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MASTER

GENERAL VALENCE BOND THEORY FOR CHEMICAL REACTIONS:
FORMULATION OF THE SOGVB WAVEFUNCTION

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SUMMARY

In this paper we present the formulation of an MCSCF wavefunction of the GVB (generalized valence - bond) type designed to deal with the changes occurring during chemical reactions. As such, this wavefunction which we have labeled SOGVB (strongly orthogonal generalized valence - bond) overcomes one of the deficiencies of the more familiar Perfect-Pairing GVB wavefunction (GVB-PP) while retaining much of the computational simplicity of the Perfect-Pairing approximation.

To understand the rationale behind the SOGVB approach¹ let us first consider the more well-known GVB-PP wavefunction.² In essence, this wavefunction results from a relaxation of the double-occupation restriction placed upon the restricted Hartree-Fock (RHF) wavefunction. That is, in GVB-PP, we replace an RHF doubly-occupied orbital by a pair of nonorthogonal singlet coupled orbitals. For example, the RHF wavefunction

$$\Psi = A \phi_1^2 \phi_3 \alpha \beta \alpha = \begin{array}{|c|} \hline \phi_1 \phi_1 \\ \hline \phi_3 \\ \hline \end{array} \quad (1)$$

becomes

$$\Psi = \frac{1}{\sqrt{2}} A (\phi'_{11} \phi'_{21} + \phi'_{21} \phi'_{11}) \phi_3 \alpha \beta \alpha = \begin{array}{|c|} \hline \phi'_{11} \phi'_{21} \\ \hline \phi_3 \\ \hline \end{array} \quad (2a)$$

However, while the orbitals in each such pair are allowed to be nonorthogonal we require that they be orthogonal to all other orbitals. Thus, in (2a) we impose the constraints

$$\langle \phi'_{11} | \phi_3 \rangle = \langle \phi'_{21} | \phi_3 \rangle = 0 \quad (2b)$$

If we now express each nonorthogonal pair in terms of the corresponding orthogonal natural orbitals such that

$$\begin{aligned} \phi'_{11} &= (\sqrt{\lambda_{11}} \phi_{11} + \sqrt{\lambda_{21}} \phi_{21}) / (\lambda_{11} + \lambda_{21})^{1/2} \\ \phi'_{21} &= (\sqrt{\lambda_{11}} \phi_{11} - \sqrt{\lambda_{21}} \phi_{21}) / (\lambda_{11} + \lambda_{21})^{1/2} \end{aligned} \quad (3)$$

we obtain an MC wavefunction involving only orthogonal orbitals. For example, (2a) then becomes (taking $\lambda_{11}^2 + \lambda_{21}^2 = 1$)

$$\Psi = A (\lambda_{11} \phi_{11}^2 - \lambda_{21} \phi_{21}^2) \phi_3 \alpha \beta \alpha \quad (4)$$

$$= \lambda_{11} \begin{array}{|c|} \hline \phi_{11} \phi_{11} \\ \hline \phi_3 \\ \hline \end{array} - \lambda_{21} \begin{array}{|c|} \hline \phi_{21} \phi_{21} \\ \hline \phi_3 \\ \hline \end{array}$$

Since the GVB-PP wavefunction can be written as an MC wavefunction involving orthogonal orbitals in which the configurations differ by at least a doubly-occupied orbital the energy expression has a form identical to that of an open-shell HF wavefunction³

$$E = 2 \sum_i f_i \langle \phi_i | h | \phi_i \rangle + \sum_{i,j} [a_{i,j} J_{i,j} + b_{i,j} K_{i,j}] \quad (5)$$

As a consequence, solving for a GVB-PP wavefunction is not much more difficult than solving for an RHF wavefunction. The essential difference is that the {f,a,b} energy coefficients involving paired orbitals are functions of the pair coefficients {λ} which must also be solved for self-consistently. In addition, there are more Fock operators to deal with since each paired orbital has a unique one of its own.³

Because GVB-PP uses two nonorthogonal orbitals in describing a typical chemical bond it serves as an excellent wavefunction for near-equilibrium molecular geometries. In addition, it is capable of describing rudimentary processes such as the formation of H₂ from two hydrogen atoms. However, in general it is not flexible enough to describe typical chemical reactions. For example, consider the formation of CH²Π from C³P and H¹S. In the separated atom limit the two carbon p-orbitals are triplet coupled so that

$$\Psi_\infty = \frac{1}{\sqrt{6}} A \cdots \phi_{pZ} \phi_{pY} \phi_H (2\alpha\alpha\beta - \alpha\beta\alpha - \beta\alpha\alpha) = \begin{array}{|c|c|} \hline \dots & \dots \\ \hline \phi_{pZ} & \phi_H \\ \hline \phi_{pY} & \\ \hline \end{array} \quad (6a)$$

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(where . . . represents all other orbitals) whereas in the product a carbon p-orbital and the hydrogen orbital must become singlet coupled in order to describe the C-H so that

$$\psi_{eq} = \begin{array}{|c|} \hline \dots \\ \hline \phi_{PZ} \phi_H \\ \hline \phi_{PY} \\ \hline \end{array} \quad (6b)$$

Clearly, regardless of how the orbitals change, GVB-PP wavefunction (6b) which gives a good description of $CH^2\Pi$ at equilibrium can never describe the separated atom limit. Conversely, (6a) which describes this limit cannot possibly describe a strong C-H bond (Fig. 1). The only way to properly describe this reaction is to employ a wavefunction which incorporates both of these coupling schemes, such as

$$\psi = \xi_{eq} \begin{array}{|c|} \hline \dots \\ \hline \phi_{PZ} \phi_H \\ \hline \phi_{PY} \\ \hline \end{array} + \xi_{\infty} \begin{array}{|c|} \hline \dots \\ \hline \phi_{PZ} \phi_H \\ \hline \phi_{PY} \\ \hline \end{array} \quad (6c)$$

in which we must solve not only for the optimal orbitals but for the optimal coupling coefficients $\{\xi\}$ as well.

The inability of the GVB-PP wavefunction to deal with chemical reactions goes beyond the obvious example given above. It also extends to cases where the coupling between product orbitals is the same as that between reactant orbitals. An example of this is seen in the formation of $CH^2\Delta$ from C^1D and H^1S . Since this state arises from the formation of a bond between a hydrogen orbital and one of the carbon sp-pair orbitals (the GVB picture of carbon has two sp-orbitals in place of the RHF $2s^2$ orbital) the product wavefunction is

$$\psi_{eq} = \begin{array}{|c|} \hline \dots \\ \hline \phi_{SZ} \phi_H \\ \hline \phi_{SZ} \\ \hline \end{array} \quad (7a)$$

whereas in the separated-atom wavefunction the hybrid sp-orbitals in C 'D are singlet coupled so that

$$\psi_{\infty} = \begin{array}{|c|} \hline \dots \\ \hline \phi_{SZ} \phi_{SZ}^- \\ \hline \phi_H \\ \hline \end{array} \quad (7b)$$

Since in either limit the system can be described by a perfect-pairing coupling scheme it might be expected that this reaction could be studied using a GVB-PP wavefunction. However, when GVB-PP calculations are performed we find that this is not the case. Rather, if we start at the separate-atom limit and move inward we climb a repulsive curve which does not lead to the bound molecular state (Fig. 2). Likewise, if we start with the molecular state and move outward we follow a potential curve which does not tend toward the proper atomic limit. Therefore, while the GVB-PP approximation is adequate at either limit it is quite inappropriate at intermediate internuclear separations. In order to obtain a smoothly varying adiabatic description of this reaction a more flexible wavefunction is clearly required.

Relaxing the constraints imposed upon the GVB-PP wavefunction while still remaining within the framework of an independent-particle model leads to the unrestricted GVB wavefunction. In this approximation all orbitals are allowed to be nonorthogonal and, while retaining the desired overall spin multiplicity, these orbitals are coupled in a fully general manner.⁴ For example, the three-electron doublet GVB wavefunction can be written as

$$\psi = \xi_1 \begin{array}{|c|} \hline \phi_1 \phi_2 \\ \hline \phi_3 \\ \hline \end{array} + \xi_2 \begin{array}{|c|} \hline \phi_1 \phi_3 \\ \hline \phi_2 \\ \hline \end{array} \quad (8)$$

Unfortunately, because of the computational complexities involved, unrestricted GVB calculations are practical only for small systems. Furthermore, extending this method through inclusion of closed-shell and/or perfect-pair orbitals is nontrivial. However, GVB calculations on small but representative systems have been performed and from the results it becomes apparent that the full generality of this wavefunction is usually not required. To illustrate, consider the simple colinear $H_2 + D \rightarrow H + HD$ reaction. Initially the system consists of a hydrogen molecule and a deuterium atom whereas in the products we have an HD molecule and a hydrogen atom. Since the reactant and product wavefunctions are

$$\psi_R = \begin{array}{|c|} \hline \phi_H \phi_{H'} \\ \hline \phi_D \\ \hline \end{array} \quad \text{and} \quad \psi_P = \begin{array}{|c|} \hline \phi_H \phi_D \\ \hline \phi_{H'} \\ \hline \end{array} \quad (9a)$$

the GVB wavefunction for this reaction can be written as

$$\psi = \xi_1 \begin{array}{|c|} \hline \phi_1 \phi_2 \\ \hline \phi_3 \\ \hline \end{array} + \xi_2 \begin{array}{|c|} \hline \phi_1 \phi_3 \\ \hline \phi_2 \\ \hline \end{array} \quad (9b)$$

From plots of the orbital changes involved in the GVB description of this reaction (Fig. 3)⁵ we see that as the reaction proceeds, orbital ϕ_2 , which is initially associated with the H' nucleus, slowly delocalizes in a symmetric manner over to the deuterium nucleus and finally relocalizes there. Simultaneously, orbital ϕ_3 , which is initially centered on the deuterium, delocalizes in an antisymmetric manner over to the H' center and finally relocalizes there. The result is that orbitals ϕ_1 and ϕ_2 always remain highly overlapping while ϕ_3 remains nearly orthogonal to both of them. Thus, these orbitals remain essentially strongly orthogonal at all times. However, the coupling between them does not remain fixed. In fact, the coupling changes drastically and, up through the saddle point, closely resembles what one would expect were the reaction to proceed via a purely localized orbital mechanism (Fig. 4).

As the above examples have served to illustrate,⁶ in order to describe a typical chemical reaction it is necessary to allow the orbitals involved in bond breaking/forming processes to couple with one another in a completely general manner. However, it is usually not necessary to relax all orthogonality constraints since the orbitals tend to remain strongly orthogonal anyway. Therefore, in the SOGVB

approximation we allow the orbitals to couple in a general manner, but nonetheless group them into strongly orthogonal pairs. For example, the three-electron doublet SOGVB wavefunction has the form of the unrestricted GVB wavefunction but involves orbitals constrained to be strongly orthogonal

$$\Psi = \xi_1 \begin{array}{|c|c|} \hline \phi_{11}' & \phi_{21}' \\ \hline \phi_3 & \\ \hline \end{array} + \xi_2 \begin{array}{|c|c|} \hline \phi_{11}' & \phi_3 \\ \hline \phi_{21}' & \\ \hline \end{array} \quad (10a)$$

$$= \begin{array}{|c|c|} \hline \phi_{11}' & \phi_{21}' \\ \hline \phi_3 & \\ \hline \end{array}$$

$$\langle \phi_{11}' | \phi_3 \rangle = \langle \phi_{21}' | \phi_3 \rangle = 0. \quad (10b)$$

As with the GVB-PP wavefunction, it is computationally convenient to write the SOGVB wavefunction in terms of orthogonal orbitals by expressing each nonorthogonal pair in terms of orthogonal natural orbitals. This leads to an MC wavefunction in which each orthogonal configuration either contains only one orbital of a pair with that orbital being doubly-occupied or it contains both orbitals of a pair triplet coupled. For example, substituting (3) into (10a) gives

$$\Psi = A_1 \begin{array}{|c|c|} \hline \phi_{11} & \phi_{11} \\ \hline \phi_3 & \\ \hline \end{array} + A_2 \begin{array}{|c|c|} \hline \phi_{21} & \phi_{21} \\ \hline \phi_3 & \\ \hline \end{array} + A_3 \begin{array}{|c|c|} \hline \phi_{11} & \phi_3 \\ \hline \phi_{21} & \\ \hline \end{array} \quad (11a)$$

where

$$A_1 = \sqrt{2} \xi_1 \lambda_{11};$$

$$A_2 = \sqrt{2} \xi_1 \lambda_{21}; \quad A_3 = 2\sqrt{\lambda_{11} \lambda_{21}} \xi_2 \quad (11b)$$

and the two-pair four-electron singlet wavefunction is

$$\Psi = A_1 \begin{array}{|c|c|} \hline \phi_{11} \phi_{11} \\ \hline \phi_{12} \phi_{21} \\ \hline \end{array} + A_2 \begin{array}{|c|c|} \hline \phi_{11} \phi_{11} \\ \hline \phi_{22} \phi_{22} \\ \hline \end{array} + A_3 \begin{array}{|c|c|} \hline \phi_{21} \phi_{21} \\ \hline \phi_{12} \phi_{12} \\ \hline \end{array} + A_4 \begin{array}{|c|c|} \hline \phi_{21} \phi_{21} \\ \hline \phi_{22} \phi_{22} \\ \hline \end{array} + A_5 \begin{array}{|c|c|} \hline \phi_{11} & \phi_{21} \\ \hline \phi_{21} & \phi_{22} \\ \hline \end{array} \quad (12)$$

subject to the constraint $A_1 A_3 = A_2 A_4$. As a consequence, the SOGVB energy expression for NG orbitals involving NGP pairs is

$$E = 2 \sum_i^{NG} f_i h_{i,i} + \sum_{i,j}^{NG} [a_{i,j} J_{i,j} + b_{i,j} K_{i,j}] + 4 \sum_m^{NGP} \left\{ \sum_{i \neq 1m, 2m}^{NG} c_{mi} \langle \phi_{1m} | K_i | \phi_{2m} \rangle + \sum_{n>m}^{NGP} [d_{nm}^{(1)} (\phi_{1m} \phi_{1n} | \phi_{2n} \phi_{2m}) + d_{nm}^{(2)} (\phi_{1m} \phi_{2n} | \phi_{1n} \phi_{2m})] \right\} \quad (13a)$$

where

$$h_{i,i} = \langle \phi_i | \hat{h} | \phi_i \rangle = \langle \phi_i | T + \hat{V} | \phi_i \rangle$$

$$J_{i,j} = (\phi_i \phi_i | \phi_j \phi_j)$$

$$= \langle \phi_i(1) \phi_j(2) | r_{12}^{-1} | \phi_i(1) \phi_j(2) \rangle \quad (13b)$$

$$K_{i,j} = (\phi_i \phi_j | \phi_j \phi_i)$$

$$= \langle \phi_i(1) \phi_j(2) | r_{12}^{-1} | \phi_j(1) \phi_i(2) \rangle$$

and where the coefficients $\{f, a, b, c, d\}$ are functions of the configuration coefficients $\{A\}$ which in turn are functions of the pair and coupling coefficients $\{\lambda, \xi\}$.

Since (13a) contains only diagonal one-electron terms, inclusion of closed-shell, perfect-pairing, and open-shell multiplet orbitals in the wavefunction is straightforward. This is of considerable importance since in most chemical reactions only a few orbitals are actually involved in the bonding process. However, nonparticipating orbitals must also be taken into account since changes in these orbitals can be important. To treat all orbitals at a generalized coupling (GC) level is unnecessary and computationally impractical. By allowing the SOGVB wavefunction to explicitly include these less correlated orbitals we arrive at a wavefunction in which each group of orbitals is treated at an appropriate level of correlation and with an appropriate amount of computational effort. Thus, generalizing (13a) to include NS closed-shell and perfect-pair orbitals and NM multiplet-shell orbitals the energy expression for all N orbitals becomes

$$E = 2 \sum_i^N f_i h_{i,i} + \sum_{i,j}^N [a_{i,j} J_{i,j} + b_{i,j} K_{i,j}]$$

$$+ 4 \sum_m \left\{ \sum_{i \neq 1m, 2m}^{NGP \quad NG+NM} c_{mi} \langle \phi_{im} | K_i | \phi_{2m} \rangle \right.$$

$$\left. + \sum_{n>m}^{NGP} [d_{nm}^{(1)} (\phi_{1m} \phi_{1n} | \phi_{2n} \phi_{2m}) \right.$$

$$\left. + d_{nm}^{(2)} (\phi_{1m} \phi_{2n} | \phi_{1n} \phi_{2m}) \right\} \quad (14)$$

Having arrived at the general energy expression for the SOGVB wavefunction we can now consider the task of developing the equations for its self-consistent solution. For the present, let us ignore the problem of optimizing the pair and coupling coefficients and concentrate on orbital optimization. From the Variational Principle we know that the orbitals will be self-consistent when the energy is stationary through first-order for any changes in the orbitals provided these changes preserve orbital orthogonality at least through first-order. Allowing the orbitals in (14) to vary according to the prescription

$$\phi_i \Rightarrow \phi_i + \delta_i ;$$

$$[\langle \delta_i | \phi_j \rangle + \langle \delta_j | \phi_i \rangle + \langle \delta_i | \delta_j \rangle]^{(1)} = 0 \quad (15a)$$

this variational condition is found to be

$$\delta E^{(1)} = \sum_i^N [\langle \delta_i | F_i | \phi_i \rangle + \langle \delta_i | R_i \rangle] = 0 \quad (15b)$$

where

$$F_i = f_i h + \sum_j^N [a_{j,i} J_j + b_{j,i} K_j]$$

$$+ \sum_m^{NGP} c_{mi} [(\phi_{1m} | \phi_{2m}) + (\phi_{2m} | \phi_{1m})] \quad (15c)$$

and where we define the exchange-like operator $(\phi_i | \phi_j)$ by

$$\langle \phi_i | (\phi_j | \phi_k) | \phi_l \rangle = (\phi_i \phi_j | \phi_k \phi_l) \quad (15d)$$

If orbital i is not a GC pair orbital then $R_i = 0$. If however it corresponds to pair orbital ϕ_{km} then

$$R_{km} = \left(\sum_{j \neq 1m, 2m}^{NG+NM} c_{mj} K_j + \sum_{n \neq m}^{NGP} [d_{nm}^{(k)} (\phi_{1n} | \phi_{2n}) \right.$$

$$\left. + d_{nm}^{(3-k)} (\phi_{2n} | \phi_{1n}) \right] | \phi_{(3-k), m} \rangle \quad (15e)$$

If we define the operator R_i' by

$$R_i' = R_i \langle \phi_i | \quad (16a)$$

then we can write (15b) in the more usual form

$$0 = \sum_i^N \langle \delta_i | F_i' | \phi_i \rangle \quad (16b)$$

where

$$F_i' = F_i + R_i' \quad (16c)$$

However, we prefer to work with the quantities defined in (15) since these arise directly from (14) whereas those of (16) do not.

Now let us consider the problem of optimizing any one orbital while keeping all others fixed. If only orbital ϕ_i is varied then (15b) becomes

$$0 = \langle \delta_i | F_i | \phi_i \rangle + \langle \delta_i | R_i \rangle \quad (17)$$

However, this is subject to the constraint that $\langle \delta_i | \phi_j \rangle = 0$ for all ϕ_j . Therefore, if only one orbital is varied it can only be changed with respect to the space orthogonal to all orbitals. Keeping this in mind, if we isolate from (14) all terms involving ϕ_i and replace this orbital with the improved orbital

$$\phi_i^1 = (\phi_i + \Delta \phi_i) / (1 + \Delta_i^2)^{1/2} ;$$

$$\Delta_i^2 = \langle \Delta \phi_i | \Delta \phi_i \rangle \quad (18a)$$

upon expansion through second-order in $\Delta\phi_i$ we obtain

$$\begin{aligned} \epsilon_i(1 + \Delta_i^2) &= \langle \phi_i | F_i | \phi_i \rangle + \langle \phi_i | R_i \rangle \\ &+ 2[\langle \Delta\phi_i | F_i | \phi_i \rangle + \langle \Delta\phi_i | R_i \rangle] \\ &+ \langle \Delta\phi_i | F_i + 2a_{i,i}K_i | \Delta\phi_i \rangle \end{aligned} \quad (18b)$$

where for simplicity we have taken $b_{i,i} = 0$. Expressing $\Delta\phi_i$ in terms of the basis space $\{\chi\}$ orthogonal to all orbitals

$$\Delta\phi_i = \sum_k C_{ki} \chi_k \quad (18c)$$

where

$$\langle \chi_k | \phi_j \rangle = 0; \quad \langle \chi_k | \chi_\ell \rangle = \delta_{k,\ell} \quad (18d)$$

the solution through second-order for the improved orbital in the field of all other ones is obtained by diagonalizing the matrix X where

$$\begin{aligned} X_{0,0} &= \langle \phi_i | F_i | \phi_i \rangle + \langle \phi_i | R_i \rangle \\ X_{0,k} &= X_{k,0} = \langle \chi_k | F_i | \phi_i \rangle + \langle \chi_k | R_i \rangle \end{aligned} \quad (18e)$$

$$X_{k,\ell} = \langle \chi_k | F_i | \chi_\ell \rangle + 2a_{i,i} \langle \chi_k | K_i | \chi_\ell \rangle; \quad k, \ell \neq 0$$

and choosing the desired root (usually on the basis of either lowest eigenvalue or least change).

If ϕ_i is a closed-shell orbital, $R_i = 0$. Furthermore, if we neglect the second-order self-correction term $2a_{i,i} \langle \chi_k | K_i | \chi_\ell \rangle$, the X matrix simply becomes a matrix over the Fock operator F_i . Since the Fock operators for all closed-shell orbitals can be made identical, solutions for all such orbitals could then be obtained through a single diagonalization. Since this offers considerable computational advantage and since experience has shown that these terms are relatively unimportant, we normally follow this procedure. For open-shell multiplet orbitals these terms do not appear in the first place. For all other orbitals the Fock operators are different and no real advantage is gained in neglecting these terms.

Examining the terms involved in (18) we see that for closed-shell and perfect-pair orbitals these equations involve only the same operator matrices that are required for a GVB-PP calculation. For the remaining orbitals the only additional matrices required are those over the GC-pair operators ($\phi_{1n} | \phi_{2n}$). Therefore, only a little more computational effort is required here than would be the case for the corresponding GVB-PP calculation.

Equations (18) provide us with the prescription for iteratively optimizing the orbitals with respect to unoccupied space. There now remains the problem of optimizing them with respect to one another. Since the orbitals must always remain orthogonal the only way to do this is to vary at least two of them simultaneously. If orbitals ϕ_i and ϕ_j are

simultaneously varied while keeping all others fixed, (15b) becomes

$$\begin{aligned} 0 &= \langle \delta_i | F_i | \phi_i \rangle + \langle \delta_i | R_i \rangle \\ &+ \langle \delta_j | F_j | \phi_j \rangle + \langle \delta_j | R_j \rangle \end{aligned} \quad (19a)$$

subject to the condition

$$[\langle \delta_i | \phi_j \rangle + \langle \delta_j | \phi_i \rangle + \langle \delta_i | \delta_j \rangle]^{(1)} = 0. \quad (19b)$$

through first-order. To obtain the equation for the optimal mixing between these two orbitals we isolate all terms involving them from (14) and substitute the improved orbitals

$$\phi_i^1 = (\phi_i + \Delta\phi_i) / (1 + \Delta_i^2)^{1/2} \quad (20a)$$

$$\phi_j^1 = (\phi_j + \Delta\phi_j) / (1 + \Delta_j^2)^{1/2}$$

Realizing that if

$$\Delta\phi_i = \gamma_{ij} \phi_j \quad (20b)$$

then we must have

$$\Delta\phi_j = -\gamma_{ij} \phi_i \quad (20c)$$

we expand through second-order in γ_{ij} to obtain

$$\begin{aligned} \epsilon_{ij}(1 + \gamma_{ij}^2) &= \langle \phi_i | F_i | \phi_i \rangle + \langle \phi_i | R_i \rangle + \langle \phi_j | F_j | \phi_j \rangle + \langle \phi_j | R_j \rangle \\ &+ \gamma_{ij}^2 [\langle \phi_i | F_j | \phi_i \rangle + \langle \phi_j | F_i | \phi_j \rangle + Q_{ij}] \\ &+ 2\gamma_{ij} [\langle \phi_i | F_i - F_j | \phi_j \rangle + \langle \phi_j | R_i \rangle - \langle \phi_i | R_j \rangle] \end{aligned} \quad (20d)$$

where the second-order correction term Q_{ij} is given by

$$\gamma_{ij} Q_{ij} = \langle \phi_i | \Delta F_i - \Delta F_j | \phi_j \rangle + \langle \phi_j | \Delta R_i \rangle - \langle \phi_i | \Delta R_j \rangle \quad (21a)$$

and where ΔF and ΔR are the first-order changes in the corresponding operators. For example, if either orbital is a closed-shell or perfect-pair orbital or if neither is a GC pair orbital

$$\begin{aligned} Q_{ij} &= Q_{ij}^0 = 2(a_{i,i} + a_{j,j} - 2a_{i,j})K_{i,j} \\ &+ (b_{i,i} + b_{j,j} - 2b_{i,j})[J_{i,j} + K_{i,j}] \end{aligned} \quad (21b)$$

whereas if orbital ϕ_i is in GC pair m and orbital ϕ_j is a multiplet or unpaired GC orbital

$$Q_{ij} = Q_{ij}^0 - 2c_{mj} \langle \phi_{1m} | J_j + K_j | \phi_{2m} \rangle \quad (21c)$$

Letting

$$\begin{aligned} c_{ij}^{(1)} &= \langle \phi_i | F_i - F_j | \phi_j \rangle - \langle \phi_j | R_i \rangle - \langle \phi_i | R_j \rangle \\ c_{ij}^{(2)} &= \langle \phi_j | F_i - F_j | \phi_j \rangle - \langle \phi_i | F_i - F_j | \phi_i \rangle \\ &\quad - \langle \phi_i | R_i \rangle - \langle \phi_j | R_j \rangle + Q_{ij} \end{aligned} \quad (22a)$$

mixing coefficient γ_{ij} is obtained by solving

$$0 = c_{ij}^{(1)} [\gamma_{ij}^2 - 1] - c_{ij}^{(2)} \gamma_{ij} \quad (22b)$$

and choosing the appropriate root.

In principle, the orbitals can be iteratively optimized with respect to one another using (22). However, to redefine all affected matrix elements after each such orbital-pair rotation is computationally unacceptable and experience has shown that by not doing so the overall orbital changes tend to be too large. To see if there is a simple way to overcome this problem let us now consider simultaneously optimizing all orbitals with respect to one another by taking the improved orbitals to be

$$\phi_i^1 = N_i \left[\bar{\phi}_i - \sum_{k < i} \langle \bar{\phi}_i | \phi_k^1 \rangle \phi_k^1 \right] \quad (23a)$$

with

$$\bar{\phi}_i = \phi_i + \sum_{j \neq i} \gamma_{ji} \phi_j \quad ; \quad \gamma_{ij} = -\gamma_{ji} \quad (23b)$$

Upon substituting these orbitals into (14) and expanding through second-order in $\{\gamma_{ij}; i > j\}$ the result is a rather complicated expression involving many two-electron integrals not required in either (22) or (18). All such integrals, however, only appear in terms involving the product of two different mixing coefficients. If we now content ourselves with a pairwise mixing scheme by neglecting all such mixed coefficient terms, we find that the mixing coefficients can be determined by diagonalizing the matrix \underline{B} where

$$\begin{aligned} B_{0,0} &= 0 \\ B_{0,ij} &= B_{ij,0} = c_{ij}^{(1)} \\ B_{ij,kl} &= 0 \text{ for } ij \neq kl \\ B_{ij,ij} &= c_{ij}^{(2)} \end{aligned} \quad (23c)$$

and where $c_{ij}^{(1)}$ and $c_{ij}^{(2)}$ are given by (22a). While diagonalization of this matrix and choosing the appropriate root still constitute only a pairwise optimization scheme, it has been found to be superior to simple sequential usage of (22) since each mixing coefficient is now weighted relative to its importance in lowering the total energy.

Equations (18) and (23) provide us with the prescriptions for optimizing the orbitals to self-consistency for fixed pair and coupling coefficients. We will now turn our attention to determining these coefficients. First of all, let us consider any perfect-pair coefficients. If orbitals ϕ_{1k} and ϕ_{2k} are perfectly paired, the coefficients in (14) which depend upon pair coefficients λ_{1k} and λ_{2k} are

$$f_{ik} = a_{ik,ik} = \lambda_{ik}^2 / (\lambda_{1k}^2 + \lambda_{2k}^2) \quad ; \quad i = 1, 2$$

$$b_{1k,2k} = b_{2k,1k} = -\lambda_{1k} \lambda_{2k} / (\lambda_{1k}^2 + \lambda_{2k}^2)$$

$$a_{ik,j} = a_{j,ik} = 2f_{ik} f_j \quad ;$$

$$i = 1, 2 \quad ; \quad \phi_j \neq \phi_{1k}, \phi_{2k}$$

$$b_{ik,j} = b_{j,ik} = -f_{ik} f_j \quad ;$$

$$i = 1, 2 \quad ; \quad \phi_j \neq \phi_{1k}, \phi_{2k}$$

(24a)

Isolating these terms in (14) gives

$$\begin{aligned} E_k (\lambda_{1k}^2 + \lambda_{2k}^2) &= \lambda_{1k}^2 H_{1k,1k} + \lambda_{2k}^2 H_{2k,2k} \\ &\quad + 2\lambda_{1k} \lambda_{2k} H_{1k,2k} \end{aligned} \quad (24b)$$

where

$$H_{ik,ik} = 2 h_{ik,ik} + J_{ik,ik}$$

$$+ 2 \sum_{j \neq 1k, 2k}^N f_j (2J_{ik,j} - K_{ik,j})$$

$$H_{1k,2k} = H_{2k,1k} = -\frac{1}{2} K_{1k,2k} \quad (24c)$$

Therefore, we solve for λ_{1k} and λ_{2k} by diagonalizing this 2×2 \underline{H} matrix and choosing the root which minimizes E_k . If there is more than one perfect pair involved, the pair coefficients for each pair are optimized iteratively through sequential application of (24) until self-consistency is achieved.

We are now left with the task of optimizing the GC pair and coupling coefficients which, in turn, define the $\{f, a, b, c, d\}$ energy coefficients involving GC orbitals. In general, the relationship between these coefficients is not straightforward and is most easily established by first expressing the wavefunction (ignoring all but GC orbitals) as

$$\Psi = \sum_i A_i \psi_i \quad (25)$$

where the configuration coefficients $\{A\}$ are known functions of the GC pair and coupling coefficients $\{\lambda, \xi\}$. Determining the energy expression for Ψ and rearranging it to the form of (13a) then establishes the relationship between $\{A\}$ and the coefficients in (13a).

In general, the coefficients $\{A\}$ in (25) are not all linearly independent. Therefore, they cannot be determined simply by diagonalizing the hamiltonian over the configurations involved. To do this we recast the wavefunction into the general form

$$\Psi = A \prod_i^{NGP} [\lambda_{1i} \phi_{1i}^2 - \lambda_{2i} \phi_{2i}^2 + \sqrt{\lambda_{1i} \lambda_{2i}} (\phi_{1i} \phi_{2i} - \phi_{2i} \phi_{1i})] \phi_m \dots \phi_n \times (\sum_j \xi_j X_j) \quad (26)$$

where $\{X\}$ is a set of appropriate orthogonal spin eigenfunctions. Concentrating on pair k , (26) can be written as

$$\Psi = (\lambda_{1k} \phi_{1k,1k} - \lambda_{2k} \phi_{2k,2k}) \sum_u \xi(k)_u X(k)_u + 2 \sqrt{\lambda_{1k} \lambda_{2k}} \phi_{1k,2k} \sum_v \xi(k)_v X(k)_v \quad (27a)$$

where

$$\phi_{ik,jk} = A \phi_{ik} \phi_{jk} \prod_{\ell \neq k}^{NGP} [\lambda_{1\ell} \phi_{1\ell}^2 - \lambda_{2\ell} \phi_{2\ell}^2 + \sqrt{\lambda_{1\ell} \lambda_{2\ell}} (\phi_{1\ell} \phi_{2\ell} - \phi_{2\ell} \phi_{1\ell})] \times \phi_m \dots \phi_n \quad (27b)$$

and where $X(k)_u$ [$X(k)_v$] is the u^{th} spin eigenfunction in which the electronic positions of pair k are singlet (triplet) coupled. If we now let

$$\psi_{k,v}^{(i)} = \phi_{ik,ik} X(k)_v \quad ; \quad i = 1, 2$$

$$\psi_{k,v}^{(3)} = \phi_{1k,2k} X(k)_v$$

$$\sigma_{k,v} = 2 \sqrt{\lambda_{1k} \lambda_{2k}} \xi(k)_v \quad (27c)$$

we can solve for $\lambda_{1k}, \lambda_{2k}$ and $\{\xi(k)\}$ by taking

$$\Psi = \lambda_{1k} \left[\sum_u \xi(k)_u \psi_{k,u}^{(1)} \right] + \lambda_{2k} \left[-\sum_u \xi(k)_u \psi_{k,u}^{(2)} \right] + \sum_v \sigma_{k,v} \psi_{k,v}^{(3)} \quad (27d)$$

and diagonalizing the hamiltonian matrix over the configurations involved. If we then rewrite (27d)

as

$$\Psi = \sum_u \xi(k)_u [\lambda_{1k} \psi_{k,u}^{(1)} - \lambda_{2k} \psi_{k,u}^{(2)}] + \sum_v \sigma_{k,v} \psi_{k,v}^{(3)} \quad (27e)$$

we can determine $\{\xi(k), \xi(k)\}$ by diagonalizing the hamiltonian matrix over the indicated configurations. Therefore, by constructing the hamiltonian matrix over the basic configurations of (25) and then by performing a series of contractions and diagonalizations the optimum GC pair and coupling coefficients can be iteratively obtained. In the course of evaluating the required matrix elements the presence of any closed-shell or perfect-pair orbitals in the total wavefunction is taken into account by using the modified one-electron operator

$$h' = h + \sum_i^{NS} f_i (2J_i - K_i) \quad (28a)$$

and the presence of any multiplet-shell orbitals is taken into account by formalizing the matrix element expressions for $NG + 1$ electrons. This leads to terms involving the multiplet-shell exchange operator

$$K_M = \sum_i^{NM} K_i \quad (28b)$$

Early experience has shown that because of the high degree of correlation existing between the GC orbitals, it is quite advantageous to fully optimize the GC orbitals with respect to one another during each iteration of the SCF cycle. Therefore, we usually ignore terms in (23) which mix the GC orbitals and perform this mixing during the GC pair and coupling coefficient optimization stage. To do this we define the improved orbitals as in (23a, 23b) but with the summations running only over GC orbitals. Upon substituting these orbitals in (25) and expanding through second-order we obtain

$$\Psi^1 = \Psi + \sum_{ij} \gamma_{ij} \psi_{ij} + \sum_{ij,kl} \gamma_{ij} \gamma_{kl} \psi_{ij,kl} \quad (29a)$$

If we then define the matrices \underline{H} and \underline{S} by

$$H_{0,0} = \langle \Psi | H | \Psi \rangle$$

$$H_{ij,0} = H_{0,ij} = \langle \Psi | H | \psi_{ij} \rangle$$

$$H_{ij,kl} = \langle \psi_{ij} | H | \psi_{kl} \rangle + \langle \Psi | H | \psi_{ij,kl} \rangle (1 + \delta_{ij,kl})$$

$$S_{0,0} = \langle \Psi | \Psi \rangle$$

$$S_{ij,0} = S_{0,ij} = \langle \psi | \psi_{ij} \rangle$$

$$S_{kj,k\ell} = \langle \psi_{ij} | H | \psi_{k\ell} \rangle$$

$$+ \langle \psi | \psi_{ij,k\ell} \rangle (1 + \delta_{ij,k\ell}), \quad (29b)$$

the mixing coefficients $\{\gamma_{ij}; i>j\}$ can be obtained through second-order in the energy by solving the secular equation

$$(\underline{H} - \underline{E} \underline{S}) \underline{\gamma} = 0. \quad (29c)$$

Once the improved orbitals have been found we redefine all required hamiltonian matrices for them and once again solve (27) for new pair and coupling coefficients. This process is continued until self-consistency within the current GC space is achieved.

To summarize, the SCF cycle which we employ to solve for an SOGVB wavefunction consists of the following distinct steps:

- 1) Optimization of all GC pair and coupling coefficients using equations (27);
- 2) Optimization of the GC orbitals with respect to one another using equations (29);
- 3) Optimization of all perfect-pair coefficients using equations (29);

- 4) Optimization of orbitals with respect to one another (excluding mixing between GC orbitals) using equations (23); and
- 5) Optimization of all orbitals with respect to unoccupied space using equations (18).

Steps 1) and 2) are performed together until self-consistent. Step 3) is continued until all perfect-pair coefficients are self-consistent. Steps 4) and 5) are performed only once per SCF iteration (i.e., they are not continued until self-consistent).

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