A generalized direct inversion in the iterative subspace approach for generalized valence bond wave functions

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We present a greatly improved method for converging generalized valence bond (GVB) self-consistent wave functions. This method starts with the direct inversion in the interative subspace (DIIS) ideas of Pulay. Previously implemented DIIS methods were limited to special cases: closed-shell Hartree–Fock (HF), restricted open-shell HF, or a single pair GVB wave function. Here we extend this method to general wave functions including arbitrary numbers of closed-shell, restricted open-shell, and GVB orbitals (including second-order orbital mixing terms). The efficacy of GVB-DIIS is illustrated by applying it to several cases (including GVB wave functions with up to ten pairs) and comparing with other standard methods.

I. INTRODUCTION

Essentially, all methods for calculating the electronic wave functions (i.e., solving the Schrödinger equation) of atoms, molecules, and solids include a first step involving optimization of orbitals (atomic orbitals, molecular orbitals, or band orbitals).

The most common starting point for accurate wave functions is the Hartree–Fock (HF) method in which a product of orbitals and spins is antisymmetrized (using a Slater determinant) and the orbitals optimized self-consistently (SCF for self-consistent field).

For systems where the description in terms of doubly occupied orbitals is adequate, this might then be used as the starting point for more accurate configuration interaction (CI) (e.g., singles and doubles CI, HF-SD) or perturbation theory (e.g., MP2 and MP3) calculations by including excitations where various numbers of electrons are excited from the occupied orbitals of the HF wave function to unoccupied or *virtual* orbitals.

An alternative approach is the generalized valence bond method[1,2] (GVB) in which (i) each pair of electrons is described with two orbitals (rather than one, as in HF); (ii) the form of the wave function is generalized from a Slater determinant to a form that ensures that the Pauli principle and spin symmetry are both satisfied; and (iii) the orbitals are optimized self-consistently.

The GVB orbitals generally localize uniquely to regions near a bond or atom and each pair can be viewed as involving one orbital very similar to a localized occupied HF orbital and the other involving an optimized unoccupied (virtual) HF orbital. Thus for the simple closed-shell case with N electrons in which HF involves $N/2$ doubly occupied orbitals, the N orbitals of the GVB wave function can be viewed as a localized set of $N/2$ HF-like occupied orbitals plus $N/2$ localized unoccupied HF orbitals optimized for electron correlation. With GVB one can correlate just a subset of HF pairs, leading to localized orbitals similar to the full GVB wave function. As with HF, many GVB calculations are followed by some kind of CI; however, since the dominant correlating orbitals have been solved self-consistently, the GVB wave function often allows an accurate description of the wave function to be obtained with very compact CIs. These GVB-based methods have proved most advantageous for examining excited states,[3] transition metal complexes,[4] organometallics,[5] reaction pathways,[6] reactions at surfaces,[7] and catalysis,[8] where the description in terms of doubly occupied orbitals would be quite poor.

GVB is a special case of multiconfiguration SCF (MCSCF) methods [including complete active space self-consistent field (CAS-SCF)] for which the methods in this paper also prove useful; however, we focus here on GVB.

Because of the two-electron interactions, optimization of the wave function is nonlinear. Hence critical to such SCF methods as HF or GVB is an iterative approach that converges quickly and reliably to the desired state.

The variational principle leads directly to the Euler–Lagrange condition[9]

$$F_i\phi_i=\epsilon_i\phi_i \tag{1.1}$$

that must be satisfied for ϕ_i to be the optimum orbital, where the Fock operator F_i contains fields due to all other orbitals. The earliest approaches for solving Eq. (1.1) involved using the orbitals from a previous iteration $\{\phi_j^I\}$ to evaluate F_i^I and then solving

$$F_i^I\phi_i^{I+1}=\epsilon_i\phi_i^{I+1} \tag{1.2}$$

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to obtain new orbitals. Using various convergence schemes to average or extrapolate orbitals, such approaches were often successful for closed-shell HF wave functions (all orbitals doubly occupied). However for GVB, wave functions for such methods were much less successful and in 1970 Hunt, Dunning, and Goddard (HDG)[10] developed a general approach for including the higher-order corrections to the variational equations for GVB and open-shell HF wave functions. This leads to an approach that can be quadratically convergent (given good trial functions). However, practical implementations[9] of HDG generally ignore some coupling terms, often leading to pseudolinear convergence.

There are two classes of self-consistent wave functions: (i) Hartree–Fock, unrestricted Hartree–Fock, GVB-PP (perfect pairing), which can be calculated without transformations of the two-electron integrals, and (ii) more general MC-SCF methods including CAS-SCF, general GVB, which do require full integral transformations. Class *b* is restricted to much smaller systems than class *a*, but with fully transformed two-electron integrals it is possible to obtain quadratic convergence.[15,22] With class *a* one could do integral transformations and also get quadratic convergence; however, this is often not practical and hence other convergence methods are necessary.

A breakthrough for convergence of HF wave functions was the development in the early 1980s by Pulay of the direct inversion of the iterative subspace (DIIS)[11–13] method. Instead of extrapolating *orbitals* from iteration to iteration, DIIS methods average the *Fock matrices* from different iterations to obtain a new trial Fock matrix for the orbitals of the next iteration. Because GVB and open-shell wave functions have *different* Fock operators for different orbitals, generalizing DIIS for such wave functions is not trivial. However, DIIS has been successfully applied to closed-shell HF,[11,12] restricted open-shell HF (ROHF),[13] and single-pair GVB wave functions.[13] In Sec. III we extend the DIIS methodology to be appropriate for general GVB wave functions. In this process we include in the Fock operator all second-order terms from HDG. This leads to very rapid convergence for GVB, comparable to that for HF-DIIS.

Section II summarizes aspects of GVB used in subsequent sections and Sec. IV illustrates the methods by application to several systems and comparison to results using previous methods.

II. SUMMARY OF GVB METHODS

A. The GVB-PP wave function and general energy expressions

The GVB wave function[1] involves a product of orbitals with a general spin function χ which is an eigenfunction of the total spin operator $[\hat{S}^2\chi=S(S+1)\chi]$:

$$\Phi^{\mathrm{GVB}}=\mathscr{A}[\phi_i,\ldots,\phi_N\chi], \tag{2.1}$$

where both the orbitals and spin functions are optimized. More commonly, the perfect pairing (PP) restriction[2] is made in which each pair of electrons is written as a valence bond (VB) pair:

$$(\phi_a\phi_b+\phi_b\phi_a)(\alpha\beta-\beta\alpha). \tag{2.2a}$$

The GVB formalism allows any number of electrons ($2n_{\mathrm{core}}$) to be described with doubly occupied orbitals (Φ_{core}) and any number of electrons (n_{open}) to be high-spin coupled ($S=n_{\mathrm{open}}/2$), leading to the composite wave function[1,17]

$$\Psi=\mathscr{A}[\Psi_{\mathrm{core}}\Psi_{\mathrm{open}}\Psi_{\mathrm{pair}}], \tag{2.3}$$

where $\mathscr{A}$ is the antisymmetrizer, where

$$\Psi_{\mathrm{core}}=\prod_{i=1}^{n_{\mathrm{core}}}(\phi_i^c\alpha)(\phi_i^c\beta), \tag{2.4a}$$

$$\Psi_{\mathrm{open}}=\prod_{i=1}^{n_{\mathrm{open}}}(\phi_i^o\alpha), \tag{2.4b}$$

$$\Psi_{\mathrm{pair}}=\prod_{i=1}^{n_{\mathrm{pair}}}(\phi_{ai}^g\phi_{bi}^g+\phi_{bi}^g\phi_{ai}^g)(\alpha\beta-\beta\alpha), \tag{2.4c}$$

where $\{\phi_i^c\}$, $\{\phi_i^o\}$ are orthogonal spacial orbitals, and where α and β are spin functions. Here ϕ_{ai}^g and ϕ_{bi}^g denote the GVB orbitals in pair *i*, and normalization of the total wave function is ignored. Within a pair, the GVB orbitals overlap, $S_i=\langle\phi_{ai}|\phi_{bi}\rangle$. However, in the PP restriction we take the orbitals of pair *i* as orthogonal to all *other* pairs (and to $\{\phi_i^c\}$ and $\{\phi_j^o\}$). For computational purposes it is convenient to rewrite the GVB wave function (2.2a) as

$$(C_{gi}\phi_{gi}\phi_{gi}+C_{ui}\phi_{ui}\phi_{ui}) \tag{2.2b}$$

and Eq. (2.4c) as

$$\Psi_{\mathrm{pair}}=\prod^{n_{\mathrm{pair}}}(C_{gi}\phi_{gi}\phi_{gi}+C_{ui}\phi_{ui}\phi_{ui})(\alpha\beta-\beta\alpha), \tag{2.4d}$$

where

$$\phi_{gi}=\frac{(\phi_{ai}+\phi_{bi})}{\sqrt{2(1+S_i)}}, \tag{2.5a}$$

$$\phi_{ui}=\frac{(\phi_{ai}-\phi_{bi})}{\sqrt{2(1-S_i)}} \tag{2.5b}$$

are orthogonal GVB natural orbitals. Here the GVB configuration interaction (CI) coefficients satisfy

$$\frac{C_{ui}}{C_{gi}}=\frac{1-S_i}{1+S_i} \tag{2.6a}$$

and

$$C_{gi}^2+C_{ui}^2=1. \tag{2.6b}$$

The wave function (2.3) leads to the general energy expression for GVB-PP wave functions,[9]

$$E=\sum_i^{\mathrm{occ}}2f_ih_{ii}+\sum_{i,j}^{\mathrm{occ}}(a_{ij}J_{ij}+b_{ij}K_{ij}), \tag{2.7}$$

where the standard definitions for the one-electron, Coulomb, and exchange energies are used:

$$h_{ii}=\langle\phi_i|\mathbf{h}|\phi_i\rangle, \tag{2.8}$$

$$J_{ij}=(ii|jj)=\int d^3r_1\,\phi_i(1)\mathbf{J}^j(1)\phi_i(1), \tag{2.9a}$$

$$\mathbf{J}^j(1)=\int d^3r_2\,\frac{\phi_j(2)\phi_j(2)}{r_{12}}, \tag{2.9b}$$

$$K_{ij}=(ij|ij)=\int d^3r_1\,\phi_i(1)\mathbf{K}^j(1)\phi_i(1), \tag{2.10a}$$

$$\mathbf{K}^j(1)=\int d^3r_2\,\frac{\phi_j(2)\tau_{12}\phi_j(2)}{r_{12}}, \tag{2.10b}$$

and τ_{12} is the transposition operator. Here $\mathbf{h}$ may include effective core potentials[14] in addition to kinetic energy and nuclear attraction terms.

The orbital occupation coefficient f_i in Eq. (2.7) is given by

$$\begin{aligned} &f_i=1 \quad \textit{if } i \textit{ is a core orbital,}\\ &f_i=\tfrac{1}{2} \quad \textit{if } i \textit{ is an open orbital,}\\ &f_i=(C_i)^2 \quad \textit{if } i \textit{ is a pair orbital with coefficient } C_i. \end{aligned} \tag{2.11}$$

The two-electron coefficients in Eq. (2.7) can then be written as

$$\begin{aligned} &a_{ij}=2f_if_j,\\ &b_{ij}=-f_if_j \end{aligned} \tag{2.12}$$

except that

$$a_{ij}=\tfrac{1}{2},\quad b_{ij}=-\tfrac{1}{2} \quad \textit{if } i \textit{ and } j \textit{ are both open orbitals,} \tag{2.13a}$$

$$a_{ii}=f_i,\quad b_{ii}=0 \quad \textit{if } i \textit{ is a pair orbital,} \tag{2.13b}$$

$$a_{ij}=0,\quad b_{ij}=C_iC_j \quad \textit{if } i\neq j \textit{ are in the same pair.} \tag{2.13c}$$

Another useful case is the open-shell singlet

$$(\phi_i\phi_j+\phi_j\phi_i)(\alpha\beta-\beta),$$

where ϕ_i and ϕ_j are orthogonal. In this case

$$\begin{aligned} &a_{ii}=b_{ii}=0,\\ &a_{ij}=2,\quad b_{ij}=1 \quad \textit{if } i\neq j. \end{aligned} \tag{2.13d}$$

The general condition for convergence is that the first-order change in the energy is zero. With the energy expression (2.7) this leads to[9]

$$\sum_i \langle\delta\phi_i|F^i|\phi_i\rangle=0, \tag{2.14}$$

where F_i is the Fock operator for the orbital ϕ_i,

$$F_i=f_i\mathbf{h}+\sum_j^{\text{occ}}(a_{ij}\mathbf{J}^j+b_{ij}\mathbf{K}^j) \tag{2.15}$$

(for an unoccupied or virtual orbital j we define $F^j=0$). Because the $\mathbf{J}^j$ and $\mathbf{K}^j$ operators depend on the orbitals [Eqs. (2.9) and (2.10)], the solution of the set of variational equation (2.14) is nonlinear and must be solved iteratively. The general condition for orbitals to be optimal[9,15] is that the matrix

$$A_{ij}=\langle i|(F^j-F^i)|j\rangle \tag{2.16}$$

be zero for all pairs of orbitals ϕ_i and ϕ_j (including virtuals).

B. GVB2P5 orbital optimization

The standard method[9] of orbital optimization for wave functions with Fock operators of the form in Eq. (2.15) is a two-step procedure. The first step (ROTATE) mixes occupied orbitals with each other to optimize the energy.[9] The second step, called *orthogonality constrained basis set expansion* (OCBSE),[9] consists of diagonalizing each Fock operator in the space spanned by the virtual orbitals plus the occupied orbitals associated with the same Fock operator (all n_{core} doubly occupied orbitals for the closed-shell Hamiltonian, all n_{open} high-spin coupled orbitals for the open-shell Hamiltonian, always a single occupied orbital for GVB pairs).

For ROTATE we write the (orthogonal) matrix T that transforms an initial set of orbitals $\{\phi_i^0\}$ into a final set of orbitals $\{\phi_i^1\}$ as[15]

$$T=e^{\Delta} \tag{2.17}$$

and calculate the antisymmetric matrix Δ that generates the optimum transformation. Expanding Eq. (2.7) through second-order in orbital changes, leads to[10,15]

$$\Delta_{ij}=-\frac{A_{ij}}{B_{ij,ij}}, \tag{2.18}$$

where A_{ij} is in Eq. (2.16) and

$$\begin{aligned} &B_{ij,ij}=\langle i|(F_j-F_i)|i\rangle-\langle j|(F_j-F_i)|j\rangle+\gamma_{ij},\\ &\gamma_{ij}=2(a_{ii}+a_{jj}-2a_{ij})K_{ij}+(b_{ii}+b_{jj}-2b_{ij})(J_{ij}+K_{ij}). \end{aligned} \tag{2.19}$$

The OCBSE equations for mixing occupied orbitals with virtuals is

$$F_iU_i=U_i\epsilon_i, \tag{2.20}$$

where a single Fock operator F_i is constructed for all orbitals (given by the columns of U_i) in shell i [which have the same f, a, and b coefficients in Eqs. (2.11)–(2.13)]. Thus, one diagonalization is needed for closed-shell HF, two are needed for open-shell HF, and $2n_{\text{pair}}+1$ Fock operators are needed for a GVB case having a core plus n_{pair} GVB pairs. These Fock operators are constructed in the space spanned by the occupied orbitals in shell i plus all virtuals.

In addition to the above orbital optimizations, the GVB CI coefficients in Eq. (2.6) are optimized each iteration, leading a two-by-two diagonalization for each GVB pair j:

$$\mathbf{Y}_j\mathbf{C}_j=\mathbf{C}_jE_j, \tag{2.21a}$$

where

$$Y_{guj}=K_{gu}, \tag{2.21b}$$

$$Y_{xxj}=F_x/f_x \quad for\ g\ or\ u.$$

Because only Coulomb and exchange operators are involved in the above energy expression (2.7) and orbital optimization expressions (2.17)–(2.21), the requisite quantities can be evaluated directly from a list of integrals (an N^4 procedure) without carrying out an integral transformation (an N^5 procedure).[9,10]

III. DIIS METHODOLOGY

A. Introduction

Writing Eq. (1.1) for iteration n as

$$F_i^{(n)}\phi_i^{(n)}-\epsilon_i^{(n)}\phi_i^{(n)}=e_i^{(n)} \tag{3.1}$$

(where the field terms in $F_i^{(n)}$ include the orbitals from iteration n) the convergence condition is that the error vector $e_i^{(n)}$ be zero for all occupied orbitals i. The DIIS procedure uses the errors for various iterations to find a "best" combination:

$$\sum_n^{n_{\text{iter}}} q_n\, \mathbf{e}^n \approx \mathbf{0}, \tag{3.2}$$

where the errors for iterations n are grouped into a supervector $\mathbf{e}^{(n)}$. The next iteration then uses the best Fock operator

$$F^{\text{opt}}=\sum_n^{n_{\text{iter}}} q_n F^{(n)}, \tag{3.3}$$

where F^n is the *general* Fock operator at iteration n. Diagonalizing this predicted Fock operator F^{opt} (rather than the newest Fock operator $F^{n_{\text{iter}}}$, as in an eigenvalue method) leads to accelerated convergence.

For closed-shell HF the variation equation (1.1) becomes

$$F^{\text{cs}}\phi_i=\epsilon_i\phi_i, \quad i=1,\ldots,n_{\text{occ}} \tag{3.4}$$

and it is convenient to define the error vector as[11]

$$e^n=\sum_{k=1}^{n_{\text{occ}}} [F^{\text{cs}}|k\rangle\langle k|-|k\rangle\langle k|F^{\text{cs}}]. \tag{3.5}$$

This has the property that

$$e_{ij}^n=0 \quad if\ i,\ j\ are\ occupied,$$

$$e_{i\mu}^n=-F_{i\mu}^{\text{cs}} \quad if\ i\ is\ occupied\ and\ \mu\ is\ unoccupied,$$

$$e_{\mu i}^n=F_{\mu i}^{\text{cs}} \quad if\ i\ is\ occupied\ and\ \mu\ is\ unoccupied,$$

$$e_{\mu\nu}^n=0 \quad if\ \mu,\nu\ are\ unoccupied.$$

Moreover, in terms of the atomic orbital basis $\{\chi_\sigma\}$:

$$\phi_k=\sum_\sigma \chi_\sigma C_{\sigma k},$$

Eq. (3.5) can be expressed as

$$e_{\sigma\eta}^n=\sum_k [F_{\sigma k}^{\text{cs}}\langle k|\chi_\eta\rangle-\langle\chi_\sigma|k\rangle F_{k\eta}^{\text{cs}}]$$

or

$$\mathbf{e}^n=\mathbf{F}^n\mathbf{D}^n\mathbf{S}-\mathbf{S}\mathbf{D}^n\mathbf{F}^n, \tag{3.6}$$

where $\mathbf{S}_{\alpha\beta}=\langle\chi_\alpha|\chi_\beta\rangle$ and

$$D_{\sigma\eta}=\sum_k C_{\sigma k}C_{\eta k}$$

is the density matrix.

For multishell systems the choice of the error vector is not straightforward,[13] and we propose in Sec. III B a general approach.

Given a sequence of error vectors $\{\mathbf{e}^{(1)},\ldots,\mathbf{e}^{n_{\text{iter}}}\}$, the weights $\{q_n\}$ in Eq. (3.3) are determined[11–13] by minimizing

$$\mathbf{e}^{\text{new}}=\sum_{n=1}^{n_{\text{iter}}} q_n\mathbf{e}^{(n)} \tag{3.7a}$$

under the constraint that

$$\sum_{n=1}^{n_{\text{iter}}} q_n=1. \tag{3.7b}$$

This leads to the equations[11]

$$\mathbf{P}\cdot\mathbf{q}=\mathbf{f} \tag{3.8a}$$

of order $n_{\text{iter}}+1$ where

$$P_{ij}=\mathbf{e}^{(i)}\cdot\mathbf{e}^{(g)} \quad for\ i,j>0, \tag{3.8b}$$

$$\begin{aligned} &P_{oi}=P_{io}=-1 \quad for\ i>0,\\ &P_{oo}=0,\\ &f_i=0 \quad for\ i>0,\\ &f_o=-1, \end{aligned} \tag{3.8c}$$

where $\{q_i,\ i=1,\ n_{\text{iter}}\}$ are used in Eq. (3.3) to obtain the orbitals of the new interation where q_o is a Lagrange multiplier corresponding to half the norm of the new vector (3.7a).

B. General Fock operators

The Fock operator (2.15) represents the first-order change in the energy with respect to mixing various pairs of orbitals. Pure diagonalization (i.e., eigenvalue) methods for multishell cases generally give slow convergence because only first-order changes in the energy are considered. A major advantage to DIIS is that through extrapolation it can provide the fast convergence generally only seen in second-order methods. The question is how to choose the error vector and Fock matrix for GVB wave functions.

1. Combine separate Fock operators, $\mathcal{F}^1$

The simplest definition of a multishell Fock operator $\mathcal{F}$ satisfying the convergence criteria in Eq. (2.16) is

$$
\begin{aligned}
&\mathcal{F}^1_{ij}=F^I_{ij},\quad \textit{where } i,\ j \textit{ are orbitals in shell } I,\\
&\mathcal{F}^1_{ij}=F^I_{ij}-F^J_{ij},\quad \textit{where } i,\ j \textit{ are in different}\\
&\qquad \textit{occupied shells } I,\ J,\\
&\mathcal{F}^1_{ij}=F^I_{ij},\quad \textit{where } i \textit{ is an orbital in shell } I,\ j\\
&\qquad \textit{is unoccupied},\\
&\mathcal{F}^1_{ij}=F^{\mathrm{core}}_{ij},\quad \textit{where } i,\ j \textit{ are unoccupied orbitals.}
\end{aligned}
\tag{3.9}
$$

$\mathcal{F}^1$ is the operator used in the GAMESS[16] program suite for DIIS convergence of one-pair GVB wave functions.

We find that DIIS methods based on $\mathcal{F}^1$ work well when the wave function is sufficiently close to convergence but have difficulty with less optimal starting guesses. Moreover, this method is inherently unsuited to cases with multiple GVB pairs because two or more pairs may be degenerate (e.g., the two OH bonds in water). With $\mathcal{F}^1$ the diagonal elements for degenerate pairs are equivalent and diagonalization delocalizes the GVB natural orbitals over the equivalent pairs.

Further difficulties with $\mathcal{F}^1$ occur in the mixing due to off-diagonal elements. In a matrix diagonalization, the coupling between i and j is proportional to

$$\frac{M_{ij}}{M_{jj}-M_{ii}}, \tag{3.10}$$

where near convergence one has $M_{ij}\ll|M_{jj}-M_{ii}|$. With $\mathcal{F}^1$, the mixing between two occupied orbitals becomes

$$\frac{F^J_{ij}-F^I_{ij}}{F^J_{jj}-F^I_{ii}}. \tag{3.11}$$

However, from Eqs. (2.16)–(2.18) and (2.19), the correct second-order form for the mixing between two occupied orbitals is

$$\frac{F^J_{ij}-F^I_{ij}}{F^I_{ii}-F^J_{ii}+F^J_{jj}-F^I_{jj}-\gamma_{ij}}. \tag{3.12}$$

Ignoring the γ_{ij} terms for the moment, the most striking part of Eq. (3.11) is that it has the *wrong sign* for the combination of F^J_{jj} and F^I_{ii} in the denominator. This can cause the denominator to be small (or even zero) and the mixing terms consequently to become very large and unstable. The lack of γ_{ij} terms in Eq. (3.11) prevents the wave function from converging with equivalent sets of orbitals such as in H_2CO or H_2O (which would have $F^J_{jj}=F^I_{ii}$). In this case all of the terms in Eqs. (3.11) and (3.12) approach zero as the wave function converges except γ_{ij} (which is large for localized orbitals). The γ_{ij} term causes Eq. (3.12) to go to zero upon convergence, while Eq. (3.11) leads to very large mixing. The absence of F^I_{jj} and F^J_{ii} terms in Eq. (3.11) further adds to the convergence problems.

2. The Pulay method

Pulay[13] has used as the multishell Fock operator,

$$
\begin{aligned}
&\mathcal{F}^P_{ij}=F^{\mathrm{core}}_{ij},\quad \textit{where } i,\ j \textit{ are both in shell } I\\
&\qquad \textit{or } i,\ j \textit{ are both unoccupied orbitals},\\
&\mathcal{F}^P_{ij}=F^I_{ij}-F^J_{ij},\quad \textit{where } i,\ j \textit{ are in different}\\
&\qquad \textit{occupied shells},\\
&\mathcal{F}^P_{ij}=\mathcal{F}^I_{ij},\quad \textit{where } i \textit{ is occupied, and } j\\
&\qquad \textit{is unoccupied.}
\end{aligned}
\tag{3.13}
$$

The advantage to $\mathcal{F}^P$ is that the denominator of the mixing term in Eq. (3.10) becomes $F^{\mathrm{core}}_{jj}-F^{\mathrm{core}}_{ii}$ which is a somewhat better approximation than the $F^J_{jj}-F^I_{ii}$ of Eq. (3.11). However, $\mathcal{F}^P$ has an obvious problem for cases like H_2O where the orbital pairs become equivalent. Thus $F^{\mathrm{core}}_{ii}=F^{\mathrm{core}}_{jj}$, leading to problems as in the above section.

3. Page and McIver

Page and McIver[17] suggested that the problems associated with the Fock matrix definition in Eq. (3.13) can be avoided by incorporating the proper orbital mixing terms into the Fock operator and then scaling them by the difference in the diagonal elements so that the proper mixing terms are obtained when the matrix is diagonalized. A further improvement is made if pseudocanonical orbitals are used by diagonalizing each shell individually before forming the Fock operator. This allows an artificial diagonal term, say

$$F^D_{ii}=i, \tag{3.14}$$

to be used and then divided out.

4. The GVB-DIIS multishell Fock operator, $\mathcal{F}^g$

For GVB-DIIS, following Page and McIver, we use the following form for the multishell Fock operator:

$$
\begin{aligned}
&\mathcal{F}^g_{ij}=F^D_{ii}\delta_{ij},\quad \textit{where } i,\ j \textit{ are both in shell } I \textit{ or}\\
&\qquad \textit{both unoccupied},
\end{aligned}
\tag{3.15a}
$$

$$
\begin{aligned}
&\mathcal{F}^g_{ij}=-\frac{A_{ij}}{B_{ij,ij}}\,(F^D_{jj}-F^D_{ii}),\\
&\qquad \textit{where } i,\ j \textit{ are in different shells},
\end{aligned}
\tag{3.15b}
$$

$$
\begin{aligned}
&\mathcal{F}^g_{ij}=\frac{F^I_{ij}(F^D_{jj}-F^D_{ii})}{F^I_{ii}},\quad \textit{where } i \textit{ is occupied, } j\\
&\qquad \textit{is unoccupied.}
\end{aligned}
\tag{3.15c}
$$

In Eq. (3.15b) the A_{ij} and $B_{ij,ij}$ are as defined in Eqs. (2.16) and (2.19), leading to

$$\mathcal{F}^g_{ij}=\frac{(F^J_{ij}-F^I_{ij})(F^D_{jj}-F^D_{ii})}{F^J_{jj}+F^I_{ii}-F^J_{ii}-F^I_{jj}+\gamma_{ij}}. \tag{3.15b'}$$

Multiplying the off-diagonal blocks with $(F^D_{jj}-F^D_{ii})$ removes the effect of the division by this term when the matrix is diagonalized [see Eq. (3.10)]. This allows us to choose in Eq. (3.15b) the correct second-order terms as in Eq. (2.18). This approach reduces exactly to the standard approach in the limit that all off-diagonal elements of Eq. (3.15) go to zero. We should emphasize that the term $(F_{jj}^{D}-F_{ii}^{D})$ in Eq. (3.15b′) is *not* included to scale the off-diagonal elements, but rather to ensure that the correct second-order mixing strength is included when the matrix $\mathscr{F}$ is diagonalized.

The error vector for iteration n is defined as the supervector

$$e_{ij}^{(n)}=\mathscr{F}_{ij}^{g}, \quad \textit{where } i\leqslant n_{\mathrm{occ}} \textit{ and } j\geqslant i, \tag{3.16}$$

where all quantities in $\mathscr{F}$ are for iteration n. With GVB-DIIS, the basis used in constructing $\mathrm{e}^{(n)}$ is the current set of orbitals at each iteration [rather than the atomic orbital basis as in Eq. (3.6)]. This matrix is then transformed to the atomic orbital basis so that all error matrices are in terms of the same basis.

C. Related DIIS issues

Pulay[13] has found the use of level shifting and off-diagonal element scaling useful in improving DIIS convergence. For GVB-DIIS we find satisfactory convergence for a wide variety of cases *without* resorting to such methods. Indeed, for GVB-DIIS we have seen no improvement when such methods are introduced.

The DIIS extrapolation scheme, Eqs. (3.3) and (3.7), requires that the Fock matrices and error vectors must be saved for each iteration. This can result in large values for the q_n coefficients in Eq. (3.3) as the number of iterations becomes large. Pulay uses scaling terms when solving Eq. (3.7) to resolve this problem. We have found it useful to save only ten iterations. For each iteration past the tenth, we overwrite the matrix which had the lowest q_n coefficient in the previous extrapolation. We have seen no decrease in the efficiency of the GVB-DIIS method from using this simplification.

D. Hierarchical convergence strategies

While the introduction of second-order terms [Eq. (3.16)] greatly increases the radius of convergence for GVB-DIIS, and while quality initial guesses (GVB-INIT) most often put the starting point of a calculation within this radius of convergence, it is still possible to find systems for which the initial guess is outside the radius of convergence of GVB-DIIS. To be fail safe, we install a threshold $e_{\max}$, corresponding to the maximum value of the error vector e, above which standard convergence method iterations are used. The results presented herein use $e_{\max}=1.0$ as this threshold, which we find to be optimal for minimizing overall computation time. Using a lower value for $e_{\max}$ the standard (non-DIIS) methods may take a long time to reach $e_{\max}$. Using a higher value for $e_{\max}$ there is a chance the wave function will be outside of the radius of convergence for DIIS. With the GVB-INIT scheme discussed in Sec. III E is used, generally no more than one non-DIIS iteration is necessary.

E. Initial guesses for GVB wave functions, GVB-INIT

A recent paper[19] presents a very general, automatic, and fast procedure, GVB-INIT, for constructing initial guesses for GVB wave functions. This involves (i) building an HF-like wave function based on the SCF orbitals of the *individual atoms* and (ii) piecewise localizing this HF trial wave function in an automatic way to obtain the first and second natural orbitals for the trial GVB orbitals. We used GVB-INIT for all cases unless noted otherwise.

F. Sequence of operations

Once the calculation is within the DIIS radius of convergence, the sequence of operations within a DIIS iteration is: (i) calculation of J and K operators; (ii) calculation of GVB-CI coefficients; (iii) formation of the general Fock operator and error matrix; (iv) determination of iteration coefficients from the DIIS equations; and (v) diagonalization of the composite Fock operator to obtain new orbitals. If the wave function is not converged, the calculation then proceeds back to (i) for another iteration.

IV. RESULTS

The GVB-DIIS method as described above provides excellent convergence for a wide variety of wave functions. For one-pair GVB wave functions we compare GVB-DIIS to the convergence methods in both GVB2P5[20] and GAUSSIAN90[21] and to the DIIS convergence in GAMESS.[16] The DIIS scheme in GAMESS cannot handle more than one GVB pair and cannot handle open-shell orbitals combined with a GVB pair. GAUSSIAN90 does not use DIIS for GVB wave functions. Thus for more complex wave functions, we compare GVB-DIIS only to GVB2P5 and GAUSSIAN90 standard (i.e., non-DIIS) convergence.

All cases used the GVB-INIT initial guess. We should emphasize that reliable convergence does require a reliable automatic procedure for initial guesses and that GVB-INIT is very effective. Thus the convergence reported here for the GVB2P5, GAUSSIAN90, and GAMESS programs is generally much better than with the default procedures.

The convergence criteria used in the following examples requires that

$$\mathrm{SQCDF}\equiv \sum_{\mu=1}^{NBF} \sum_{j=1}^{N} (C_{\mu j}^{I}-C_{\mu j}^{I+1})^2$$

satisfy $\mathrm{SQCDF}\leqslant 10^{-9}$. This is usually a much more stringent requirement than the more commonly used criteria of energy changes between iterations being less than 10^{-9}. All cases report the number of iterations from trial guess to convergence.

A. One-pair GVB wave functions

1. H_2O, one bond stretched

The first example tests the ability of GVB-DIIS to converge a wave function with a single correlated σ bond. Here we calculated the wave function for H_2O using a GVB pair for one of the O–H σ bonds. We stretched the correlated O–H bond from equilibrium (0.94 Å) to near

TABLE I. (a) Number of iterations to converge the one-pair GVB wave function for H_2O as one OH bond is dissociated. The starting geometry ($R_{OH}=0.94$ Å, $\alpha_{HOH}=105.98°$) was the optimum geometry for the HF wave function with an STO-3G basis. The 6-31G** basis set was used with the GVB-INIT initial guess. (b) Initial guess based on localizing the orbitals of the HF wave function (rather than GVB-INIT).

	ΔR_{OH}(Å)	Energy (h)	GVB-DIIS	GVB2P5	GAMESS	G90
(a)	0.0	−76.043 561	13	24	dnc[a]	41
	0.2	−76.023 038	13	23	dnc[a]	26
	0.5	−75.963 830	11	23	22	24
	1.0	−75.904 616	12	19	20	22
	2.0	−75.883 588	11	20	22	26
(b)	0.0	−76.043 561	13	22	dnc[a]	34
	0.2	−76.023 038	12	21	dnc[a]	26
	0.5	−75.963 830	11	19	dnc[a]	24
	1.0	−75.904 616	11	37	19	46
	2.0	−75.883 588	10	107	27	392

[a] dnc = did not converge.

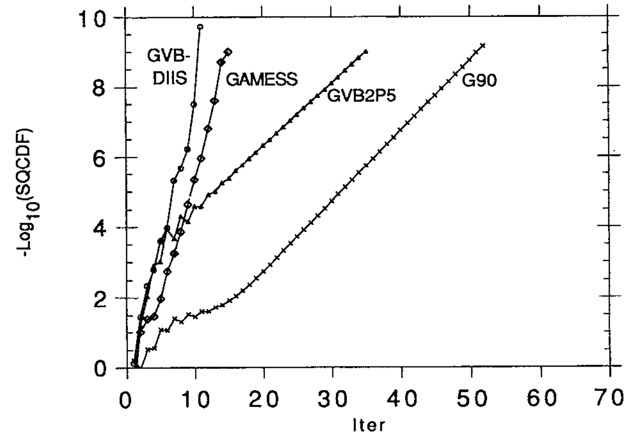

FIG. 1. Convergence of the one-pair GVB wave function for formaldehyde with various methods. These calculations used the 6-31G** basis set and GVB-INIT. The geometry is $R_{CO}=1.18$ Å, $R_{CH}=1.09$ Å, $\alpha_{HCO}=122.15°$ from an STO-3G minimization.

dissociation (2.94 Å). In each case we calculated the wave function using the GVB-DIIS, GVB2P5, GAUSSIAN90, and GAMESS programs (starting from the GVB-INIT guess for all programs).

The results are in Table I A. GVB-DIIS showed excellent convergence (11 to 13) iterations in all cases. GVB2P5 took about twice as long in most cases. The GAMESS DIIS convergence scheme does about as well as GVB2P5 for the three most stretched cases, but does not converge for the two cases closer to the equilibrium geometry. This is probably due to mixing between the first GVB natural orbital and the uncorrelated O–H bond, which results from using the $\mathscr{F}^1$ multishell Fock operator, Eq. (3.9), which would have near-identical matrix elements along the diagonal for these two orbitals. GVB-DIIS has no difficulty whatsoever with these degeneracies (see discussion in Sec. III B). GAUSSIAN90 uses a GVB convergence scheme based upon GVB2P5, resulting in the same general trends as GVB2P5. However, GAUSSIAN90 takes slightly longer for each case, with convergence much slower than for GVB-DIIS.

We investigated the effect of using a guess based on a converged HF wave function *before* generating the GVB orbitals (see Table I B). These guesses are significantly more expensive than the guesses used in Table I A. In every case GVB-DIIS saves one or two iterations with these guesses. However, the saved iteration hardly justifies the expense of obtaining the guess. On the other hand, while GVB2P5 does work slightly better for some of the less distorted geometries, it behaves very poorly for the more distorted geometries. This is because the HF orbitals are poor descriptions for chemical bonds at very distorted geometries leading to a poor basis for initial guesses. The convergence in GAUSSIAN90 is also improved slightly for the less distorted geometries but does poorly for the more distorted geometries. GAMESS failed to converge three of the five cases. The general conclusion is that added accuracy of the guesses based on using the converged HF wave function to generate the initial GVB orbitals does not justify the added expense. The remainder of the paper uses the less expensive GVB-INIT method (as in Table I A).

2. Twisted ethylene

We examined the one-pair GVB wave function to describe twisting of the π bond in C_2H_4 from 0° to 90°. The results and various details[18] are in Table II. We report the total number of iterations required to converge the wave function from the trial guess to a SQCDF less than 10^{-9}.

At the equilibrium structure all methods display acceptable convergence, but as the bond twists above 45° GVB2P5, GAUSSIAN90, and GAMESS have increasing difficulty. GVB2P5 and GAUSSIAN90 take a large number of

TABLE II. Number of iterations for the one-pair GVB wave function of C_2H_4 as a function of twisting about the C—C bond. Starting geometry: $R_{CC}=1.334$ Å, $R_{CH}=1.081$ Å, $\alpha_{HCH}=117.4°$ (Ref. 18). The 6-31G** basis set was used with GVB-INIT.

Twist (deg)	Energy (h)	GVB-DIIS	GVB2P5	GAMESS	G90
0	−78.066 047	7	11	13	27
30	−78.022 104	12	19	21	23
60	−77.906 403	12	29	25	31
90	−77.748 431	21	46	dnc[a]	74

[a] dnc = did not converge.

TABLE III. Same as Table I (a) except that both bonds are simultaneously dissociated and a two-pair GVB wave function is used to correlate both O—H σ bonds.

Δ_{OH_1}/(Å)	Δ_{OH_2}/(Å)	Energy (h)	GVB-DIIS	GVB2P5	G90
0.0	0.0	−76.063 303	14	24	89
0.0	1.0	−75.925 219	15	31	36
1.0	1.0	−75.799 411	14	17	61
0.0	2.0	−75.904 235	14	32	40
1.0	2.0	−75.778 726	15	56	65
2.0	2.0	−75.756 784	18	13	dnc[a]

[a] dnc = did not converge.

TABLE IV. Number of iterations for the two-pair GVB wave function of C_2H_4 as a function of C—C bond dissociation. The GVB pairs correlate both the C–C σ and π bonds. Otherwise the same as Table II.

$\Delta_{CC}/(\text{Å})$	Energy (h)	GVB-DIIS	GVB2P5	G90
0.0	−78.075 751	10	15	26
0.5	−77.975 870	13	36	40
1.0	−77.862 122	8	14	70
2.0	−77.800 986	15	54	74
3.0	−77.798 767	15	39	125

iterations for the 90° geometry, and GAMESS does not converge at all. In contrast, GVB-DIIS shows rapid convergence in every example.

3. Formaldehyde, one pair

Using a single GVB pair to correlate the π bond of H_2CO leads to the results in Fig. 1 which shows $-\log_{10}(\text{SQCDF})$ vs iteration number for GVB-DIIS, GVB2P5, GAUSSIAN90, and GAMESS methods. GVB-DIIS has the fastest convergence of the four programs. GAMESS also displays the rapid convergence typical of DIIS methods. GVB2P5 takes much longer than either of the DIIS methods to converge, and GAUSSIAN90 takes even longer. These calculations illustrate how standard methods often slow down close to convergence. In contrast the DIIS methods continue the rapid rate of convergence for the entire sequence.

B. Multiple pair GVB wave functions

1. Dissociating both bonds of H_2O

We used a two-pair GVB wave function to describe the simultaneous dissociation of both bonds of H_2O. This is not a significant pathway for most physical processes in H_2O, but it provides a good test for the methods. The bonds are stretched from equilibrium (0.94 Å) to over three times the equilibrium distance (2.94 Å). We report in Table III the total number of iterations from the GVB-INIT trial guess to $\text{SQCDF} < 10^{-9}$.

GVB-DIIS converges quickly (14 to 18 iterations) for every case reported. We see that the convergence using GVB2P5 can be quite poor (up to 56 iterations), although GVB2P5 converges in fewer iterations than GVB-DIIS for one case. GAUSSIAN90 does significantly worse than either of the other programs for all cases and does not converge for one.

TABLE V. Number of iterations for converging the three-pair GVB wave function of CH_3 radical for symmetric dissociation of the three C—H bonds. The geometry is kept planar with bond angles of 120°. The 6-31G** basis set was used with GVB-INIT.

$R_{CH}/(\text{Å})$	Energy (h)	GVB-DIIS	GVB2P5	G90
1.0	−39.585 824	14	17	28
1.2	−39.583 762	12	15	28
1.4	−39.492 389	11	18	30
1.6	−39.382 916	11	21	39
1.8	−39.281 492	11	22	41
2.0	−39.196 612	10	21	67
2.2	−39.127 903	12	20	111
2.4	−39.072 965	12	18	191
2.6	−39.029 350	14	17	249

TABLE VI. Number of iterations for converging GVB wave functions for glycine, $H_2N–CH_2–C(O)OH$. The 6-31G** basis set was used with GVB-INIT. The geometry was from an STO-3G HF minimization: $R_{NH}=1.03$ Å, $R_{NC}=1.48$ Å, $R_{CH}=1.09$ Å, $R_{CC}=1.55$ Å, $R_{CO}=1.22$ Å, $R_{C—OH}=1.37$ Å, $R_{OH}=0.99$ Å, $\alpha_{HNH}=104.25°$, $\alpha_{HCH}=107.54°$, $\alpha_{HNC}=107.24°$, $\alpha_{NCC}=113.59°$, $\alpha_{CCO}=125.67°$, $\alpha_{OCO}=122.44°$, $\alpha_{COH}=104.75°$, $\tau_{HNCC}=55.98°$, $\tau_{HCCO}=-122.00°$, all heavy atoms and the hydroxyl H are coplanar.

N_{pair}	Description	Energy (h)	GVB-DIIS	GVB2P5	G90
0	HF	−282.837 281	12	48	16[a]
1	CO π bond	−282.864 831	13	26	30
5	all NC, CC, CO bonds	−282.932 640	20	162	111
6	CO π, CH, NH, OH	−282.953 850	17	42	42
10	all bonds	−283.019 396	20	90	75

[a] HF DIIS convergence used in Gaussian.

2. Dissociation of the double bond in ethylene

Dissociating a double bond is a stiff test of the convergence method. We considered dissociation of C—C double

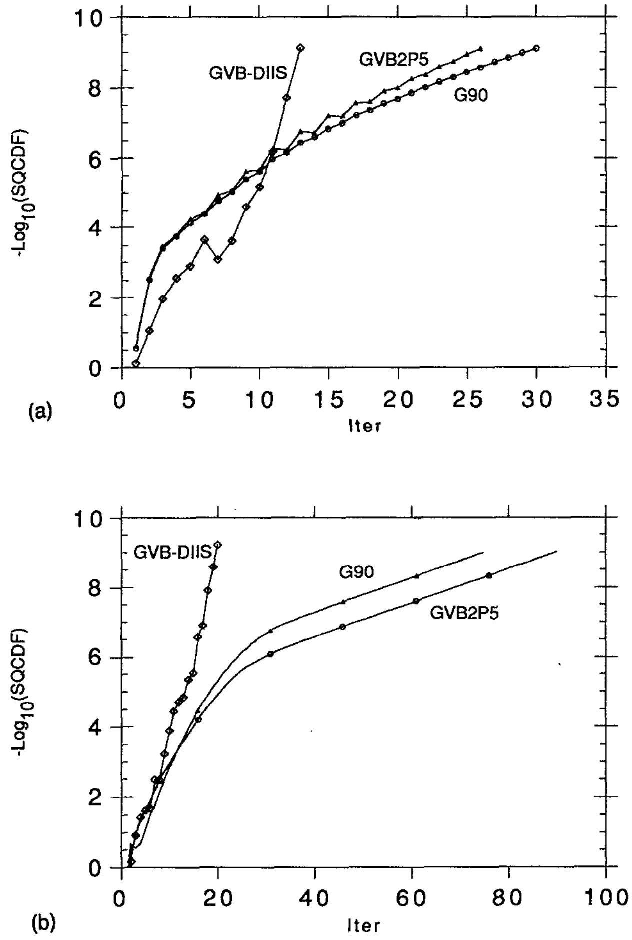

FIG. 2. (a) Convergence of the one-pair GVB wave function for glycine (C—O π bond correlated). See Table VI for details. (b) Convergence of the ten-pair GVB wave function for glycine.

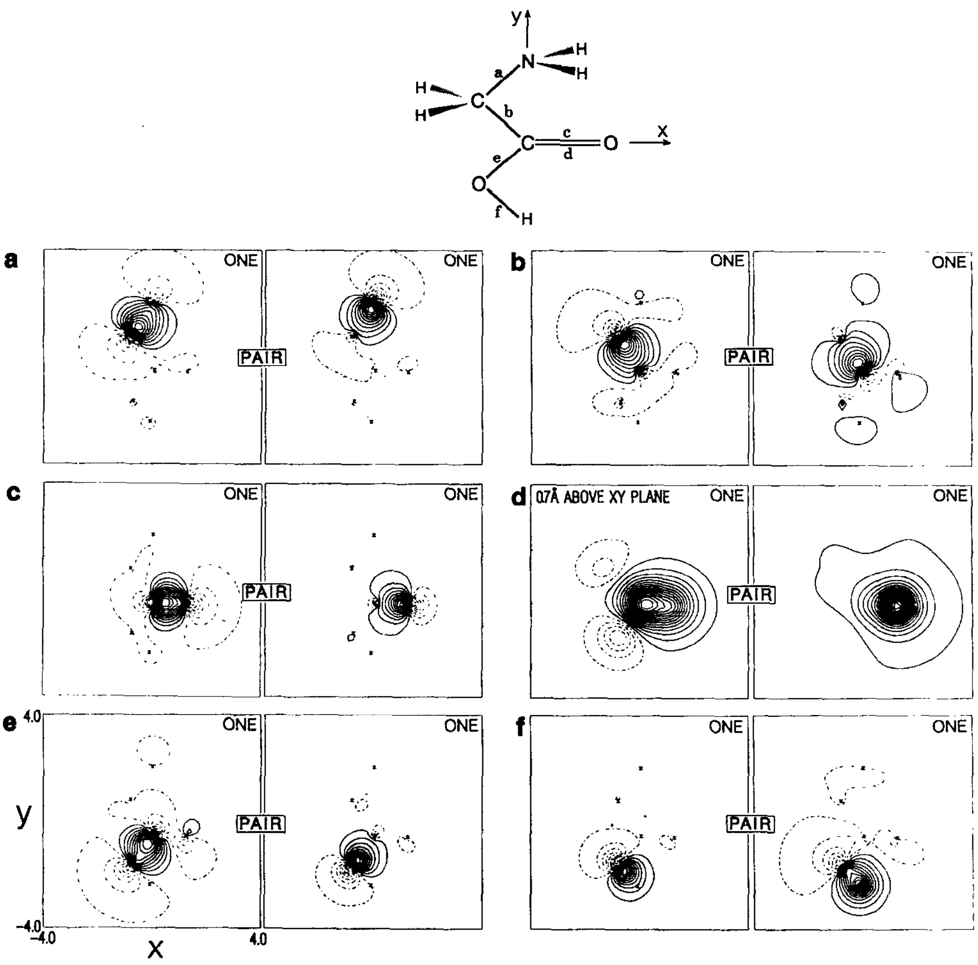

FIG. 3. The GVB orbitals for glycine (with all ten bond pairs correlated). (a) C—N σ bond; (b) C—C σ bond; (c) C—O σ bond; (d) C—O π bond; (e) C—O σ bond; (f) O—H σ bond. Not shown are the two CH bonds and two NH bonds out of the plane. Each plot is for a GVB orbital containing one electron. Contours of the orbitals are plotted in the xy plane (increments of 0.05 a.u., zero not shown) except for the C—O π bond (d), which is plotted 0.7 Å above the xy plane.

bond in C_2H_4 using two GVB pairs for the wave function (correlating the σ and π bonds). We use the same (planar) geometry[18] as in Table II and stretched the bond from 1.334 to 4.334 Å. As summarized in Table IV, GVB-DIIS is dramatically faster than the other two programs for every geometry, requiring no more than 15 iterations from initial guess to SQCDF $< 10^{-9}$ for any case. GVB2P5, on the other hand, takes no less than 14 and as many as 54 iterations, while GAUSSIAN90 requires from 26 to 125 iterations for these same geometries.

3. Dissociating three bonds of methyl radical

The next example (Table V) examines the effect of an open-shell orbital on the convergence rate. We use the CH_3 radical (6-31G** basis) as our test molecule in a planar geometry (120° bond angles). We vary the C—H bond distances from 1.0 to 2.6 Å, and calculate the wave function of the doublet state at each geometry. Once again, GVB-DIIS requires 10–14 iterations whereas GVB2P5 leads to 13–22 while GAUSSIAN90 has increasing difficulty as the molecule dissociates (28 to 249 iterations).

4. Correlating all ten bond pairs of glycine

For glycine we examined the convergence for wave functions with up to 10 GVB pairs. We correlated zero pairs (the regular HF wave function), one pair (correlating the C—O π bond), five pairs (correlating all bonds between heavy atoms, four σ and one π bonds), six pairs (correlating the C—O π bond, the three C—H σ bonds, and the two N—H σ bonds), and ten pairs (correlating all bonds). Table VI reports the results: GVB-DIIS requires from 12 to 20 iterations to converge these wave functions, while GVB2P5 requires from 26 to 162 iterations, and GAUSSIAN90 from 16 to 111 iterations.

Figure 2 illustrates these cases graphically for GVB-DIIS, GVB2P5, and GAUSSIAN90. We see consistently rapid convergence for GVB-DIIS. Both GVB2P5 and GAUSSIAN90 require many additional iterations with a rate of convergence that slows as the iterations increase.

Figure 3 shows the GVB orbitals of glycine. Electron correlation leads naturally to localized optimum orbitals closely related to simple valence bond concepts. The various bonds between heavy atoms (C, N, O) all involve

sp^2-like orbitals with one electron more on the left and the other more on the right. Similarly each M—H bond pair has one orbital that is very H_{1s}-like while the other corresponds to an sp^2- or sp^3-like orbital on M. This localization is a virtue for correlating very large systems, since the virtual orbitals in the CI can be restricted to the region near the orbitals being correlated.

V. DISCUSSION

The results presented in the previous sections reflects a number of significant points. GVB-DIIS in general converges much more quickly than the standard method (GVB2P5). GAUSSIAN90 convergence follows the same general trends as does GVB2P5, but generally takes significantly longer, leading to convergence far inferior to that for GVB-DIIS. Finally, the radius of convergence for GVB-DIIS, while perhaps not as wide as that of GVB2P5, is a significant improvement over the DIIS scheme in GAMESS (restricted to one GVB pair).

GVB-DIIS (in conjunction with GVB-INIT) allows fast and reliable convergence of wave functions having arbitrary numbers of core, open, and GVB orbitals. This makes it possible now to use physically accurate wave functions to calculate force fields, to describe bond distortion and dissociation processes, and to obtain highly converged wave functions for the purpose of calculating molecular properties such as charges and dipole moments.

The GVB-DIIS convergence scheme has already been implemented in the PS-GVB electronic structure program. We expect that the pseudospectral approach, when combined with the methods detailed here, should allow GVB calculations on much larger systems than have been possible before.

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[1] R. C. Ladner and W. A. Goddard III, J. Chem. Phys. **51**, 1073 (1969); W. A. Goddard III, T. H. Dunning, Jr., W. J. Hunt, and P. J. Hay, Acc. Chem. Res. **6**, 368 (1973); W. A. Goddard III and L. B. Harding, Annu. Rev. Phys. Chem. **29**, 363 (1978); W. A. Goddard III, Science **227**, 917 (1985).

[2] W. J. Hunt, P. J. Hay, and W. A. Goddard III, J. Chem. Phys. **57**, 738 (1972); P. J. Hay, W. J. Hunt, and W. A. Goddard III, J. Am. Chem. Soc. **94**, 8293 (1972).

[3] P. J. Hay, W. J. Hunt, and W. A. Goddard III, Chem. Phys. Lett. **13**, 30 (1972); S. L. Guberman and W. A. Goddard III, Phys. Rev. A **12**, 1203 (1975); B. J. Moss and W. A. Goddard III, J. Chem. Phys. **63**, 3523 (1975); L. B. Harding and W. A. Goddard III, J. Am. Chem. Soc. **97**, 6293 (1975); J. Am. Chem. Soc. **97**, 6300 (1975).

[4] E. V. Anslyn, M. J. Brusich, and W. A. Goddard III, Organometallics **7**, 98 (1988).

[5] E. A. Carter and W. A. Goddard III, J. Am. Chem. Soc. **109**, 579 (1987); Organometallics **7**, 675 (1988).

[6] W. A. Goddard III and R. C. Ladner, Int. J. Quantum Chem. Symp. **III**, 63 (1969); W. A. Goddard III, J. Am. Chem. Soc. **92**, 7520 (1970); W. A. Goddard III and R. C. Ladner, *ibid.* **93**, 6750 (1971); L. B. Harding and W. A. Goddard III, *ibid.* **100**, 7180 (1978); A. K. Rappé and W. A. Goddard III, *ibid.* **104**, 448, 3287 (1982).

[7] J. J. Barton, W. A. Goddard III, and T. C. McGill, J. Vac. Sci. Technol. **16**, 1178 (1979).

[8] A. K. Rappé and W. A. Goddard III, J. Am. Chem. Soc. **102**, 5114 (1980); Nature **285**, 311 (1980); J. N. Allison and W. A. Goddard III, J. Catal. **92**, 127 (1985); in *Solid State Chemistry in Catalysis*, edited by R. K. Grasselli and J. F. Brazdil, ACS Symp. Ser. No. 279 (American Chemical Society, Washington, DC, 1985), pp. 23–36; J. J. Low and W. A. Goddard III, J. Am. Chem. Soc. **108**, 6115 (1986); E. A. Carter and W. A. Goddard III, J. Catal. **112**, 80 (1988).

[9] F. W. Bobrowicz and W. A. Goddard III, in *Modern Theoretical Chemistry: Methods of Electronic Structure Theory*, edited by H. F. Schaefer III (Plenum, New York, 1977), Vol. 3, p. 79.

[10] W. J. Hunt, W. A. Goddard III, and T. H. Dunning, Jr., Chem. Phys. Lett. **6**, 147 (1970); see also Chem. Phys. Lett. **4**, 231 (1969); **3**, 606 (1969).

[11] P. Pulay, J. Comput. Chem. **3**, 556 (1982).

[12] P. Pulay, Chem. Phys. Lett. **73**, 393 (1980).

[13] T. P. Hamilton and P. Pulay, J. Chem. Phys. **84**, 5728 (1986).

[14] C. F. Melius and W. A. Goddard III, Phys. Rev. A **10**, 1528 (1974); A. Redondo, W. A. Goddard III, and T. C. McGill, Phys. Rev. B **15**, 5038 (1977); A. K. Rappé, T. A. Smedley, and W. A. Goddard III, J. Phys. Chem. **85**, 1662 (1981); P. J. Hay and W. R. Wadt, J. Chem. Phys. **82**, 270 (1985).

[15] L. G. Yaffe and W. A. Goddard III, J. Chem. Phys. **67**, 1777 (1977).

[16] GAMESS program suite, M. W. Schmidt, K. K. Baldridge, J. A. Boatz, J. H. Jensen, S. Doseki, M. S. Gordon, K. A. Nguyen, T. L. Windus, and S. T. Elbert (unpublished).

[17] M. Page and J. W. McIver, Jr., J. Chem. Phys. **79**, 4985 (1983).

[18] R. Krishnan, J. S. Binkley, R. Seeger, and J. A. Pople, J. Chem. Phys. **72**, 650 (1980).

[19] J.-M. Langlois, T. E. Yamasaki, R. P. Muller, and W. A. Goddard III (unpublished).

[20] R. A. Bair, F. W. Bobrowicz, W. J. Hunt, P. J. Hay, and W. A. Goddard (unpublished); see R. A. Bair, Ph.D. thesis, Caltech (1981).

[21] M. J. Frisch, M. Head-Gordon, G. W. Trucks, J. B. Foresman, H. B. Schlegel, K. Raghavachari, M. A. Robb, J. S. Binkley, C. Gonzales, D. J. Defrees, D. J. Fox, R. A. Whiteside, R. Seeger, C. F. Melius, J. Baker, R. L. Martin, L. R. Kahn, J. J. P. Stewart, S. Topiol, and J. A. Pople, GAUSSIAN90, Gaussian, Inc., Pittsburgh, PA (1990).

[22] H.-J. Werner and P. J. Knowles, J. Chem. Phys. **82**, 5053 (1985); P.-A. Malmqvist, A. Randell, and B. O. Roos, J. Phys. Chem. **94**, 5477 (1990); R. Shepard, I. Shavitt, and J. Simons, J. Chem. Phys. **76**, 543 (1982).