The Self-Consistent Field Equations for Generalized Valence Bond and Open-Shell Hartree–Fock Wave Functions

Frank W. Bobrowicz and William A. Goddard III

1. Introduction

The basic starting point for calculating ab initio wave functions of molecules is generally the Hartree–Fock (HF) wave function, which in the simplest case involves two electrons (one with each spin) in each orbital $\phi_i$ with the total wave function antisymmetrized in order to satisfy the Pauli principle

$$\alpha[\phi_1\alpha)(\phi_1\beta)(\phi_2\alpha)(\phi_2\beta)\cdots(\phi_n\alpha)(\phi_n\beta)] = \alpha(\phi_1\phi_1\phi_2\phi_2\cdots\phi_n\phi_n)abab\cdots ab)$$

(1)

Here $\alpha$ is the antisymmetrizer or determinant operator and $\alpha$ and $\beta$ are the usual spin functions. In Eq. (1) as elsewhere, we arrange products of spatial functions and spin functions in order of increasing electron numbers. |
As is well known, this type of wave function generally does not lead to an adequate description of bond dissociation, nor does it provide a consistent level of treatment for excited states. A simple generalization of Eq. (1) is used to allow selected electron pairs to be described in terms of overlapping singly occupied orbitals,

$$\phi_i(1)\phi_i(2) \rightarrow \left[ \phi_u(1)\phi_u(2) + \phi_d(1)\phi_d(2) \right]$$  \hspace{1cm} (2)

as in the simple valence bond wave function. If the various orbitals of such a wave function are solved for self consistency, the resulting wave function is referred to as a generalized valence bond (GVB) wave function.\(^{1-3}\) In this chapter we will develop the variational equations which are solved to obtain GVB wave functions, and we will describe the various steps for solving the GVB wave functions of general systems. This discussion necessarily includes open-shell Hartree-Fock wave functions as a special case and the procedures developed are also appropriate for more general wave functions.

A common procedure for solving SCF wave functions\(^{4}\) has been to consider all occupied orbitals as fixed except for one, say \(\phi_u\), and to require that the first-order change in the energy be zero upon variation of this orbital, consistent with maintaining orthogonality between all occupied orbitals. A typical approach is to write the variational equations as pseudoeigenvalue equations and to solve these equations iteratively. Although often successful, this procedure is not reliable for complicated wave functions.

Our approach is to start with the expression for the total energy and to expand it (through second order) in terms of simultaneous corrections in all orbitals.\(^{5,6}\) Because of the orthogonality conditions the variations in different orbitals are coupled. Including these couplings, we derive the equations for the optimal simultaneous correction in each orbital. Solution of these equations leads to quadratic convergence to the optimum orbitals. Various simplifications are also discussed.

2. The Energy Expression

Given the usual nonrelativistic Hamiltonian

$$H = \sum_{p=1}^{N} h(p) + \sum_{p>q=1}^{N} \frac{1}{r_{pq}}$$  \hspace{1cm} (3)

where \(N\) is the number of electrons and the operator \(h(p)\) contains all one-electron terms involving electron \(p\), the total energy of any electronic wave function can be written as\(^{7}\)

$$E = \sum_{i} \sum_{i,j} D_{ii}^i h_{ii} + \sum_{i,j} \sum_{k,l} D_{kk}^l (ik|jl)$$  \hspace{1cm} (4)

where

$$h_{ii} = \langle \phi_i | h | \phi_i \rangle$$

$$(ik|jl) = \langle \phi_i(1)\phi_i(2) | (1/r_{ij})(1/r_{kl}) | \phi_j(1)\phi_j(2) \rangle$$

and \(\phi_i\) is a set of \(n\) orbital basis functions in terms of which the wave function is described. Here \(D_{ii}\) and \(D_{kl}\) are appropriate density matrix elements.

For a wide class of useful wave functions (including open-shell HF and important cases of GVB), once appropriately expressed in terms of orthonormal orbitals

$$\langle \phi_j | \phi_i \rangle = \delta_{ij}$$

the one- and two-electron density matrices in (4) can be brought into diagonal form so that the only nonzero elements are

$$D_{ii} = 2f_i, \quad D_{ij} = a_{ij}, \quad D_{kl} = b_{ij}$$

where the energy coefficients \(f_i, a_{ij}, b_{ij}\) are independent of the orbitals \(\phi_i\). For such wave functions the energy expression takes on the greatly simplified form,

$$E = 2 \sum_{i=1}^{N} f_i h_{ii} + \sum_{i,j=1}^{N} (a_{ij} J_{ij} + b_{ij} K_{ij})$$  \hspace{1cm} (6)

where

$$J_{ii} = \langle ii|ii\rangle = \langle \phi_i | J_i | \phi_i \rangle$$

$$K_{ij} = \langle jj|ij\rangle = \langle \phi_i | K_j | \phi_i \rangle$$

indicate the usual Coulomb and exchange energies, respectively. The Coulomb and exchange operators \(J_i\) and \(K_i\) are defined here for later convenience. In this chapter we will be concerned mainly with the problem of solving for the self-consistent solutions of wave functions whose energy expressions conform to Eq. (6).

3. Wave Functions

While Eq. (6) does not apply to all electronic wave functions, this energy expression is applicable to many of the most important wave functions useful in dealing with chemical problems at the conceptual level. In this section we will examine such wave functions, paying particular attention to both the simplifying aspects of their functional forms and their inherent limitations.
3.1. Hartree–Fock Wave Functions

The HF wave function is of singular importance in our basic understanding of atomic and molecular electronic structure. For mainly historical reasons, however, this wave function defies a neat unambiguous definition, since a fairly wide variety of wave functions of differing forms are classified under this appellation. Therefore, we will discuss HF wave functions by way of representative examples, without attempting an exhaustive treatment.

3.1.1. Closed Shell

Consider the four-electron singlet wave function involving two doubly occupied orbitals,

\[ a[\phi_1, \alpha \phi_1, \beta \phi_2, \alpha \phi_2] = a[\phi_1, \phi_2, \alpha \beta, \alpha \beta] \]  

(7)

Allowing orbitals \( \phi_1 \) and \( \phi_2 \) to be nonorthogonal,

\[ \langle \phi_1 | \phi_1 \rangle = S_{12}, \quad \langle \phi_2 | \phi_2 \rangle = 1 \]  

(8)

the energy of (7) is

\[ E = [2(1 - S^2_{12}) + J_{11} + J_{22} + 2(2 - S^2_{12})]K_{12} - 4S_{12}(U_{12} + J_{12})/(1 - S^2_{12}) \]  

(9)

However, writing \( \phi_2 \) as

\[ \phi_2 = \phi_2' + \lambda \phi_1 \]

where

\[ \langle \phi_1 | \phi_2' \rangle = 0 \]  

(10)

(7) becomes

\[ a[\phi_1, \phi_2, \phi_2', \alpha \beta, \alpha \beta] = a[\phi_1, \phi_2', \alpha \beta, \alpha \beta] + \lambda a[\phi_1, \phi_2, \alpha \beta, \alpha \beta] + \lambda a[\phi_1, \phi_2', \alpha \beta, \alpha \beta] + \lambda^2 a[\phi_1, \phi_2', \alpha \beta, \alpha \beta] \]  

(11)

But, because of the Pauli principle (as embodied in the antisymmetrizer \( a \)), we find that

\[ a[\phi_1, \phi_2, \phi_2', \phi_\alpha, \alpha \beta, \alpha \beta] = a[\phi_1, \phi_2', \phi_\alpha, \alpha \beta, \alpha \beta] = 0 \]  

(12)

Therefore, (11) reduces to simply

\[ a[\phi_1, \phi_2, \phi_2', \alpha \beta, \alpha \beta] = a[\phi_1, \phi_2', \alpha \beta, \alpha \beta] \]  

(13)

That is, the antisymmetrizer projects away any nonorthogonality, and hence it is no restriction to take these orbitals as orthogonal in the first place.\(^\dagger\) In this case the energy expression (9) becomes

\[ E_c = 2h_{11} + 2h_{22} + J_{11} + J_{22} + 4J_{12} - 2K_{12} \]  

(14)

Since

\[ J_a = K_a \]  

(15)

we can add and subtract these \( J \) terms to obtain the more symmetric expression

\[ E_c = 2h_{11} + 2h_{22} + (2J_{11} - K_{11}) + (2J_{22} - K_{22}) + (4J_{12} - 2K_{12}) \]  

(16)

which is of the form of (6) with

\[ f_1 = f_2 = 1 \]

\[ a_{11} = a_{22} = a_{12} = 2 \]

\[ b_{11} = b_{22} = b_{12} = -1 \]

Since \( \phi_1 \) and \( \phi_2 \) are maximally occupied \((f = 1)\), we refer to them as \( \text{closed-shell} \) orbitals. Orbitals leading to \( f \neq 1 \) are referred to collectively as \( \text{open-shell} \) orbitals. A closed-shell orbital can be (and always is) taken to be orthogonal to all other orbitals, without restriction. A wave function composed entirely of closed-shell orbitals

\[ a[\phi_1, \phi_2, \phi_2', \alpha \beta, \alpha \beta] \]  

is called a closed-shell wave function and has the general energy expression\(^\dagger\)

\[ E_c = \sum_i \frac{\hbar_i^2}{2m_i} + \sum_j (2J_{jj} - K_{jj}) \]  

(18)

3.1.2. Closed-Shell/Open-Shell Energy Partitioning

Generally, wave functions involving open-shell orbitals also contain several closed-shell orbitals as well. Therefore, it is convenient to develop a

\(^\dagger\) Also because of the antisymmetrizer we find that starting with two orbitals \( \phi_1 \) and \( \phi_2 \) and transforming to a new set of orbitals \( \tilde{\phi}_1 \) and \( \tilde{\phi}_2 \),

\[ \tilde{\phi}_i = \sum_j \phi_j U_{ij} \]

leads to

\[ a[\tilde{\phi}_1, \tilde{\phi}_2, \phi_\alpha, \alpha \beta, \alpha \beta] = (\det U)^2 a[\phi_1, \phi_2, \phi_\alpha, \alpha \beta, \alpha \beta] \]

Thus the closed-shell wave function is \( \textit{invariant} \) under orthogonal transformations.

\(^\dagger\) We have seen that the form of (18) is invariant under orthogonal transformations of the orbitals.
scheme whereby energy expressions may be derived without explicitly considering the closed-shell orbitals. Consider the doublet wave function

$$a[\phi_1\phi_1\phi_2\phi_2\alpha\beta\alpha\beta]$$

(19)

Since all the orbitals can be taken as orthonormal, the energy of (19) is

$$E = (2h_{11} + 2h_{22}) + h_{33} + (2J_{11} - K_{11} + 2J_{22} - K_{22} + 4J_{12} - 2K_{12}) + (2J_{13} - K_{13} + 2J_{23} - K_{23})$$

(20)

Hence

$$f_1 = f_2 = f_3 = 2f_3 = 1$$

$$a_{11} = a_{22} = a_{12} = a_{13} = a_{23} = 2$$

$$b_{11} = b_{22} = b_{12} = b_{13} = b_{23} = -1$$

$$a_{33} = b_{33} = 0$$

Comparing with (16) we see that (20) can be written as

$$E = E_c + h_{33} + 2J_{13} - K_{13} + 2J_{23} - K_{23}$$

$$= E_c + h^c_{33}$$

(21)

where

$$h^c = h + 2J_1 - K_1 + 2J_2 - K_2$$

Thus, insofar as the open-shell orbital (\(\phi_3\)) is concerned all effects due to the closed-shell orbitals are included in the new “one-electron” operator \(h^c\).

In general, if orbital \(i\) is a closed-shell orbital and orbital \(j\) is any other orbital, the only nonvanishing density matrix elements in (4) involving both of these orbitals are

$$D_{ij} = 2D_{ji}^1$$

$$D_{ij}^2 = -D_{ji}^2$$

As a consequence, the energy for any wave function involving both closed-shell and open-shell orbitals has the form

$$E = E_c + \sum_{\text{open}} D_{ij}^1 h_{ij}^c + \sum_{\text{closed}} D_{ij}^2 (ik|lj)$$

(22)

where

$$h_{ij}^c = h + \sum_{\text{closed}} (2J_{ij} - K_{ij})$$

$$E_c = 2 \sum_{\text{closed}} h_{pp} + \sum_{k<l} (2J_{pq} - K_{pq})$$

(23)

If the open-shell energy can be simplified to the form of (6), then (22) reduces to

$$E = E_c + \sum_{\text{open}} D_{ij}^1 h_{ij}^c + \sum_{\text{closed}} (a_{ij}J_{ij} + b_{ij}K_{ij})$$

(24)

Hence, letting \(\{core\}\) denote the presence of an arbitrary number of closed-shell orbitals,

$$\{core\} = \phi_{1\alpha}\phi_{2\alpha}\phi_{3\beta}\phi_{4\beta}\cdots\phi_{m\alpha}\phi_{n\beta}$$

(25)

the energy for the doublet wave function

$$a[\{core\}\phi_1\alpha\phi_2\alpha]$$

(26)

becomes simply

$$E = E_c + h_{nn}^c$$

(27)

3.1.3. High-Spin Open Shell

For the wave function

$$a[\{core\}\phi_1\alpha\phi_2\alpha\alpha]$$

(28)

where the electrons in orbitals \(\phi_1\) and \(\phi_2\) are coupled into a triplet state, we see from the analysis in (10)–(13) that it is no restriction to take these two orbitals as orthogonal. Therefore, the energy of (28) is

$$E = E_c + h_{11}^c + h_{22}^c + J_{12} - K_{12}$$

(29)

Adding and subtracting self-terms leads to the more symmetric expression

$$E = E_c + h_{11}^c + h_{22}^c + \frac{1}{2}(J_{11} - K_{11}) + \frac{1}{2}(J_{22} - K_{22}) + J_{12} - K_{12}$$

(30)

so that

$$f_1 = f_2 = a_{11} = a_{22} = a_{12} = -b_{11} = -b_{22} = -b_{12} = \frac{1}{2}$$

For the general high-spin open-shell wave function,

$$a[\{core\}\phi_1\alpha\phi_2\alpha\cdots\phi_m\alpha]$$

(31)

we obtain the energy expression*

$$E = E_c + \sum_{i} h_{ii}^c + \frac{1}{2} \sum_{i<j} (J_{ii} - K_{ii})$$

(32)

We refer to wave functions such as (31) as ‘multiplet’ wave functions and to the high-spin coupled open-shell orbitals involved as the ‘multiplet-shell’ orbitals.

*Under a transformation \(U\) of the open-shell orbitals of a high-spin open-shell wave function, the total wave function changes as (det \(U\)). Thus at most a sign change occurs under orthogonal transformations. As a result, the form of (32) is invariant under orthogonal transformations among the high-spin orbitals.
3.1.4. Orthogonality Restrictions

If in the open-shell singlet wave function,
\[ a[(\text{core})\phi_1\phi_2(\alpha\beta - \beta\alpha)] = a[(\text{core})\phi_1(\phi_2 + \phi_3)\alpha\beta] \] (33a)
(where the electrons in \( \phi_1 \) and \( \phi_2 \) are coupled into a singlet pair), we take \( \phi_1 \) and \( \phi_2 \) as orthogonal,
\[ \langle \phi_1 | \phi_2 \rangle = 0 \] (33b)
the energy expression is
\[ E = E_c + h_1^1 + h_2^2 + J_{12} + K_{12} \] (34)
so that
\[ f_1 = f_2 = a_{12} = b_{12} = \frac{1}{2} \]
\[ a_{11} = a_{22} = b_{11} = b_{22} = 0 \]
In this case, the energy expression cannot be put into a more symmetric form by adding and subtracting self-terms.

For all the HF wave functions considered in Sections 3.1.1–3.1.3, we found that because of the functional form of these wave functions the antisymmetrizer projected away any orbital nonorthogonalities. Thus, the sole effect of constraining the orbitals to be orthogonal was to permit us to express energies in the simplified form of (6), rather than (4). However, if in (33a) we allow \( \phi_1 \) and \( \phi_2 \) to be nonorthogonal,
\[ \langle \phi_1 | \phi_2 \rangle = S_{12} \]
and rewrite \( \phi_2 \) as
\[ \phi_2 = \phi_2' + \lambda \phi_1 \]
where
\[ \langle \phi_1 | \phi_2' \rangle = 0 \]
then expansion of (33a) leads to
\[ a[(\text{core})\phi_1\phi_2'(\alpha\beta - \beta\alpha)] + 2\alpha a[(\text{core})\phi_1\phi_1\alpha\beta] \] (35)
The second term in (35) is nonvanishing, and hence in this case imposing orthogonality between \( \phi_1 \) and \( \phi_2 \) does, in general, represent a restriction. Thus, in this instance (33b) is not just a convenient computational tool.*

The restrictive nature of the orbital orthogonality constraint, which is always imposed upon HF wave functions, is not confined solely to the two orbitals comprising an open-shell singlet pair. It applies in general with respect to all open-shell orbitals which are not multiplet (high-spin) coupled to one another. For example, in the wave function
\[ a[\phi_1\phi_2\phi_3\phi_4\alpha\beta(\alpha\beta - \beta\alpha)\alpha\alpha] \] (36)
while the conditions,
\[ \langle \phi_i | \phi_i \rangle = 0, \quad i = 2, 3, 4, 5 \]
\[ \langle \phi_2 | \phi_3 \rangle = 0 \] (37)
are completely unrestricted, the constraints,
\[ \langle \phi_2 | \phi_i \rangle = 0, \quad k = 2, 3 \text{ and } l = 4, 5 \]
\[ \langle \phi_2 | \phi_3 \rangle = 0 \] (38)
are actual restrictions. Whether or not (38) is imposed upon (36) can have a significant effect upon the energy (and potential usefulness) of this wave function.

3.2. GVB Wave Functions

3.2.1. General Considerations

The Hartree–Fock wave function forms the conceptual basis for understanding the electronic structures of broad classes of molecules. However, upon applying HF wave functions to studies of chemical reactions, a serious deficiency becomes apparent. These wave functions are generally incapable of describing bond dissociation. To illustrate, consider the case of the hydrogen molecule. Near the equilibrium internuclear distance \( R \), the ground state molecule is adequately described by the closed-shell HF wave function
\[ a[\phi_1\phi_1\beta\alpha] \] (39)
However, in the dissociative limit the system consists of two isolated hydrogen atoms and is accurately described by the open-shell singlet HF wave function
\[ a[\phi_1\phi_2(\alpha\beta - \beta\alpha)] \quad \langle \phi_1 | \phi_2 \rangle = 0 \] (40)
Since (39) consists of a single doubly occupied orbital, it can never describe the separated-atom limit. Conversely, the required orthogonality between \( \phi_1 \) and \( \phi_2 \) prevents (40) from describing the molecular bond. Hence, while each limit is described by an HF wave function, the inherent restrictions of the HF formalism preclude the possibility of smoothly going from one limit to the other.
Frank W. Bobrowicz and William A. Goddard III

The obvious solution of this dilemma is to relax the orthogonality restriction in (40), thereby giving rise to the GVB wave function

$$a[\phi_1^1\phi_2^2(\alpha\beta - \beta\alpha)] = a[(\phi_1^1\phi_2^2 + \phi_2^1\phi_1^1)\alpha\beta]$$

(41)

where

$$\langle \phi_1^1|\phi_2^2 \rangle = S_{12} \neq 0$$

Since in (41) no restrictions are placed upon either $\phi_1^1$ or $\phi_2^2$, this wave function can behave properly at all internuclear separations with $S_{12}$ (for the optimum orbitals) varying from zero at infinite separation $[(41) = (40)]$ to $-0.8$ at $R_2$ [that is, (41) = (39)].

Furthermore, the added functional freedom associated with this wave function allows for the incorporation of optimal ionic and covalent character in the wave function, thereby leading to a significantly stronger chemical bond than does (39). That is, wave function (41) allows the electrons to better correlate their motions, thus reducing the energy of the system.

For workers conditioned to thinking of chemical systems in terms of traditional molecular HF wave functions it is useful to regard (41) as being a generalization of (39), in which we replace the conventional closed-shell orbital description of a singlet electron pair by a GVB pair consisting of two nonorthogonal orbitals coupled into a singlet,

$$\phi_{s1}\phi_{s2}(\alpha\beta - \beta\alpha)$$

(42a)

or equivalently

$$\phi_{s1}\phi_{s2}(\alpha\beta - \beta\alpha)$$

(42b)

Using this pair correlation prescription (42), the HF wave function

$$a[\phi_1^1\phi_2^2(\alpha\beta - \beta\alpha)]$$

where

$$\langle \phi_1^1|\phi_2^2 \rangle = S_{12}$$

In (43) each singlet electron pair is allowed to correlate. However, for most chemical problems many such correlations can be ignored. Since only selected electron pairs need be represented by GVB pairs (e.g., those describing chemical bonds), we normally generalize (42c) to a wave function of the form

$$a[\phi_1^1\phi_2^2(\alpha\beta - \beta\alpha)\cdot\phi_{m1}\phi_{m2}(\alpha\beta - \beta\alpha)\phi_{m+1}\alpha\cdot\phi_n\alpha]$$

(43)

(44)

For example, the excitation energies between the lower electronic states of $O_2$ are essentially unaffected by correlation effects involving the 1s core orbitals of each oxygen. Indeed, for the lower few states it is not necessary to correlate even the 2s core orbitals of each oxygen.

In wave functions such as (43) or (44) it is computationally useful to require that all orbitals other than the two within a given singlet pair be orthogonal. This strong orthogonality constraint (45) is of course a restriction. However, since it applies between orbitals that are normally not expected to overlap significantly, strong orthogonality is usually not a serious restriction.

The wave function developed here singlet couples as many orbital pairs as is possible for a given eigenstate of spin. Thus for a four-electron singlet state we have

$$a[\phi_{s1}\phi_{s2}(\alpha\beta - \beta\alpha)]$$

(45)

However this perfect pairing is not the only coupling scheme possible. For example,

$$a[\phi_{s1}\phi_{s2}(\alpha\beta - \beta\alpha)\phi_{m1}\phi_{m2}(\alpha\beta - \beta\alpha)]$$

represents another linearly independent way of coupling these orbitals into a singlet state. The unrestricted GVB wave function (46) allows for these other possibilities as well, having the form

$$a[\phi_1^1\phi_2^2\cdot\phi_n\theta(1\cdots n)]$$

(46)

where the spin function $\theta$ is allowed full functional freedom within the confines of being an eigenstate of spin

$$S^2\theta = S(S+1)\theta$$

Furthermore, in the GVB wave function no orbital orthogonality conditions are imposed. The perfect-pairing spin function is especially inappropriate for systems such as the allyl radical (11) or benzene, (12) in which two or more bonding schemes are of comparable importance, and for describing the dissociation of molecules leading to triplet or higher spin states on the separated fragments (e.g., $O_2$). However, for most cases the orbital obtained from GVB–PP are quite adequate.

The GVB wave function, in which the perfect pairing and strong orthogonality restrictions are both imposed, (10) is referred to as the GVB–PP (perfect pairing) wave function to distinguish it from the general GVB wave function. In addition, we have developed an intermediate level of calculation in which the spin function is optimized while retaining the strong orthogonality

*These orthogonality conditions have been relaxed in several cases (1, 2, 5) where it has been found that the orbitals in different singlet pairs of perfect pairing wave functions such as (43) and (44) generally have small overlaps (this arises basically from the Pauli principle).
restrictions. This has been quite useful, for example, for considering allyl systems. These more general GVB wave functions lead to an energy expression not conforming to (6), and hence in this chapter we will restrict ourselves to the GVB–PP approximation.

3.2.2. The GVB–PP Energy Expression (The Natural Orbital Representation)

The energy of the simplest GVB wave function (41) is

\[ E = (1 + S_{12})^{-1} \left[ h_{11} + h_{22} + 2S_{12}h_{12} + J_{12} + K_{12} \right] \]  

(47)

an expression not conforming to (6). However, letting

\[ \phi_1' = (\sigma_1^{1/2}\phi_1 + \sigma_2^{1/2}\phi_2)/(\sigma_1 + \sigma_2)^{1/2} \]
\[ \phi_2' = (\sigma_1^{1/2}\phi_1 - \sigma_2^{1/2}\phi_2)/(\sigma_1 + \sigma_2)^{1/2} \]

(48)

where \( \sigma_1 > 0, \sigma_2 > 0, \) and \( \langle \phi_i | \phi_j \rangle = 0 \) allows (41) to be rewritten as

\[ a\left[ (\sigma_1\phi_1|\phi_1 - \sigma_2\phi_2|\phi_2) | \alpha \beta \right] = \sigma_1 a\left[ \phi_1|\phi_1 | \alpha \beta \right] - \sigma_2 a\left[ \phi_2|\phi_2 | \alpha \beta \right] \]

(49)

giving rise to the energy expression

\[ E = \frac{\sigma_1^2}{\sigma_1^2 + \sigma_2^2} (2h_{11} + J_{11}) + \frac{\sigma_2^2}{\sigma_1^2 + \sigma_2^2} (2h_{22} + J_{22}) - 2\sigma_1\sigma_2 K_{12} \]

(50)

Equation (50) does have the desired form of (6), differing from a typical HF expression only in that the energy coefficients \( f, a, b \) are now functions of the pair coefficients \( \sigma_1, \sigma_2 \), rather than being fixed.

Thus, while it is conceptually the nonorthogonal GVB orbitals that are the most useful, computationally it is much more convenient to replace the GVB pair,

\[ \phi_1' \phi_2' (\alpha \beta - \beta \alpha), \quad \langle \phi_1' | \phi_2' \rangle = S_{12} \]

(51)

with its natural orbital\(^{(14)}\) representation,

\[ (\sigma_1\phi_1, \sigma_2\phi_1 - \sigma_2\phi_2, \sigma_1\phi_2, \sigma_2\phi_2) | \alpha \beta \]

(52)

where

\[ \phi_1'' = (\sigma_1^{1/2}\phi_{11} + \sigma_2^{1/2}\phi_{22})/(\sigma_1 + \sigma_2)^{1/2} \]
\[ \phi_2'' = (\sigma_1^{1/2}\phi_{11} - \sigma_2^{1/2}\phi_{22})/(\sigma_1 + \sigma_2)^{1/2} \]

(53)

and where for future convenience we take

\[ \sigma_1^2 + \sigma_2^2 = 1 \]

(54)

Once written in terms of these natural orbital pairs, the energy of any GVB–PP wave function always has the form of (6). For example, casting the two-pair wave function,

\[ a\left[ (\text{core})|\phi_1'\phi_2'|\phi_3'\phi_4'(\alpha \beta - \beta \alpha) | (\alpha \beta - \beta \alpha) \right] \]

(55)

in its natural orbital form

\[ a\left[ (\text{core})|\sigma_1\phi_1|\phi_1 - \sigma_2\phi_2|\phi_2 (\sigma_3\phi_3|\phi_3 - \sigma_4\phi_4|\phi_4) | \alpha \beta \right] \]

(56)

leads to

\[ E = E_0 + \frac{4}{\sum i=1} \sigma_i^2 (h_{ii} + J_{ii}) + 2 \sum_{i=1}^{4} \sum_{j=1}^{5} \sigma_i^2 \sigma_j^2 (J_{ij} - K_{ij}) - 2\sigma_1\sigma_2 K_{12} \]

(57)

Thus, the GVB–PP wave function (in natural orbital form) having the general form

\[ a\left[ (\text{core}) (\text{pair}) (\text{open}) \right] \]

(58)

where

\[ (\text{core}) = \phi_{11} \phi_{21} \alpha \beta \phi_{22} \phi_{11} \alpha \beta \cdots \]
\[ (\text{pair}) = (\sigma_{11} \phi_{11} \phi_{21} - \sigma_{22} \phi_{21} \phi_{22}) \alpha \beta (\sigma_{33} \phi_{33} \phi_{43} - \sigma_{44} \phi_{43} \phi_{44}) \alpha \beta \cdots \]
\[ (\text{open}) = \phi_{11} \phi_{21} \alpha \cdots \]

leads to an energy expression in the desired form (6), where

\[ f_i = 1 \quad \text{if } \phi_i \text{ is a core orbital} \]
\[ f_i = \sigma_i^2 \quad \text{if } \phi_i \text{ is a pair orbital} \]
\[ f_i = \frac{1}{2} \quad \text{if } \phi_i \text{ is an open orbital} \]
\[ a_i = 2 f_i f_j \]
\[ b_i = -f_i f_j \]

except that

\[ b_i = -\frac{1}{2} \quad \text{if } \phi_i \text{ and } \phi_j \text{ are both open orbitals} \]
\[ a_i = f_i \quad \text{if } \phi_i \text{ is a pair orbital} \]
\[ b_i = 0 \quad \text{if } \phi_i \text{ is a core orbital} \]
\[ a_i = 0 \quad \text{if } \phi_i \text{ and } \phi_j \text{ are in the same pair} \]
\[ b_i = -\sigma_i f_i \]

*The [open] wave function can also be taken of the form in (33) or as a product of (33) with a multiplet open shell. The modifications of the coefficients (59) are straightforward.
Upon solving for the GVB natural orbitals $\phi_{1i}$ and $\phi_{2i}$ and the pair coefficients $\sigma_{1i}$ and $\sigma_{2i}$, the GVB orbitals $\phi_{1i}'$ and $\phi_{2i}'$ are obtained from (48), where the overlap $S_i$ is given by

$$S_i = \frac{\sigma_{1i} - \sigma_{2i}}{\sigma_{1i} + \sigma_{2i}} \quad (60)$$

### 3.3. Separated-Pair Wave Functions

Written in its natural orbital form, we see that another prescription for obtaining a GVB–PP wave function from the usual HF wave function is

$$\phi_{i} = (\sigma_{1i}\phi_{1i} + \sigma_{2i}\phi_{2i})\alpha \beta, \quad \langle \phi_{1i}|\phi_{2j}\rangle = 0 \quad (60a)$$

That is, an electron pair normally described by a closed-shell orbital in the HF wave function is instead described by a geminal expansion consisting of two orthogonal doubly occupied orbitals. In a separated-pair wave function\(^{(15,16)}\) this pair correlation prescription is extended to the general form,*

$$\phi_{i} = \sum_{j=1}^{n_e} \sigma_j \phi_{j}\alpha \beta, \quad \langle \phi_{im}|\phi_{mn}\rangle = \delta_{in} \quad (60b)$$

so that the pair functional consists of an expansion of arbitrary length. That these orbitals can be taken as orthogonal without restriction becomes obvious upon realizing that the general singlet functional,

$$\sum_{i,j} d_{ij}\phi_{1i}'\phi_{1j}'\alpha \beta$$

where

$$\langle \phi_{1i}'|\phi_{1j}'\rangle = \delta_{ij}, \quad d_{ij} = d_{ji}$$

is directly related to (60b) through a general orthogonal transformation of the form

$$\phi_{1i}' = (\phi_{1i} + \lambda_i \phi_{2i})/(1 + \lambda_i^2)^{1/2}, \quad \lambda_i = -\lambda_j \quad \text{for all } i \text{ and } j$$

Thus, a separated-pair functional can, in principle, be used to introduce any amount of correlation between the two singlet coupled electrons by taking $n_e$ to be arbitrarily large. In practice, all significant correlation effects can normally be taken into account using a relatively small expansion through an optimal choice of the orbitals involved.\(^{(15,16)}\)

*Note that for two-term wave functions we define a minus sign with $\sigma_2$ so that $\sigma_1, \sigma_2 > 0$. For separated-pair wave functions we let all terms enter with $+\sigma_i$ coefficient so that some $\sigma_i < 0$.

The ability of (60b) to correlate the two electrons within a given singlet pair to an arbitrary degree can at times be quite important and can obviously lead to results that are quantitatively superior to those possible using the GVB pair functional (60a). However, for most chemical problems the dominant correlations (both qualitative and quantitative) can usually be accomodated by the simpler GVB pair functional. Additional effects, which could be incorporated through use of (60b) with $n_e > 2$, are generally of less importance, especially when compared with other types of correlations possible in a many-electron system.

The GVB wave function (46) obtained by relaxing the perfect-pairing and strong orthogonality constraints associated with a GVB–PP wave function can incorporate many of these additional kinds of correlations as well, and we regard the GVB–PP wave function as a restricted GVB wave function, not as a restricted separated-pair wave function. This distinction, which on the basis of comparing (60a) and (60b) is rather obscure, crystallizes upon recalling that the GVB pair functional in (60a) is simply a computationally convenient representation for a pair of nonorthogonal orbitals coupled into a singlet. Therefore, just as is the case for HF and GVB wave functions, a GVB–PP wave function is readily susceptible to physical interpretation through the fundamental conceptualization of associating each electron with a special orbital. On the other hand, for a separated-pair wave function ($n_e > 2$) this is not possible since each correlated electron pair is described in terms of more than two orbitals.

On a computational level, however, there really is no formal distinction. That is, using the conventional normalization criterion

$$\sum_{i=1}^{n_e} \sigma_i^2 = 1$$

the energy expression and actual energy coefficients as given in (59) are the same for both GVB–PP and separated-pair wave functions and hybrids thereof. The only difference is that now a “pair” can be composed of more than two orbitals. This being the case, we find it convenient to refer to such wave functions collectively as correlated-pair wave functions and the orbitals involved in such pairs are then simply called correlated-pair orbitals.

### 4. The Basic Variational Equations

Having demonstrated that energy expression (6) is applicable to a wide range of useful wave functions, we will now concern ourselves with the task of solving for the optimal (self-consistent) orbitals of (6); generally those leading to the lowest energy. Since we will be dealing solely with (6), where the energy coefficients ($f_0, a_0, b_0$) are regarded as arbitrary parameters, the results obtained are quite general in that they apply to any wave function (actual or