quad (8)$$

which has the form appropriate for general HF and many types of MC SCF wavefunctions. [In (8) $h_k \equiv \langle k | h | k \rangle$ and J_{kl} and K_{kl} are the normal Coulomb and exchange integrals.]

Using the variational principle, one obtains the self-consistent field equations^{8,15b}

$$\tilde{H}_k \phi_k = [H_k - \sum_{j \neq k} |j\rangle \langle j| H_j] \phi_k = \epsilon_k \phi_k, \\ k = 1, 2, \dots, M, \quad (9)$$

where $H_k = f_k h + \sum_l a_{kl}J_l + b_{kl}K_l$ and M is the number of distinct orbitals. (J and K are the usual Coulomb and exchange operators from HF theory.) In general, there are fewer than M such equations to solve, since all doubly occupied orbitals can be taken as eigenfunctions of the same closed-shell Hamiltonian.

In the homogeneous approach normally used in solving SCF equations,¹⁶ one explicitly constructs each \tilde{H}_k for a set of trial functions $\{\phi^0\}$ and solves (9) for the ϕ_k to use in the next iteration. We have found this approach to be unsatisfactory and instead we use the method suggested in Ref. 15(c) where each iteration

consists of three distinct steps:

(1) The Hamiltonian matrices \mathbf{H}_k are constructed using the trial functions $\{\phi_j^0\}$ and trial CI coefficients $\{C_i^0\}$, and a new set of CI coefficients is obtained by solving the 2×2 matrix equations for each pair.

(2) Each Hamiltonian matrix \mathbf{H}_k is diagonalized according to the orthogonality constrained basis set expansion (OCBSE)^{15a} procedure. In this approach the eigensolutions of \mathbf{H}_k are obtained in the space orthogonal to the vectors of shells k' , where $k' \neq k$, thereby avoiding the necessity of using coupling operators in the SCF equations.

(3) Since step (2) does not permit mixing of occupied orbitals of shell k with occupied orbitals of other shells, we obtain this optimum mixing by using the set of old orbitals $\{\phi_i^0\}$ as a basis for the expansion of the new (unknown) orbitals $\{\phi_i\}$,

$$\phi_i = \phi_i^0 + \sum_{v>i} \phi_v^0 \Delta_{vi} - \sum_{v<i} \phi_v^0 \Delta_{iv},$$

and optimize the mixing of occupied orbitals with each other by solving for the correction coefficients

$$\{\Delta_{vi}, v > i, i = 1, M\}$$

as in Ref. 15(c). Since this procedure optimizes the mixing of natural orbitals, terms such as

$$C_{12}(\phi_1 \phi_2 + \phi_2 \phi_1)$$

need not appear in the expansion [Eq. (6)] of the GVB pair.

The above iterative procedure ensures that when the SCF equations have converged, one has obtained the optimum set of orbitals. Although for step (2) the orbitals of shell k are restricted to be in a space orthogonal to the orbitals of other shells, this space changes from iteration to iteration as the occupied orbitals mix in virtual orbital components in step (2) and occupied orbital components in step (3). This differs from some previous strongly orthogonal geminal calculations¹⁷⁻¹⁹ where each geminal was obtained in a partitioned subspace of the basis, but where the partition was imposed at the beginning of the calculation and not optimized.

C. Comparison with Other Methods

With the exceptions of strongly orthogonal geminal calculations on small diatomic molecules^{7,12,20} and of several multiconfiguration SCF calculations,^{16,21-23} previous calculations on wavefunctions of the form (3) have not optimized the orbitals within a given basis to a level comparable to the degree of convergence obtained in Hartree-Fock calculations.

Several types of calculations have been carried out using strongly orthogonal geminals as in (4) including approximate treatments by McWeeny and Ohno¹⁹ on

the water molecule and Parks and Parr¹¹ on formaldehyde. Silver, Mehler, and Ruedenberg¹² obtained fully optimized SOG wavefunctions for Be, LiH, BH, and NH using more than two NO's in each geminal, and Scarzafava²⁴ carried out similar calculations on H₂O. Ahrlich and Kutzelnigg^{7,20} also used a procedure similar to ours on Be and LiH.

Calculations by Franchini *et al.*¹⁷ have employed the procedure of localizing the Hartree-Fock orbitals and expanding each geminal in a CI wavefunction as in (5) with a fixed partition of the basis set. In this scheme, the orbitals are not fully optimized since the space available to each geminal was arbitrarily determined before the calculation.

McWeeny and Klessinger^{18,25} have carried out minimum basis self-consistent group calculations on many molecules by starting with a set of symmetrically orthogonalized hybridized atomic orbitals and carrying out a two by two CI calculation on each geminal. Since the energy was optimized as a function of only one hybridization parameter per atom, the resulting orbitals were not completely optimum. For several molecules this has resulted in very poor descriptions of the barriers to internal rotation^{18b} (e.g., ethane is calculated to have a barrier of 5.1 kcal with the *eclipsed* configuration lower).

Wahl and Das²¹ have carried out extensive MC SCF calculations on a large number of first row diatomic molecules while including more general configurations than appear in GVB.

Although several authors have discussed ways of relaxing orthogonality constraints,^{26,27} the complications involved are excessive. Hinze^{28,29} has developed an approach for general MC SCF wavefunctions in which the mixings of occupied orbitals with each other are optimized through successive 2×2 rotations, leading to fully optimized orbitals.

Harrison and Allen³⁰ have used VB configurations with orbitals based on atomic HF calculations not solving for the optimum VB orbitals. Multiconfiguration techniques for diatomic molecules using elliptic basis functions were discussed by Taylor and Harris.³¹ VB CI methods have also been used on LiH and BeH⁺ by Miller *et al.*³² and on He₂ potential curves by Klein³³ and Gupta and Matsen.³⁴

Particularly promising approaches are the MC SCF method as developed by Wahl and Das²¹ and the use of iterative natural orbitals in conjunction with a standard scheme for generating configurations (INO CI) as developed by Schaefer and Bender.^{35,36}

The GVB method is related to these INO CI and MC SCF methods but is more restricted since the wavefunction must have a form compatible with a valence bond type wavefunction. The emphasis in the GVB approach is more on using these orbitals to understand the role of electronic structure in chemical processes (such as chemical reactions). However, as

discussed in Sec. VI (for O₂), the GVB orbitals can be used to construct a simple CI wavefunction with results similar to (but still less extensive than) those obtained with the MC SCF and INO CI methods.

III. TESTS OF STRONG ORTHOGONALITY AND "PERFECT PAIRING"

In order to test the validity of the restrictions involved in GVB calculations, we will compare the results of GVB and SOGI calculations for several systems. This forms a useful test of both the strong orthogonality and perfect pairing restrictions, since neither restriction is made in the SOGI method.

A. LiH and BH (¹Σ⁺)

For a four-electron singlet system, we can write the GVB and SOGI wavefunctions as

$$\psi_{\text{GVB}} = \alpha(\phi_{1a}\phi_{1b}\phi_{2a}\phi_{2b}\chi_1),$$

$$\psi_{\text{SOGI}} = \alpha[\phi_{1a}\phi_{1b}\phi_{2a}\phi_{2b}(\cos\theta\chi_1 + \sin\theta\chi_2)],$$

where χ_1 and χ_2 are the two linearly independent spin functions,

$$\chi_1 = \frac{1}{2}(\alpha\beta - \beta\alpha)(\alpha\beta - \beta\alpha),$$

$$\chi_2 = (2\sqrt{3})^{-1}[2\alpha\alpha\beta\beta + 2\beta\beta\alpha\alpha - (\alpha\beta + \beta\alpha)(\alpha\beta + \beta\alpha)].$$

In GVB the pair (ϕ_{1a}, ϕ_{1b}) is constrained to be orthogonal to pair (ϕ_{2a}, ϕ_{2b}) and the second spin function χ_2 is not used.

SOGI calculations on the ground states of LiH^{2,37} and BH⁵ have shown that contributions from spin functions other than χ_1 are negligible. Thus comparing SOGI and GVB for these systems is primarily a test of the strong orthogonality restriction. From Table I we see that for LiH at R_e , E_{GVB} is 0.0296 hartree lower than E_{HF} and only 0.0008 hartree higher than E_{SOGI} . Similar results were also obtained for BH at R_e where E_{GVB} was only 0.0018 hartree greater than E_{SOGI} while 0.045 hartree lower than E_{HF} . In comparing the GVB and SOGI orbitals of these systems (see Fig. 1 for BH), we find that the main effect involves orthogonality of the GVB valence orbital to the core orbitals; the

TABLE I. Comparison of HF, GVB, and SOGI calculations on ground states of LiH ($R=3.015a_0$) and BH ($R=2.336a_0$).

	Energy (hartree)		D_e (eV)	Energy lowering	
	$R=R_e$	$R=\infty$		Pair	$\Delta\epsilon_i$ (hartree)
LiH					
HF ^a	-7.98326	-7.93123	1.42
GVB ^b					
1 pair	-8.00054	-7.93123	1.89	bond	-0.01728
2 pair	-8.01289	-7.94336	1.89	bond	-0.01710
				core	-0.01249
SOGI ^{b,c}	-8.01369	-7.94435	1.89
Exptl ^d			2.52		
BH					
HF ^a	-25.12820	-25.01790	2.73
GVB ^e					
2 pair	-25.16542	-25.04735	3.21	bond	-0.01443
				lone	-0.02279
3 pair	-25.17769	-25.0599	3.21	bond	-0.01436
				lone	-0.02276
				core	-0.01236
SOGI ^{e,f}	-25.18014	-25.06119	3.24
Exptl ^g			3.56		

^a Cade and Huo [J. Chem. Phys. **47**, 614 (1967)], using a more extensive basis, obtain $E = -7.9873$ and $D_e = 1.49$ for LiH and $E = -25.13137$ and $D_e = 2.77$ for BH.

^b Using a basis consisting of nine s functions⁴⁴ and three p functions on the Li contracted to a (4s, 2p) set plus four s functions and two p functions on the H contracted to (3s, 1p).

^c Palke and Goddard [J. Chem. Phys. **50**, 4524 (1969)], using a more extensive basis, obtain $E = -8.0173$ and $D_e = 1.90$.

^d See Ref. 45 and R. Velasco, Can. J. Phys. **35**, 1204 (1957).

^e Using the DZP basis from Ref. 5(b).

^f See Ref. 5(b).

^g P. G. Wilkinson, Astrophys. J. **138**, 614 (1967).

^h The energy lowering due to splitting the one pair.

TABLE II. Comparison of GVB and SOGI calculations for (a) the transition state of the $H_2+D \rightleftharpoons H+HD$ reaction at $R_{12}=R_{23}=1.8a_0$ and (b) the $^3\Pi$ and $^1\Pi$ states of BH.

	Energy (hartree)		Barrier height (kcal/mole)
	$R_{12}=R_{23}=1.8a_0$	H_2+D	
HF	-1.5930	-1.6335	25
GVB			
rlu^b	-1.5936	-1.6517	36
$gg'u^b$	-1.6035	-1.6517	30
GVB CI (3BF) ^c	-1.6178	-1.6517	21
SOGI ^d	-1.6240	-1.6517	17
CI ^e	-1.6521	-1.6696	11

	Energy (hartree)	
	$R=2.25a_0$	$R=4.0a_0$
BH $^3\Pi$		
HF	-25.11333	-25.01847
GVB	-25.12413	-25.03240
GVB CI (4BF)	-25.12800	-25.03742
SOGI ^f	-25.12874	-25.04170
BH $^1\Pi$		
HF	-25.03375	-25.02459
GVB	-25.04307	-25.03987
GVB CI (4BF)	-25.05400	-25.04964
SOGI ^f	-25.06285	-25.05242

^a Energy of saddle point ($R_{12}=R_{23}=1.8a_0$) relative to $H+HD$.

^b rlu and $gg'u$ refer to the two possible orbital configurations; see text for further discussion.

^c Complete CI using the GVB orthogonal orbitals.

^d Reference 4(a).

^e I. Shavitt, R. M. Stevens, F. L. Minn, and M. Karplus, *J. Chem. Phys.* **48**, 2700 (1968).

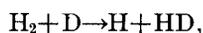
^f Reference 38.

GVB valence orbitals have a node in the core region. Otherwise the relative relationships between the valence orbitals are quite similar for these two methods. Thus we conclude that at least for these two systems the orbitals and energies are not greatly modified by the strong orthogonal restrictions.

We also carried out calculations in which the $1s$ orbitals of the LiH and BH were forced to be doubly occupied (but solved for self-consistency). Although in each case the energy is lowered about 0.012 hartree upon splitting the core orbitals, we find that this core splitting leads to a negligible modification in the valence orbitals. Thus, in the following calculations we will keep the $1s$ core orbitals paired [$f_k=1$ in (8)], but we will solve for them self-consistently with the valence orbitals.

B. $H_2+D \rightarrow H+HD$

A more significant test of the GVB approach is the description of the reaction



where SOGI calculations have shown^{4a} that the spin coupling changes from having a singlet-coupled electron pair on the H_2 for the reactants to a singlet-coupled electron pair on the HD for the products. Thus in the linear transition state with $R_{HH}=R_{HD}$, Ψ_{SOGI} contains equal contributions from the two (VB) spin couplings. GVB calculations at $R_{HH}=R_{HD}=1.8$ bohr using the Ladner^{4a} axis set yielded an energy 13 kcal/mole (0.021 a.u.) higher than E_{SOGI} (see Table II). This error in the GVB result is quite significant, being as large as for Hartree-Fock. (The calculated barrier height from the SOGI calculation is 16.9 kcal/mole.) However, the GVB orbitals have shapes somewhat similar to those of the SOGI orbitals as shown in Fig. 3. The GVB wavefunction has the form

$$\mathcal{A}[(gg'+g'g)u\alpha\beta\alpha],$$

where all orbitals have the full $D_{\infty h}$ symmetry of the molecule (g or u). An alternative description of the $^2\Sigma_u^+$ state, $\mathcal{A}[(ab+ba)u\alpha\beta\alpha]$ with a and b symmetrically related by mirror plane reflections but solved for self-consistency yielded an even higher energy.

To determine whether one can improve upon the GVB results for H_3 without a great deal of effort, we used the three GVB orbitals as a basis set and carried out an SOGI calculation. This is equivalent to a three basis function, three-electron CI calculation using all configurations. We find that this accounts for 69% of the error between GVB and SOGI, leading to a barrier 4 kcal greater than the SOGI barrier.

C. BH $^1\Pi$ and $^3\Pi$ States

Recent SOGI calculations³⁸ have shown that the lowest $^1\Pi$ and $^3\Pi$ states of BH also involve significant changes in spin coupling as the internuclear distance (R) is decreased from ∞ to V_e . Thus, this system serves as another good test case of the limitations of GVB. In the 2P state of B, Ψ_{GVB} has the form,⁵

$$\mathcal{A}\{[1s^2][sz, s\bar{z}]2p_x\alpha\beta\alpha\beta\}$$

where sz and $s\bar{z}$ have the form

$$sz = \phi_s + \lambda\phi_{pz},$$

$$s\bar{z} = \phi_s - \lambda\phi_{pz},$$

that is, these functions are sp -like hybridized orbitals polarized along the z axis.

In contrast to the $^1\Sigma$ state, where the $1s$ hydrogen orbital is singlet coupled to the px orbital, the Π states arise from breaking up the nonbonding pair to form the BH bond³⁸

$$^3\Pi: \psi_{GVB} = \mathcal{A}\{[1s^2][sz, h]s\bar{z}px\alpha\beta\alpha\beta\},$$

$$^1\Pi: \psi_{GVB} = \mathcal{A}\{[1s^2][sz, h][s\bar{z}, pz]\alpha\beta\alpha\beta\}.$$

Here we refer to the orbitals with symbols (sz , $s\bar{z}$, px , h) to denote their basic shapes, although each orbital is

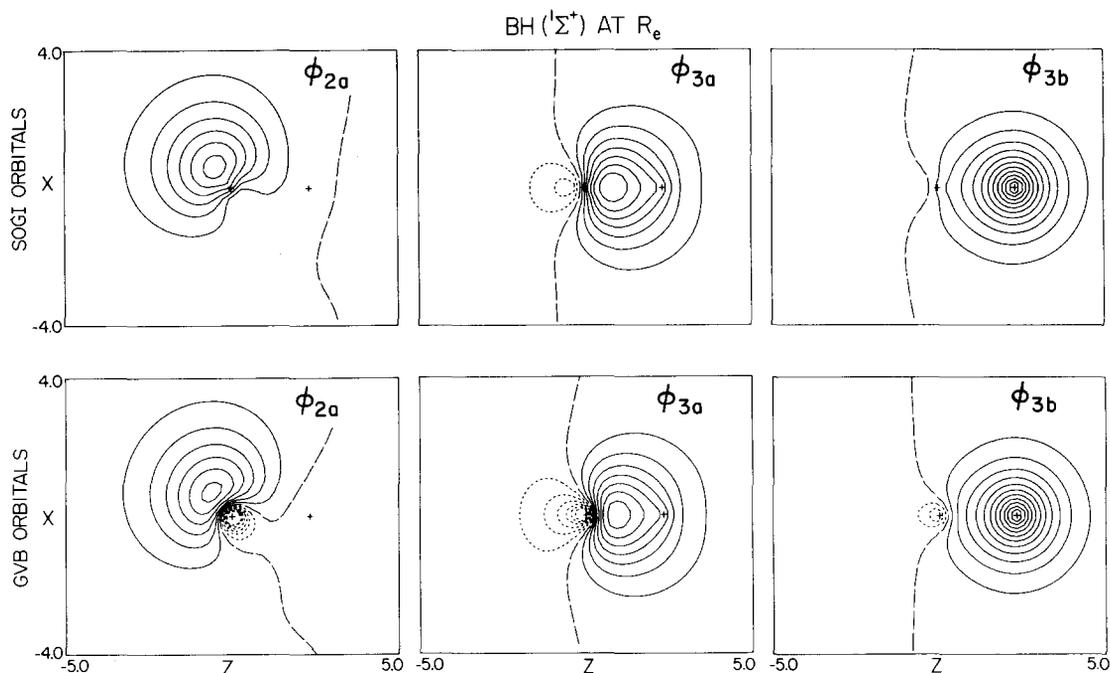


FIG. 1. Comparison of the SOGI and GVB orbitals for BH($^1\Sigma^+$). ϕ_{2a} is one of the two symmetrically related nonbonding orbitals. ϕ_{3a} and ϕ_{3b} are the bonding orbitals.

solved for self-consistency. From the results at $R=2.25$ and $R=4.0$ in Table II, it is seen that the GVB wavefunction is higher in energy than ψ_{SOGI} by amounts ranging from 0.0046 a.u. for the $^3\Pi$ state ($R=2.25$) to 0.0198 a.u. for the $^1\Pi$ ($R=2.25$).

The description of the $^1\Pi$ state is rather poor, and so we examined the improvements to be obtained by solving for the CI wavefunction using the four GVB orbitals as the basis. At $R=2.25a_0$ this accounted for 56% of the error between GVB and SOGI but still led to an energy 0.0088 greater than E_{SOGI} .

Another difficult case occurs in the $^2\Pi$ state of CH for large R . At $R=\infty$ the C atom is in the 3P state and hence two valence orbitals are coupled antisymmetrically. Coupling the H orbital symmetrically to the carbon p orbital is thus incorrect at large R . As a result, the GVB wavefunction for CH at large R is 0.35 eV above the limit of $C(^3P)+H(^2S)$. However, Bobrowicz³⁹ has shown that starting with the GVB orbitals and carrying out a three-basis-function CI (or SOGI) calculation leads to a proper description of the wavefunction at large R .

TABLE III. Comparison of calculations on the ethane molecule.^a

	Energy (hartree)			Barrier (kcal/mole)	Pair information			
	Staggered	Eclipsed	Pair		Energy lowering		Orbital overlap	
					Staggered	Eclipsed	Staggered	Eclipsed
This work								
HF	-78.8608	-78.8555	+3.3					
GVB	-78.9691	-78.9641	+3.1	CC bond	-0.0139	-0.0139	0.835	0.836
				CH bond	-0.0157	-0.0158	0.826	0.826
Klessinger^b								
HF	-78.9562	-78.9510	+3.3					
SCGF	-78.9641	-79.0188	-5.1					
Exptl^c			2.93					

^a The geometry used was taken to be that used by R. M. Pitzer and W. N. Lipscomb, J. Chem. Phys. **39**, 1995 (1963).

^b Reference 18(b).

^c S. Weiss and G. Leroi, J. Chem. Phys. **48**, 962 (1968).

D. Summary

From reflections on these studies we have concluded that:

(1) The GVB approach should lead to an adequate description of the ground state of most molecules that can be described in terms of one covalent VB structure.

(2) This method also should lead to an adequate description of bond breaking and bond formation when spin coupling changes are not important (thus, biradicals should be well described).

(3) However, the GVB approach may be of less quantitative use in describing reactions involving extensive spin coupling changes. In such cases, a simple CI calculation using the GVB natural orbitals may be satisfactory.

Further implications for CI calculations will be discussed later.

IV. THE WATER MOLECULE

The optimum GVB orbitals of the ground state of H_2O lead to a description having two equivalent bonding pairs, two equivalent nonbonding pairs, and an

oxygen 1s core pair

$$\Psi_{\text{GVB}} = \mathcal{G} \{ [1s_a, 1s_b] [b_{1a}, b_{1b}] [b_{2a}, b_{2b}] [l_{1a}, l_{1b}] [l_{2a}, l_{2b}] \chi \}.$$

This description is not forced upon the system by any arbitrary symmetry requirements, but rather is obtained by solving for the optimum 10 GVB orbitals. The orbitals for the equilibrium geometry of the H_2O molecule were obtained using a basis set³⁷ of contracted Gaussian functions including 3d oxygen polarization functions. We see from Table III that the major improvement over the Hartree-Fock wavefunction is in the description of the bonding pairs, where an energy lowering of 13 kcal/mole for each bond is obtained.

In Fig. 2 we see that each orbital of a bonding pair (ϕ_{2a} and ϕ_{2b}) is localized on a different center. The ϕ_{2a} orbital, localized on the oxygen atom, has some s character but is mainly (81.9%) p-like (corresponding to $sp^{4.7}$ bonding). Similarly, the ϕ_{2b} orbital remains essentially a hydrogenic 1s orbital, delocalized onto the oxygen atom (indicating the ionic character in the bond).

The nonbonding pairs have 59% p character ($sp^{1.46}$) and are bent back from the oxygen in the plane perpendicular to the molecular plane. Each pair consists of two

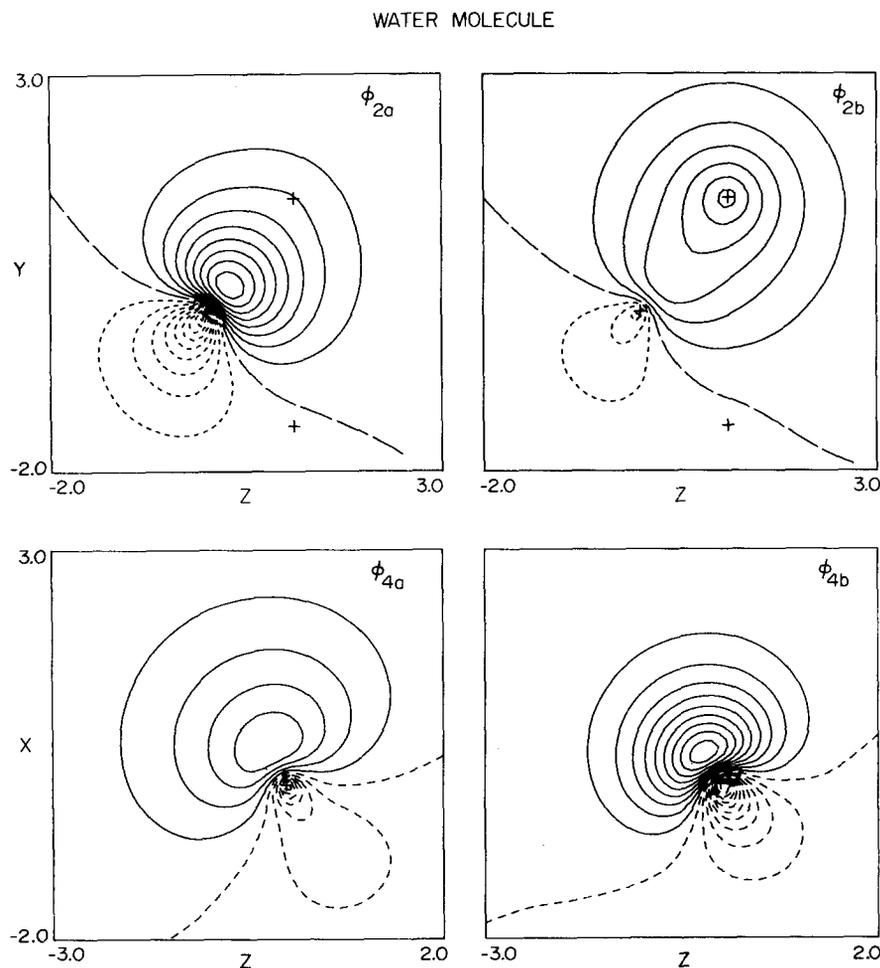


FIG. 2. The GVB orbitals for the H_2O molecule. ϕ_{2a} and ϕ_{2b} represent the orbitals of one of the two equivalent lone pairs. ϕ_{4a} and ϕ_{4b} represent the orbitals of one of the two equivalent OH bonds.

orbitals (ϕ_{4a} and ϕ_{4b} in Fig. 2) oriented in the same direction but having different radial dependencies, i.e., one being more diffuse than the other. This description is not equivalent to the case where we require the lone-pair functions to have a_1 and b_1 symmetry (i.e., symmetric and antisymmetric with the molecular plane), which in fact (see Table IV) leads to an energy only 0.0031 hartree (2 kcal/mole) higher.

The above results generally agree with previous GVB-like calculations on H₂O by other investigators. Klessinger^{18a} has carried out a group function calculation on the OH bonds in H₂O where he obtained an energy lowering of each OH bond of 0.0142 hartree compared with our value of 0.0209 hartree. The group functions of Franchini, Moccia, and Zandomeni¹⁷ are roughly equivalent in sophistication to our GVB approach, but lead to slightly worse energies because their method does not achieve full optimization. Scarzafava²⁴ obtained full orbital optimization and his uv wavefunction is comparable in energy to ours; he also obtained more general separated pair and CI wavefunctions for H₂O. A recent strongly orthogonal geminal

calculation by Shull and co-workers⁴⁰ demonstrated the transferability of geminals from H₂O to H₂O₂.

V. THE ETHANE MOLECULE

The ethane molecule is a good test case of the GVB approach since a highly restricted wavefunction might not lead to a proper description of the small (2.9 kcal/mole) rotational barrier.

For the ethane molecule, we solved for the GVB orbitals in the STO-4G minimum basis set of contracted Gaussian functions developed by Pople.⁴¹ We obtain six equivalent C-H bond pairs, one of which is shown in Fig. 3 (orbitals ϕ_{2a} and ϕ_{2b}). In contrast to the delocalized nature of molecular orbitals, we see that one of the GVB orbitals is an essentially unchanged hydrogen 1s orbital and the other is a hybrid orbital (68.5% p character, hence sp^2 .¹⁷) on the C oriented toward the H. Each C-H bond is lowered 0.0157 hartree (10 kcal) relative to the HF description. The C-C bond orbitals (orbitals ϕ_{1a} and ϕ_{1b} in Fig. 3) have a smaller energy lowering (0.0139 hartree or 9 kcal) and a higher overlap

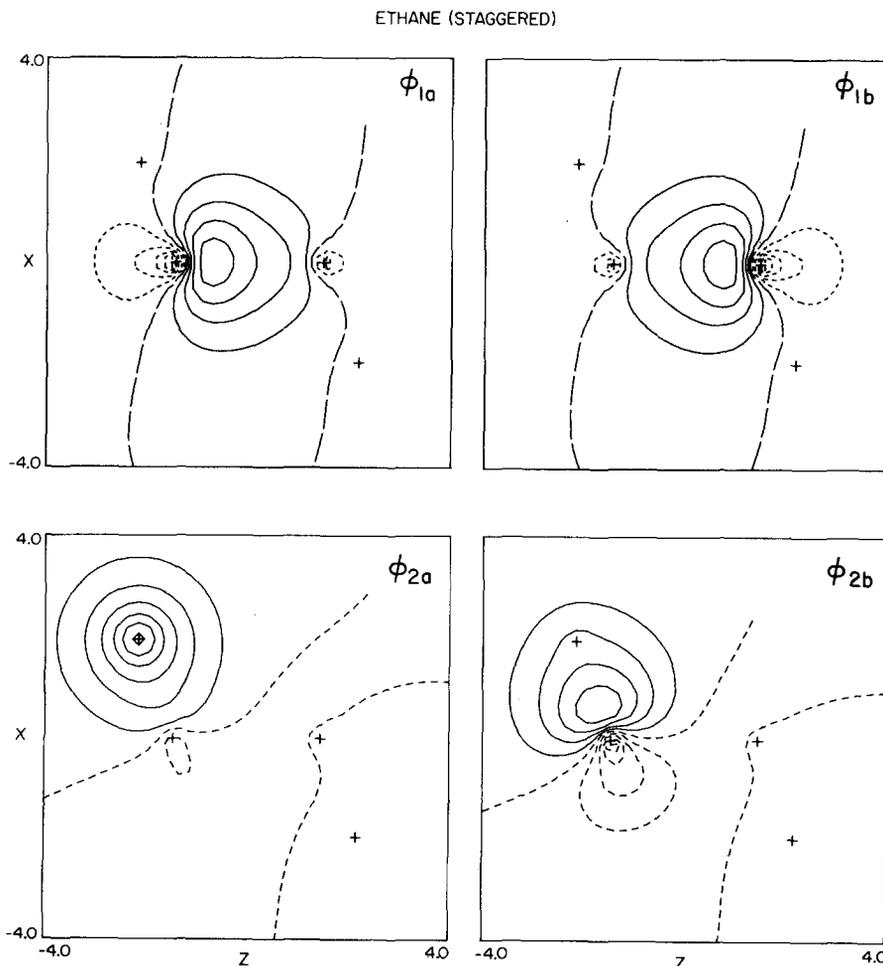


FIG. 3. The GVB orbitals for the CC bond (ϕ_{1a} and ϕ_{1b}) and a CH bond (ϕ_{2a} and ϕ_{2b}) in ethane.

TABLE IV. Calculations on the ground state of the water molecule.^a

Method	Energy	Pair information	
		Pair	$\Delta\Sigma$ Energy lowering
This work			
HF	-76.0377
GVB	-76.0988	bond(2)	-0.0207
4 pairs ($\sigma\pi$)		lone- σ	-0.0086
		lone- π	-0.0118
GVB	-76.1019	bond(2)	-0.0209
4 pairs (lobes)		lone(2)	-0.0115
GVB	-76.1118	bond(2)	-0.0209
5 pairs (lobes)		lone(2)	-0.0114
		core(1)	-0.0100
Scarzafava (Ref. 24)			
HF	-76.038		
Separated pair uv form (5 pairs) all terms	-76.110		
	-76.120		
Klessinger [Ref. 18(c)]			
HF	-75.6807		
Group function -2 pairs	-75.7139		
Franchini <i>et al.</i> (Ref. 17)			
HF	-76.0374		
Group function -4 pairs	-76.0997		
Other calculations			
HF ^b	-76.059		
HF ^c	-76.0630		
CI ^d	-76.1422		
CI ^e	-76.2205		

^a $R(\text{O-H}) = 1.811$ a.u., $\angle\text{HOH} = 104^\circ 27'$; some calculations^b used a slightly different geometry.

^b D. Neuman and J. W. Moskowitz, *J. Chem. Phys.* **49**, 2056 (1968).

^c T. H. Dunning and R. N. Pitzer (unpublished).

^d R. P. Hosteny, R. R. Gilman, T. H. Dunning, A. Pipano, and I. Shavitt, *Chem. Phys. Letters* **7**, 325 (1970).

^e C. Bender and H. F. Schaeffer (unpublished).

than the C-H bond orbitals (0.835 vs 0.826) but dissociate continuously into the p orbitals of two methyl radicals as the groups are pulled apart (the hybridization of these orbitals in ethane is 66.3% p).

We find that GVB leads to a rotational barrier of 3.1 kcal (with the staggered configuration lower) in good agreement with the HF results (3.3 kcal) and with experiment (2.9 kcal). This contrast with the barrier of -5.1 kcal (eclipsed form lower) found by Klessinger using partially optimized orbitals.

VI. THE OXYGEN MOLECULE

The failure to predict a triplet ground state for the O_2 molecule was one of the major difficulties of valence bond theory.⁴² It is therefore of interest to examine O_2 in the GVB description, which is a synthesis of the MO and VB methods. The wavefunction for the ${}^3\Sigma_g^-$ state is

$$\psi_{\text{GVB}} = \alpha \{ [\sigma_A, \sigma_B] [\pi_{xu}^2] [\pi_{yu}^2] [\pi_{zg}\pi_{yg}] \chi \},$$

where (σ_A, σ_B) is the O-O σ bonding pair [the 1s and 2s orbitals have been taken to be doubly occupied (but solved for self-consistency) and are not shown]. Little improvement in energy (0.001 hartree) is obtained by allowing the π_u orbitals to split or to become asymmetric. Thus ψ_{GVB} differs from ψ_{HF} by the presence of a split O-O σ bonding pair (σ_A, σ_B) involving the $3\sigma_g$ and $3\sigma_u$ natural orbitals.

From Table V we see that the HF and GVB results both predict the correct ordering of the ${}^3\Sigma_g^-$, ${}^1\Delta_g$, and ${}^1\Sigma_g^+$ states.⁴³ Using the GVB natural orbitals as a basis set for a small configuration interaction (CI) calculation effectively relaxes both the strong orthogonality and the spin-coupling restrictions as well as including the correlation terms involving only valence like orbitals (internal correlation). The importance of these terms has been emphasized in the theory of Silverstone and Sinanoğlu,⁴⁶ the optimized valence configuration studies of Wahl and Das,²¹ and by the first-order wavefunction calculations of Schaefer.³⁵

The calculated dissociation energy from the GVB CI calculation is in much better agreement with the experi-

TABLE V. Oxygen molecule ($R = 2.282a_0$).

	${}^3\Sigma_g^-$ state				
	E	D_e			
HF	-149.6331	0.95			
GVB (one pair)	-149.6595	1.68			
GVB CI	-149.7315	3.64			
CI ^a	-149.7944	4.72			
Exptl ^b	...	5.21			
		Excitation energies			
State	HF	GVB	GVB CI	Exptl	
${}^3\Sigma_g^-$	
${}^1\Delta_g$	1.43	1.28	0.91	0.98 ^b	
${}^1\Sigma_g^+$	2.37	2.23	1.69	1.63 ^b	
${}^1\Sigma_u^-$	5.91	6.1 ^c	
${}^3\Delta_u$	6.16	6.1 ^c	
${}^3\Sigma_u^+$	6.31	6.1 ^c	

^a Reference 35.

^b Reference 45.

^c Broad unresolved feature, Ref. 47.

TABLE VI. Characteristics of GVB electron pairs in bonds.

Pair type	System state	Basis	Pair information		
			Pair	Overlap	Energy lowering relative to HF (hartrees)
Sigma bond	CH ² Π	POL		0.8264	0.0173
	CH ⁴ Σ ⁻	POL		0.8640	0.0104
	CH ₄	POL		0.8342	0.0153
	C ₂ H ₂ ¹ Σ _g ⁺	MBS	CH	0.8413	0.0138
			CC	0.9289	0.0045
	C ₂ H ₄ ¹ A _g	MBS	CH	0.8388	0.0142
			CC	0.8930	0.0078
	C ₂ H ₆ ¹ A ₁	MBS	CH	0.8259	0.0157
			CC	0.8354	0.0139
	BeO ¹ Σ ⁺	MBS		0.8618	0.0085
	BeO ³ Π	MBS		0.9117	0.0046
	H ₂ O ¹ A ₁	POL	OH	0.8247	0.0209
Pi bond	C ₂ H ₂ ¹ Σ _g ⁺	MBS		0.6639	0.0329
	C ₂ H ₄ ¹ A _{1g}	MBS		0.5782	0.0462
	CO ¹ Σ ⁺	MBS		0.7366	0.0308
	BeO ¹ Σ ⁺	MBS		0.6662	0.0313
Lone pair	H ₂ O ¹ A ₁	POL		0.8830	0.0115
	CH ₂ ¹ A ₁	POL		0.6827	0.0214
	C ₂ ¹ Σ _g ⁺	MBS		0.3313	0.1013

mental results and with the more extensive calculation by Shaefer.^{35a} Calculations on the five lower excited states of O₂ using the natural orbitals from the ground state GVB wavefunction are also reported in Table V, where the results are in good agreement with experiment.⁴⁷

VII. GENERAL CHARACTERISTICS OF THE GVB APPROACH TO MOLECULES

The previous discussions of H₂O, C₂H₆, and O₂ illustrated some specific aspects of the GVB method; in this section we will summarize some of the results obtained for other molecules. These will be discussed more fully in future publications.

The basis sets used are MBS (minimum basis set; Pople's STO-4G basis with standard molecular exponents)⁴¹ and POL [the (4s2p) DZ set⁴⁴ augmented by one set of *d*-type uncontracted Gaussian functions on each of the B, C, N, O, and F atoms]. While MBS calculations are often inadequate to describe quantitative properties such as dissociation energies and dipole moments, comparison of results with those obtained with the POL basis indicates that the GVB characteristics (e.g., orbital overlap and pair splitting energy) are similar in both basis sets.

In Table VI we see that the two orbitals making up a sigma bond have high overlap: For C-H bonds it is 0.82-0.87 and for sigma bonds involving two first-row

atoms, 0.85-0.93. Thus, at the equilibrium distance, HF should yield a relatively good description since the energy gain in the GVB method is only 0.005-0.015 a.u. for each bond. However, pi bonds are not so well described by HF, as the GVB overlap is only 0.57-0.73 and the increase in bond energy in GVB is 0.03-0.045 a.u. (0.8-1.2 eV). Thus π bonds are much closer to the dissociated bond limit than is the case for sigma bonds.

The most drastic improvement can be noted in cases where there are two molecular orbitals—one occupied and one virtual—which are nearly degenerate. Such situations arise in biradicals (such as singlet CH₂, the trimethylene biradical,⁴⁸ benzynes,⁴⁹ the C₂ molecule) and cases where a bond is broken. In the case of C₂, the two nonbonding electrons are especially poorly described by a single 2σ_u orbital as in HF [the GVB orbitals have small overlap (0.33)] and the pair splitting energy is 63 kcal. This leads to a dissociation energy for C₂ of -22.1 kcal/mole in HF⁵⁰ as compared with 72.7 for GVB⁵⁰ and the experimental value of 144.

We conclude that the GVB method leads to useful wavefunctions and removes many difficulties and inconsistencies of the Hartree-Fock method.

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