

Pseudospectral generalized valence-bond calculations: Application to methylene, ethylene, and silylene

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The pseudospectral (PS) method for self-consistent-field calculations is extended for use in generalized valence-bond calculations and is used to calculate singlet–triplet excitation energies in methylene, silylene, and ethylene molecules and bond dissociation and twisting energies in ethylene. We find that the PS calculations lead to an accuracy in total energies of <0.1 kcal/mol and excitation energies to <0.01 kcal/mol for all systems. With effective core potentials on Si, we find greatly improved accuracy for PS.

I. INTRODUCTION

Recently, we have shown that the pseudospectral (PS) numerical method provides an attractive alternative to the usual all-integral methods of calculating Hartree–Fock (HF) wave functions for molecules.^{1–6} Thus, for a valence double-zeta plus polarization description of glycine (100 basis functions), PS calculations⁵ leading to an accuracy in the total energy of 0.04 kcal/mol now take about 75 CPU seconds on a Cray X-MP (recalculating integrals at every self-consistent iteration) vs 200 CPU seconds using GRADSCF, a fast program for the traditional all-integral approach (which calculates integrals only once). For HF wave functions the PS approach scales as M^3 (where M is the number of basis functions), whereas the all-integral approaches scale as M^4 , so that PS should become even more advantageous for very large systems. Using integral cutoffs, we have recently achieved M^2 scaling for PS for systems as small as benzene and uracil.⁶ In this paper we extend the PS approach to generalized valence-bond (GVB) wave functions (which include electron correlation) and to second-row compounds (Si) treated either with all electrons or with core effective potentials.

Earlier attempts to use purely numerical methods for electronic wave functions of polyatomic molecules have failed to provide uniform accuracy, primarily because the accurate description of the cusps at atomic centers requires an impractical number of grid points. The PS method uses both a basis set and a numerical grid and preserves the advantages of both approaches. Using a basis set for the calculation of one-electron and selected two-electron integrals accurately reproduces the description of the wave function near atomic centers. Use of a grid for the evaluation of the majority of the two-electron terms both (a) preserves the M^3 scaling of the numerical calculation with basis-set size and (b) increases the speed of calculating the integrals that must be evaluated.

In previous papers the general algorithm has been proposed and applied to atomic,¹ diatomic,² and polyatomic molecules.³ A suitable automatic grid generation scheme

has been developed,⁴ and the method has been applied to glycine.⁵ It has been demonstrated that the method promises significant reduction of computation time (even when compared with the GRADSCF program that was specifically designed for Cray computers). In all cases the PS method has shown accurate reproduction of total and relative energies to within 0.1 kcal/mol, as compared with all-integral approaches.

There remain, however, many issues to be addressed. Only a few basis sets have been used, and it has not yet been determined whether the agreement with all-integral method energies will degrade with different basis sets. Since calculations have only been performed on first-row elements, the ability to replace the core electrons with an effective core potential (ECP)—a virtually essential condition to effectively model systems with heavy atoms—has not yet been established. The calculations have not yet attempted to solve for excited electronic states, or for the broken bonds of stretched or twisted molecular conformations. Finally, no amount of electron correlation has entered into any of the calculations. In each of these areas it is necessary to test the efficacy of the PS method.

In this paper we examine the above issues for methylene, ethylene, and silylene molecules. In the methylene and silylene molecules we investigate (a) the effect of basis sets where s , p , and d orbitals have different exponents, (b) the use of diffuse functions, and (c) multiple sets of polarization functions. In silylene we also examine the use of an effective potential to replace the core electrons in the wave function. For the ethylene system we determine how well the PS method reproduces all-integral results for broken bonds and twisted geometries. In all of these systems we have examined both restricted HF wave functions and generalized valence-bond (GVB) multiple configuration wave functions for both the singlet and triplet electronic states. We find excellent agreement with all-integral results for these more complex systems, suggesting that the PS method can be applied to a variety of chemically relevant systems.

In Secs. II and III we review the relevant aspects of GVB wave functions and the PS method and indicate how the PS approach is used with GVB. In Sec. IV we report the results on CH₂, SiH₂, and C₂H₄ while Sec. V discusses some key points.

II. OVERVIEW OF THE GVB FORMALISM

A. The GVB-PP wave function

The GVB wave function for an N electron system has the general form^{7,8}

$$\Psi_{S,M_s}^{\text{GVB}} = \mathcal{A}[\phi_a^{(1)}\phi_b^{(2)}\cdots\phi_w^{(N)}\Theta_{S,M_s}(1\cdots N)], \quad (2.1)$$

where the orbitals are singly occupied and allowed to overlap, $\Theta_{S,M_s}^{(1\cdots N)}$ is a general spin eigenfunction

$$S^2\Theta_{S,M_s} = S(S+1)\Theta_{S,M_s}, \quad S_z\Theta_{S,M_s} = M_s\Theta_{S,M_s}, \quad (2.2)$$

for an N electron system, and \mathcal{A} is the antisymmetrizer. There are f_{NS} ways of combining the spin to satisfy Eqs. (2.2) so that Θ_{S,M_s} is written as

$$\Theta = \sum_{i=1}^f \gamma_i \Theta_i, \quad (2.3)$$

where each Θ_i satisfies Eqs. (2.2). (Thus $f=2$ for $N=4$ and $S=0$, and $f=5$ for $N=6$ and $S=0$.) The GVB orbitals are obtained by simultaneously optimizing the orbitals ϕ_i and spin function Θ [i.e., the γ_i for Eq. (2.3)].

A restricted form of GVB that is much more tractable for computation is the GVB-PP (for perfect-pairing) wave function, in which the spin function in Eq. (2.3) is restricted to the simple valence-bond form

$$\Theta_{\text{VB}} = \Theta_1 = (\alpha\beta - \beta\alpha)(\alpha\beta - \beta\alpha)\cdots(\alpha\beta - \beta\alpha)\alpha\alpha\cdots\alpha \quad (2.4)$$

with $(1/2)N-S$ singlet pairs and $2S$ electrons coupled high spin.

In this case the orbital functions in Eq. (2.1) corresponding to the j th singlet pair in Eq. (2.4) have the valence-bond form

$$(\phi_{1j}\phi_{2j} + \phi_{2j}\phi_{1j}). \quad (2.5)$$

For computational purposes it is convenient to rewrite Eq. (2.5) as

$$C_{gj}\phi_{gj}\phi_{gj} - C_{uj}\phi_{uj}\phi_{uj} \quad (2.6)$$

using the GVB natural orbitals

$$\phi_{gj} = (\phi_{1j} + \phi_{2j})/\sqrt{2(1+S_j)}, \quad (2.7)$$

$$\phi_{uj} = (\phi_{1j} - \phi_{2j})/\sqrt{2(1-S_j)},$$

where $S_j = \langle\phi_{1j}|\phi_{2j}\rangle$ and $C_{gj}^2 + C_{uj}^2 = 1$. Taking natural orbitals of different pairs to be orthogonal leads to the general energy expression for GVB-PP wave functions:

$$E = 2 \sum_i^{\text{occ}} f_i h_{ii} + \sum_{i,j}^{\text{occ}} (a_{ij} J_{ij} + b_{ij} K_{ij}), \quad (2.8)$$

where

$$h_{ii} = \langle\phi_i|h|\phi_i\rangle, \quad (2.9)$$

$$J_{ij} = (ii|jj) = \int d^3r_1 \phi_i(1) \hat{J}_j(1) \phi_i(1), \quad (2.10)$$

$$\hat{J}_j(1) = \int d^3r_2 \frac{\phi_j(2)\phi_j(2)}{r_{12}}, \quad (2.11)$$

$$K_{ij} = (ij|ij) = \int d^3r_1 \phi_i(1) \hat{K}_j(1) \phi_i(1), \quad (2.12)$$

$$\hat{K}_j(1) = \int d^3r_2 \frac{\phi_j(2)\tau_{ij}\phi_j(2)}{r_{12}}, \quad (2.13)$$

τ_{ij} = transposition operator

are standard expressions for the one-electron, Coulomb, and exchange energies. (Here h may include core effective potentials in addition to kinetic energy and nuclear potential terms.)

The coefficients f_i , a_{ij} , and b_{ij} in Eq. (2.8) depend on the wave function, and the general prescription is given in Ref. 9. Some special cases are that doubly occupied orbitals lead to $f_i = 1$, while a GVB natural orbital leads to $f_i = C_i^2$. For two orbitals of the same GVB pair, $a_{ii} = f_i$, $b_{ii} = 0$, $a_{1j,2j} = 0$, $b_{1j,2j} = -C_{1j}C_{2j}$. For orbitals i, j ($i \neq j$) that are doubly occupied or of different GVB pairs, $a_{ij} = 2f_i f_j$ and $b_{ij} = -f_i f_j$.

With Eq. (2.8), the general condition for the optimum orbitals is that the first-order change in the energy due to changes in the various orbitals is zero, leading to

$$\sum_i \langle\delta\phi_i|F_i|\phi_i\rangle = 0, \quad (2.14)$$

where F_i is the Fock operator

$$F_i = f_i \hat{h} + \sum_j^{\text{occ}} (a_{ij} \hat{J}_j + b_{ij} \hat{K}_j). \quad (2.15)$$

Because F_i depends on the orbitals, solution of the variational equation (2.14) is nonlinear, requiring an iterative procedure to solve. The general conditions for the orbitals to be optimal is that the matrix

$$A_{ji} = \langle j|(F_j - F_i)|i\rangle \quad (2.16)$$

be zero,

$$A_{ji} = 0, \quad (2.17)$$

for all pairs of orbitals: If j is unoccupied, then $F_j = 0$ is used in Eq. (2.16). The iterative GVB equations are based on expanding (2.8) through second order in the orbital changes and lead to the general equation

$$\sum_{vj} B_{\mu i, \nu j} \Delta_{\nu j} = -A_{\mu i}, \quad (2.18)$$

where $\nu > j$ for index νj and where j is occupied and ν is occupied or virtual. The antisymmetric matrix Δ is the generator of the orthogonal transformation matrix

$$T = e^{\Delta} \quad (2.19)$$

that transforms an initial set of orthogonal orbitals $\{\phi_i^0\}$ into a final set of orthogonal functions $\{\phi_i^1\}$ which minimizes the energy (2.8) expanded to second order in the changes. The general formulas for $A_{\mu i}$ and $B_{\mu i, \nu j}$ can be found in Refs. 9–11.

The diagonal elements of B have the form

$$B_{\mu i, \mu i} = \langle \mu | (F_i - F_\mu) | \mu \rangle + \langle i | (F_\mu - F_i) | i \rangle + \alpha_{\mu i} J_{\mu i} + \beta_{\mu i} K_{\mu i}, \quad (2.20)$$

where the $\alpha_{\mu i}$ and $\beta_{\mu i}$ depend on the a_{ij} and b_{ij} . Since only Coulomb and exchange operators are involved, the quantities required for the diagonal terms can be evaluated from a list of integrals (an M^4 procedure) without carrying out integral transformations (an M^5 procedure). On the other hand, the off-diagonal terms generally involve more complicated integrals requiring integral transformations. In the GVB2P5 program we ignore any terms that cannot be evaluated with Coulomb and exchange operators, and in the present calculations we used only the diagonal elements of B . As a result, Eq. (2.18) reduces to

$$\Delta_{\mu i} = -A_{\mu i} / B_{\mu i, \mu i}. \quad (2.21)$$

In addition to Δ , the configuration-interaction (CI) coefficients in Eq. (2.6) must be optimized each iteration, leading to the two-by-two diagonalizations⁹

$$\sum_{l=g}^u Y_{kj, lj} C_{lj} = E_{kj} C_{kj} \quad (2.22)$$

where $l=g$ or u and

$$Y_{kj, kj} = h_{kj, kj} + \frac{1}{2} J_{kj, kj} + \sum_{i \neq g, u}^{\text{occ}} f_i (2J_{i, kj} - K_{i, kj}), \quad (2.23)$$

$$Y_{gj, uj} = \frac{1}{2} K_{gj, uj}.$$

An important feature of the GVB-PP wave function is that the calculations require *only* Coulomb and exchange integrals [see Eqs. (2.8), (2.15), (2.20), and (2.23)].

B. Basis-set expansions

The standard approach to solving for the GVB-PP orbitals is to expand each orbital ϕ_i as

$$\phi_i = \sum_{\mu=1}^M \chi_\mu C_{\mu i}, \quad \delta \phi_i = \sum_{\mu=1}^M \chi_\mu (\delta C_{\mu i}) \quad (2.24)$$

in a finite basis set $\{\chi_\mu; \mu = 1 \cdots M\}$ and solve for the coefficients $\{C_{\mu i}\}$ leading to orbitals satisfying Eqs. (2.17) and (2.22). With a basis set, all quantities needed for optimizing the orbitals can be calculated in terms of the one-electron integrals,

$$h_{\mu\nu} = \langle \mu | h | \nu \rangle, \quad (2.25)$$

the matrix elements of the Coulomb operators,

$$J_{\mu\nu}^j = \langle \mu | \hat{J}_j | \nu \rangle = (\mu\nu | jj), \quad (2.26)$$

and the exchange operators,

$$K_{\mu\nu}^j = \langle \mu | \hat{K}_j | \nu \rangle = (\mu j | \nu j). \quad (2.27)$$

These operators can be calculated from the fundamental list of two-electron integrals by a simple two-index transformation:

$$J_{\mu\nu}^j = \sum_{\sigma, \eta} (\mu\nu | \sigma\eta) C_{\sigma j} C_{\eta j}, \quad K_{\mu\nu}^j = \sum_{\sigma, \eta} (\mu\sigma | \nu\eta) C_{\sigma j} C_{\eta j}, \quad (2.28)$$

so that it is never necessary to transform the two-electron set of integrals. This contrasts with more general multiconfiguration-self-consistent-field (MC-SCF) procedures where a full transformation of the two-electron integrals (a M^5 procedure) is necessary every iteration.

III. PS GVB

A. Overview

In the usual all-integral GVB calculations, a set of $M^4/8$ integrals $(\mu\nu | \sigma\eta)$ is evaluated and used to calculate the matrix elements for various Coulomb and exchange operators as in Eq. (2.28). In contrast, for PS GVB calculations, the Coulomb and exchange operators are evaluated directly using a numerical grid. This involves evaluating the $M^2/2$ quantities

$$A_{\sigma\eta}(r_g) = \int d^3r_2 \frac{\chi_\sigma(2)\chi_\eta(2)}{|r_g - r_2|} \quad (3.1)$$

directly for a set of grid points $\{r_g\}$. With Gaussian-type basis functions, $\chi_\sigma = r^l e^{-ar^2} Y_{lm}(\Theta, \Phi)$, on various centers, the potentials $A_{\sigma\eta}(r_g)$ can be evaluated analytically for each grid point.

Given the potentials (3.1), the fundamental Coulomb and exchange matrices (2.26) and (2.27) could be calculated numerically using

$$J_{\mu\nu}^j = \langle \mu | \hat{J}_j | \nu \rangle = \sum_g \chi_\mu(g) \chi_\nu(g) \sum_{\sigma\eta} C_{\sigma j} C_{\eta j} A_{\sigma\eta}(g), \quad (3.2)$$

$$K_{\mu\nu}^j = \langle \mu | \hat{K}_j | \nu \rangle = \sum_g \chi_\mu(g) \sum_{\eta} \chi_\eta(g) \sum_{\sigma} C_{\sigma j} C_{\eta j} A_{\sigma\nu}(g).$$

However, Eq. (3.2) leads to large numerical errors that can be overcome only with huge grids. The reason is that the functions

$$\hat{J}_j \chi_\nu \quad \text{and} \quad \hat{K}_j \chi_\nu \quad (3.3)$$

lead to components *outside* the basis space $\{\chi_\mu\}$ even though ϕ_i is described within this space. Use of Eq. (3.2) is equivalent to expanding $\hat{J}_j \phi_i$ and $\hat{K}_j \phi_i$ defined over the grid in terms of the basis $\{\chi_\mu\}$. If the grid were infinite, this would be acceptable, but with finite grids it leads to large errors in (3.2), referred to as the *alias*.² This manifests itself as noise in the wave function.³ The solution to this difficulty is to expand Eq. (3.3) in terms of a larger *dealiasing basis* $\{\chi_\mu^*; \sigma = 1 \cdots M^*\}$:

$$J^j(g)\chi_\nu(g) = \sum_{\sigma}^{M^*} \chi_{\sigma}^*(g) W_{\sigma,\nu}^{jJ} \quad (3.4)$$

$$K^j(g)\chi_\nu(g) = \sum_{\sigma}^{M^*} \chi_{\sigma}^*(g) W_{\sigma,\nu}^{jK},$$

used only for evaluating Eq. (3.2)

$$J_{\mu\nu}^j = \langle \mu | J^j | \nu \rangle = \sum_{\sigma}^{M^*} S_{\mu\sigma}^* W_{\sigma,\nu}^{jJ}, \quad (3.5)$$

$$K_{\mu\nu}^j = \langle \mu | K^j | \nu \rangle = \sum_{\sigma}^{M^*} S_{\mu\sigma}^* W_{\sigma,\nu}^{jK},$$

where the $S_{\mu\sigma}^* = \langle \chi_{\mu} | \chi_{\sigma}^* \rangle$ is the overlap matrix element between the normal basis and the augmented dealiasing set (normal basis functions plus dealiasing functions). This set of dealiasing functions then filters out the noise due to incompleteness of $\langle \chi_{\mu} \rangle$. The coefficients $W_{\sigma,\nu}^{jJ}$ and $W_{\sigma,\nu}^{jK}$ in Eq. (3.4) are obtained by a least-squares fit over the grid points.²

The normal basis $\langle \chi_{\mu} \rangle$ is augmented to form the dealiasing basis $\langle \chi_{\mu}^* \rangle$ by adding new radial wave functions so that the augmented basis has functions whose exponents differ by a factor of at least 1.5 and at most 2.5. When two exponents are any closer than this, linear dependencies start to appear, making the final energy unreliable. When two consecutive exponents are spaced by more than this, then the least-squares fit is less accurate, again making the final energy less reliable. In addition, the angular functions of the basis are augmented so that the d basis contains exponents corresponding to the p functions of the normal basis, and so there are f functions corresponding to the d functions of the normal basis.

With the Coulomb and exchange operators $J_{\mu\nu}^j$ and $K_{\mu\nu}^j$ in Eq. (3.5), we proceed to calculate the wave functions as in normal GVB-PP calculations.

B. The grid

The general grid generation approach is outlined in Ref. 4. For each atom in the molecule, there are angular and radial grids using Legendre polynomials and hyperbolic tangent functions, respectively. These atomic grids are then merged to form a molecular grid using Lagrange interpolation to ensure that the grid produces functions that dissociate smoothly as atoms are separated to infinity.

We use a multigrid strategy as outlined in Ref. 5. This strategy involves generating three different grids denoted as medium, fine, and ultrafine with about 200, 400, and 1100 points per carbon atom. The medium grid is used for the vast majority of the SCF iterations. Once the wave function begins to converge, the ultrafine grid is used for one iteration, followed by the fine grid for several iterations (usually three). After this reconsolidation, all subsequent iterations can be carried out using the medium grid. Fock matrix updating is used subsequent to the ultrafine grid iteration, so that the remaining iterations require increasingly less accuracy in the integrals.

The great advantage in using such a multigrid strategy is that one can obtain wave functions whose energies are more accurate than those obtained from using the medium grid alone, while using the medium grid for all but about four of the iterations. The integrals for the fine and ultrafine grids need never be stored, and consequently the storage requirement for the PS algorithm is proportional to the medium grid size. More recently, we have switched entirely to a direct SCF scheme in which no disk space is required for integral storage. Regeneration of the medium grid integrals is very inexpensive, so that with an optimized integral package and efficient cutoffs there is only a $\sim 15\%$ increase in CPU time for recalculation.

C. Monoatomic and diatomic corrections

A major challenge in using numerical methods for the wave functions of molecules is the accurate description of the core orbitals. These orbitals vary rapidly near the nucleus, requiring a large number of grid points and dealiasing functions for reasonable accuracy. An efficient way to deal with this problem is to calculate selected two-electron integrals analytically for these core orbitals. This method has been applied on two levels, which we denote as monoatomic (1C) and diatomic (2C) corrections.

1. 1C corrections

In the 1C approach the two-electron integrals having all four of the atomic orbitals centered on one atom are evaluated analytically. Such an approach is computationally inexpensive and is easy to implement. The number of two-electron integrals required is $M\eta^3/8$, where η is the number of basis functions per atom and M the total number of basis functions. For large molecules this scales as M , with a prefactor of η^3 . Since η is always small (10–20) and a large fraction of the 1C two-electron terms are zero by symmetry, the 1C calculations are always inexpensive.

The procedure is as follows. The Coulomb and exchange operators containing all one-center contributions are calculated as in Eqs. (2.26) and (2.27), but with the sum restricted to one-center terms only, to obtain

$$J_{\mu,\nu}^{j,1c} \quad \text{and} \quad K_{\mu,\nu}^{j,1c}.$$

The time required to evaluate analytically the necessary 1C two-electron integrals and to assemble these operators is negligible.

Next we must correct for these 1C terms in evaluating $J_j \chi_2$ and $K_j \chi_2$ over the grid. This is done by calculating the 1C operators on the grid using

$$J_a^{j,1c}(g) = \sum_{\sigma,\eta \in a} A_{\sigma\eta}(g) C_{\sigma j} C_{\eta j}, \quad (3.6a)$$

$$K_a^{j,1c}(g)\chi_{\nu_a}(g) = \sum_{\sigma,\eta \in a} A_{\sigma\nu_a}(g) C_{\sigma j} C_{\eta j} \chi_{\eta}(g), \quad (3.6b)$$

where the sums in Eq. (3.6) are over all basis functions of atoms a . In Eq. (3.6b) the ν_a is only for basis functions on a .

These functions Eq. (3.6) are then described with the antialiasing functions:

$$J_a^{j,1c}(g)\chi_{v_a}(g) = \sum_{\sigma}^{M^*} W_{\sigma,v_a}^{j,J,1c} \chi_{\sigma}^*(g), \quad (3.7)$$

$$K_a^{j,1c}(g)\chi_{v_a}(g) = \sum_{\sigma}^{M^*} W_{\sigma,v_a}^{j,K,1c} \chi_{\sigma}^*(g).$$

Using these quantities the total Coulomb and exchange operators are calculated as

$$J_{\mu\nu} = \sum_{\sigma}^{M^*} S_{\mu\sigma}^* (W_{\sigma,\nu}^{j,J} - \delta_{a_{\mu}a_{\nu}} W_{\sigma,\nu}^{j,J,1c}) + J_{\mu\nu}^{1c} \quad (3.8)$$

$$K_{\mu\nu} = \sum_{\sigma}^{M^*} S_{\mu\sigma}^* (W_{\sigma,\nu}^{j,K} - \delta_{a_{\mu}a_{\nu}} W_{\sigma,\nu}^{j,K,1c}) + K_{\mu\nu}^{1c},$$

where $\delta_{a_{\mu}a_{\nu}}$ ensures that basis functions μ and ν be on the same center a ($J_{\mu\nu}^{1c}$ and $K_{\mu\nu}^{1c}$ are zero for μ and ν on different centers).

2. 2C corrections

In the diatomic corrections approach, the two-electron integrals having all four of the atomic orbitals centered on one or two atoms are evaluated analytically and used to calculate

$$J_{\mu\nu}^{2c} \text{ and } K_{\mu\nu}^{2c} \quad (3.9)$$

The number of such terms is $M^2\eta^2$, and for large molecules this scales as M^2 with a prefactor of η^2 . The implementation of the diatomic correction is much more complicated than for the monatomic correction. New correction operators need to be defined for every pair of atoms,

$$J_{ab}^{j,2c}(g) = \sum_{\sigma,\eta \in a,b} A_{\sigma\eta}(g) C_{\sigma j} C_{\eta j}, \quad (3.10)$$

$$K_{ab}^{j,2c}(g)\chi_{v_a}(g) = \sum_{\sigma,\eta \in a,b} A_{\sigma\eta}(g) C_{\sigma j} C_{\eta j} \chi_{\eta}(g)$$

(where v_{ab} indicates v on either a or b). These are in turn described with antialiasing functions as in Eq. (3.7),

$$J_{ab}^{j,2c}(g)\chi_{v_a}(g) = \sum_{\sigma}^{M^*} W_{\sigma,v_a}^{j,J,2c} \chi_{\sigma}^*(g), \quad (3.11)$$

$$K_{ab}^{j,2c}(g)\chi_{v_a}(g) = \sum_{\sigma}^{M^*} W_{\sigma,v_a}^{j,K,2c} \chi_{\sigma}^*(g).$$

The Coulomb and exchange operators are then defined as

$$J_{\mu\nu}^j = \sum_{\sigma} S_{\mu\sigma}^* \left[W_{\sigma,\nu}^{j,J} - \left(\sum_b \right) W_{\sigma,\nu,b}^{j,J,2c} \right] + J_{\mu\nu}^{j,2c}, \quad (3.12)$$

$$K_{\mu\nu}^j = \sum_{\sigma} S_{\mu\sigma}^* \left[W_{\sigma,\nu}^{j,K} - \left(\sum_b \right) W_{\sigma,\nu,b}^{j,K,2c} \right] + K_{\mu\nu}^{j,2c},$$

where the sum over all the atoms, \sum_b , needs to be done if $a_{\nu} = a_{\mu}$. The number of correction operators that need to be evaluated scales as the square of the number of atoms in the molecule. The time required to include these correc-

tions is not as trivial as in the monoatomic corrections, but the diatomic corrections give results that are significantly more accurate than the monoatomic corrections.

IV. RESULTS

We picked three systems designed to test how effective the PS method would be for GVB calculations. In each case the quantity of interest is an energy difference, either between two excited states or for breaking a bond. For CH_2 and SiH_2 the quantities of interest are the excitation energy to the excited triplet state. In addition, a core effective potential was tested for Si where an issue is the accuracy of PS approaches for such cases. For C_2H_4 the quantities of interest include the π -to- π^* excitation energy, the rotational barrier for twisting the molecule by 90° about the CC bond, and the CC bond energy (energy to double the CC bond length).

A. Methylene

For CH_2 the ground state has 3B_1 symmetry with σ and π nonbonding orbitals as in Eq. (4.1a), whereas the singlet has the two nonbonding electrons spin paired as in Eq. (4.1b):



(4.1a)



(4.1b)

Because of the difference in the nonbonding orbitals, the geometries are quite different. Thus, with GVB configuration-interaction (GVB-POL-CI), Harding and Goddard¹² calculated $R_{\text{CH}} = 1.084 \text{ \AA}$, $\Theta_{\text{HCH}} = 133.2^\circ$ for the triplet state, and $R_{\text{CH}} = 1.113 \text{ \AA}$, $\Theta_{\text{HCH}} = 101.8^\circ$ for the singlet. The important quantity here, the triplet-singlet excitation energy, is $\Delta_{\text{ST}} = 9.09 \text{ kcal/mol} = 0.0145 \text{ hartrees} = 14.5 \text{ mhartrees}$.

In studying methylene, our goals are (a) to test the accuracy of the PS method for good quality basis sets [valence double-zeta plus polarization (VDZp)] and for basis sets where additional polarization or diffuse functions are added, and (b) to test the change in accuracy when GVB wave functions are used rather than HF wave functions.

All-integral HF calculations lead to excitation energies ranging from 26.1 to 25.1 kcal/mol for various basis sets, while GVB-PP leads to 9.1 to 7.8 kcal/mol. As described below, the PS-1C leads to a maximum error of 0.09 kcal/mol for both HF and GVB calculations, while PS-2C leads to a maximum error of 0.01 kcal/mol. We conclude that the PS method is quite adequate for these systems.

TABLE I. Dealiasing set for methylene.

Atom	Basis	<i>L</i> block	Exponent ^a				
C	VDZ _{<i>p</i>}	SP	10.24	20.48			
		SPD	0.32	0.64	1.28	2.56	5.12
H	VDZ _{<i>p</i>}	SP	4.0	8.0			
		SPD	0.1775	0.32	0.64	1.0	2.0
C	VDZ2 _{<i>p</i>}	SP	8.0	16.0			
		SPD	0.06	0.422	0.971	2.0	4.0
H	TZ2 _{<i>p</i>}	SP	4.0	8.0			
		SPD	0.0822	0.2246	0.6	1.38	2.0

^aExponents that already exist in the basis set are not included in the dealiasing set.

1. Geometry and basis sets

For CH₂, we used the geometries optimized by Harding and Goddard¹² with GVB-POL-CI calculations (see below).

Three different basis sets of increasing size were used:

(a) VDZ_{*p*}/DZ_{*p*}: The C uses the Dunning–Huzinaga valence double-zeta basis set^{13,14} [based on (9*s*/5*p*)] with one set of *d* functions on C ($\alpha = 0.64$). The H uses the Dunning–Huzinaga basis (based on four *s* functions contracted to two, with the exponents scaled by¹⁵ $\xi = 1.2$) and one set of *p* functions on H ($\alpha = 1.0$).

(b) VDZ2_{*p*}/TZ2_{*p*}: Here we replaced the 4*s* H basis with the 6*s* (unscaled) basis¹⁴ contracted to 3*s* triple zeta. The *d* and *p* polarization functions from VDZ_{*p*}/DZ_{*p*} were replaced by a pair of functions scaled by the factors $\sqrt{2.3}$ and $1/\sqrt{2.3}$ from the above values.

(c) VDZ2_{*pn*}/TZ2_{*p*}: To the basis in *b* was added a diffuse set of *s* and *p* functions on the C atom ($\alpha_s = 0.45$, $\alpha_p = 0.34$) optimized¹³ for the negative ion of C.

2. Grids and dealiasing basis sets

Table I shows the dealiasing basis sets used for methylene. As in previous work,⁵ the dealiasing basis sets are formed of SP and SPD blocks of atomic orbitals with the same exponents. This makes the assembly of the least-squares-fitting matrix more efficient. The molecular grid for CH₂ is generated using atomic grids similar to the ones used in studying glycine.⁵ Thus, for methylene the sizes of the grids are 181, 409, and 1114 grid points.

3. Discussion

For the triplet state, the two C–H bonds are correlated, leading to the GVB-PP (2/4) wave function. For the singlet state, the two C–H bonds and the singlet lone pair are all correlated, leading to the GVB-PP (3/6) wave function. These wave functions have the same total number of orbitals, leading to a consistent level of description for the two states.

The results for methylene are summarized in Tables II and III. In Table II we compare the total energies for the various calculations. The all-integral results are expressed in hartrees, and the PS results are expressed as the differ-

TABLE II. Total energy for CH₂ using GVB-PP wave functions.

Method	State ^a	Basis sets (carbon/hydrogen)		
		VDZ _{<i>p</i>} /VDZ _{<i>p</i>}	VDZ2 _{<i>p</i>} /TZ2 _{<i>p</i>}	VDZ2 _{<i>pn</i>} /TZ2 _{<i>p</i>}
Total energy (hartrees)				
All-ints ^b	¹ A ₁	−38.938 766	−38.942 557	−38.943 274
All-ints	³ B ₁	−38.953 285	−38.955 554	−38.955 770
Energy difference (kcal/mol) ^c				
PS-1C ^d	¹ A ₁	0.015	0.032	0.024
PS-2C ^e	¹ A ₁	−0.005	0.005	0.004
PS-1C	³ B ₁	−0.054	0.117	0.112
PS-2C	³ B ₁	<0.001	0.013	0.013

^aGVB-PP (3/6) wave function for the ¹A₁ state and GVB-PP (2/4) for the ³B₁ state.

^bAll-integrals result from the GVB2P5 program.

^cEnergy difference, $E_{PS} - E_{AI}$.

^dPS results with analytic two-electron integrals for monoatomic terms.

^ePS results with analytic two-electron integrals for diatomic terms.

ence from the all-integral results. These are quoted in kcal/mol to simplify comparison with bond energies and other chemical data.

For the singlet state using the PS-1C correction, the errors in total energy (GVB) range from 0.015 to 0.032 kcal/mol, which drops to a maximum error of 0.005 kcal/mol for PS-2C. In the triplet state the errors are a factor of 3 to 5 larger, ranging from 0.054 to 0.117 kcal/mol for PS-1C and up to 0.113 kcal/mol for PS-2C. The larger error for the triplet arises because the grid is less complete in the directions perpendicular to the molecule. The grid is more complete in directions parallel to the plane since each atom contributes its own grid. Such difficulties could be ameliorated by a more sophisticated grid design procedure. Similar energy differences are obtained for the HF wave functions, again a maximum error of about 0.120 kcal/mol was found for the triplet-state geometry with monoatomic corrections.

Table III shows the singlet–triplet gap obtained for the HF and GVB-PP wave functions. For both wave functions, the error is smaller than 0.09 kcal/mol using PS-1C corrections and smaller than 0.02 kcal/mol for the PS-2C corrections.

TABLE III. The singlet–triplet gap (ΔE_{ST}) for CH₂.^a

Method	Wave function	Basis sets (carbon/hydrogen)		
		VDZ _{<i>p</i>} /VDZ _{<i>p</i>}	VDZ2 _{<i>p</i>} /TZ2 _{<i>p</i>}	VDZ2 _{<i>pn</i>} /TZ2 _{<i>p</i>}
All-ints ^b	HF	26.11	25.48	25.13
PS-1C ^c	HF	26.18	25.41	25.06
PS-2C ^d	HF	26.11	25.48	25.12
All-ints	GVB-PP	9.11	8.16	7.84
PS-1C	GVB-PP	9.18	8.07	7.75
PS-2C	GVB-PP	9.11	8.15	7.83

^aAll energies in kcal/mol. Experimental value 9.09 kcal/mol.

^bSee footnote b of Table II.

^cSee footnote c of Table II.

^dSee footnote d of Table II.

An important result is that the errors do not increase as the size of the basis set is increased. This shows that the PS method does not have any intrinsic problems in manipulating the diffuse functions present in the largest basis set. More significant is the fact that the same grid was used for all three basis sets, so that the number of one-electron potentials (3.1) only increases as M^2 . This scaling is much better than the traditional all-integral method, where the number of two-electron integrals grows as M^4 . The PS method is thus expected to be particularly advantageous for larger basis sets.

B. Silylene

For SiH₂ the two low-lying states have the character of the two states in CH₂ as in Eq. (4.1); however, the singlet state is the ground state (see Ref. 12 for a discussion). The studies of silylene emphasize two points: (a) to test the PS method for a second-row element, and (b) to test the use of effective core potentials for PS calculations. Two sets of calculations were carried out, one with all the core electrons present and the other using the shape and Hamiltonian consistent (SHC) effective core potential to replace them.

As discussed below, we find that use of the ECP leads to an enormous improvement of the accuracy for PS without atomic corrections (i.e., so that 1C and 2C corrections are *not* necessary). For the all-electron calculations, use of 1C and 2C corrections leads to results for SiH₂ comparable with those of CH₂, suggesting that PS will be effective for the later rows of the Periodic Table.

1. Geometry and basis sets

For the ¹A₁ state, we used $R_{\text{SiH}} = 1.508 \text{ \AA}$ and $\Theta_{\text{HSiH}} = 92.4^\circ$, while for the ³B₁ state, we used $R_{\text{SiH}} = 1.471 \text{ \AA}$ and $\Theta_{\text{HSiH}} = 118.2^\circ$. [These were based on geometry optimizations using second-order Møller–Plesset perturbation theory (MP2) and unrestricted MP2 with the 6-31G** basis (valence double zeta with polarization functions on Si and H)].

When no effective core potential is used, a Huzinaga valence double-zeta basis set (11s8p/4s3p) was used for silicon and a Huzinaga unscaled double-zeta basis set (4s/2s) was used for hydrogen. A set of *d* polarization functions ($\alpha = 0.42$) was used with the silicon basis, and a set of *p* polarization functions ($\alpha = 0.6$) was used with the hydrogen basis.

The SHC effective core potential (Rappé *et al.*¹⁶) was used to eliminate the 17 core electrons of Si. The corresponding VDZ basis set (3s3p/2s2p) was augmented with the same 3*d* polarization functions as before. The same VDZ*p* basis was used for hydrogen.

2. Grids and dealiasing basis sets

The dealiasing basis sets are chosen by the same method described for methylene, but slightly different atomic grids are used. For the silicon atom, the size of the bonding region is changed from 4.5 to 6.5 bohrs for the ultrafine grid. This increases the size of the grids from 1114 of carbon to 1389 for silicon. This was found to be necessary to achieve good accuracy.

TABLE IV. Energies comparison for SiH₂.

Calculation ^a State	All-ints ^b Energy ^f	PS ^c error (kcal/mol)	PS-1C ^d error (kcal/mol)	PS-2C ^e error (kcal/mol)
(a) All-electron				
HF	³ B ₁ - 289.920 507	22.7	0.065	0.007
HF	¹ A ₁ - 289.929 006	22.6	0.080	0.025
ΔE_{ST}^g	0.008 499	0.152	-0.015	-0.019
GVB ^h	³ B ₁ - 289.940 694	22.7	0.062	0.008
GVB ⁱ	¹ A ₁ - 289.972 813	22.9	0.075	0.025
ΔE_{ST}	0.032 119	0.150	-0.013	-0.017
(b) Si core electrons replaced by the effective potential				
HF	³ B ₁ - 289.994 255	0.003	0.002	0.010
HF	¹ A ₁ - 290.003 034	0.066	0.063	0.024
ΔE_{ST}	0.008 779	-0.064	-0.061	-0.014
GVB	³ B ₁ - 290.014 773	0.003	0.001	0.004
GVB	¹ A ₁ - 290.048 020	0.068	0.063	0.024
ΔE_{ST}	0.033 247	-0.066	-0.061	-0.020

^aExperimental geometry with the VDZ*p* basis set for Si and H atoms.

^bAll-integral calculations.

^cPS results with no atomic corrections.

^dPS results with analytic bielectronic integrals for monoatomic terms.

^ePS results with analytic bielectronic integrals for diatomic terms.

^fAll total energies in hartrees.

^gSinglet–triplet gap = $E_{\text{Triplet}} - E_{\text{Singlet}}$.

^hGVB-PP (2/4) wave function for the ³B₁ state.

ⁱGVB-PP (3/6) wave function for the ¹A₁ state.

3. Discussion

The errors obtained for SiH₂ are of the same order as those for CH₂. The maximum error is 0.079 kcal/mol when PS-1C corrections are included and 0.014 kcal/mol with PS-2C corrections. As can be seen in Table IV, the errors are always similar for the HF and GVB wave functions at a given geometry.

The presence of an effective core potential improves the accuracy of the PS method. This is because the largest errors in the PS method are caused by the tight core orbitals. Thus, when no 1C or 2C corrections are made, the error in the PS result is 22 kcal/mol for all electrons, which drops to less than 0.07 kcal/mol when the core electrons are replaced by the effective potential. On the other hand, with 1C or 2C corrections, the accuracy is about the same for all electrons as for ECP; this shows that the 1C and 2C corrections are very effective in removing large errors associated with core orbitals.

Note that for the triplet state with an effective core potential, the error using the PS method is unusually small, 0.001–0.002 kcal/mol. We believe this results from a fortuitous cancellation of errors arising from the particular geometries and has nothing to do with either the effective core potential or the nature of the wave function.

C. Ethylene

In the ethylene system we shift our focus away from electronic criteria (basis sets and effective core potentials) and concentrate on the effect of larger geometric changes on the accuracy of the PS method. We considered four geometries:

TABLE V. Summary of energy differences for C_2H_4 .

State	All-integral total energy (hartrees) ^b		PS energy error (kcal/mol) ^a			
			PS-1C ^c		PS-2C ^d	
	HF	GVB ^e	HF	GVB	HF	GVB
Experimental geometry ($R_{CC} = 1.338 \text{ \AA}$, $\phi = 0^\circ$)						
3A_2	-77.931 907	-77.942 874	-0.137	-0.119	-0.036	-0.038
1A_1	-78.060 723	-78.099 240	-0.243	-0.209	-0.045	-0.045
ΔE_{ST}^f	0.128 816	0.156 366	0.106	0.089	0.008	0.007
Twisted geometry ($R_{CC} = 1.338 \text{ \AA}$, $\phi = 90^\circ$)						
3A_2	-77.973 417	-77.984 305	-0.183	-0.022	0.003	0.004
1A_1	-77.888 273	-77.981 006	0.016	-0.025	0.007	0.004
ΔE_{ST}	-0.085 144	-0.003 299	-0.199	0.003	-0.004	0.000
Barrier ^g 3A_2	-0.041 510	-0.041 431	0.046	-0.097	-0.039	-0.042
Barrier 1A_1	0.172 450	0.118 234	-0.259	-0.184	-0.053	-0.049
Stretched geometry ($R_{CC} = 2.676 \text{ \AA}$, $\phi = 0^\circ$)						
3A_2	-77.772 934	-77.884 587	-0.199	-0.196	-0.013	-0.013
1A_1	-77.726 946	-77.847 384	-0.128	-0.209	-0.038	-0.016
ΔE_{ST}	-0.045 988	0.002 797	-0.070	0.013	-0.009	0.003
Bond energy 3A_2	0.158 973	0.098 287	0.062	0.077	0.023	0.025
Bond energy 2A_1	0.333 777	0.251 856	0.115	0.000	0.007	0.029
Stretched/twisted geometry ($R_{CC} = 2.676 \text{ \AA}$, $\phi = 90^\circ$)						
3A_2	-77.773 688	-77.845 388	-0.128	-0.104	0.003	-0.013
1A_1	-77.727 351	-77.845 284	-0.139	-0.104	0.012	0.013
ΔE_{ST}	-0.046 337	-0.000 104	0.011	0.000	-0.006	-0.000

^aEnergy difference, $E_{PS} - E_{RH}$.^bAll total energies in hartrees.^cPS results with analytic bielectronic integrals for diatomic terms.^dPS results with analytic bielectronic integrals for monoatomic terms.^eGVB-PP (3/6) wave function for 1A_1 state and GVB-PP (2/4) for 3A_2 state.^fSingle-triplet gap $E_{\text{triplet}} - E_{\text{singlet}}$.^g $E(\phi = 90^\circ) - E(\phi = 0^\circ)$.

(a) Planar: The ground-state geometry with a torsion angle of $\phi = 0^\circ$, and $R_{CC} = 1.338 \text{ \AA}$. The other geometric parameters are $R_{CH} = 1.085 \text{ \AA}$, $\Theta_{HCH} = 117.8^\circ$.

(b) Twisted: The torsion angle is $\phi = 90^\circ$ but no other parameters are changed. (The equilibrium twisted geometry would have a larger CC bond and HCH angle.)

(c) Stretched: With $\phi = 0^\circ$ the CC bond distance is doubled to $R_{CC} = 2.676 \text{ \AA}$ (all other quantities fixed). At this distance the bond is broken,

(d) Stretched/twisted: With $R_{CC} = 2.676 \text{ \AA}$, we twist to $\phi = 90^\circ$. Since there is essentially no bond, the energy changes should be small.

We find that with PS-1C the errors in the GVB wave functions have a maximum error of 0.09 kcal/mol, while PS-2C leads to a maximum error of 0.007 kcal/mol. These are quite acceptable results and indicate that PS-GVB has sufficient accuracy for chemical applications.

1. Basis sets, grids, and wave functions

For all of the calculations on the ethylene system we use the VDZ_p/VDZ_p basis described above for CH₂ and the same grid and dealiasing set.

In these calculations we correlate the two pairs of electrons associated with the CC bond, leading to a GVB-PP

(2/4) wave function for the singlet and a GVB-PP (1/2) wave function for the triplet state.

2. Discussion

Table V summarizes the calculations performed on ethylene. The first two columns tabulate the standard all-integral results for both HF and GVB-PP wave functions for each of the four geometries. Included are the absolute singlet and triplet energies, the singlet-triplet gap, and the rotational barriers.

The next four columns detail the corresponding results for PS calculations. Columns three and four include results with 1C corrections, and columns five and six include results with 2C corrections. The PS results are expressed as a difference from the all-integral results and are quoted in kcal/mol to indicate the significance for bond energies and other chemical data.

We note that with 1C corrections the absolute energies for HF wave functions agree with the analytic ones to within 0.25 kcal/mol, and the relative energies agree to within 0.2 kcal/mol. For GVB wave functions the absolute energies agree to within 0.2 kcal/mol, and the relative energies to within 0.1 kcal/mol.

For calculations using the 2C corrections, the absolute energies for HF wave functions agree with the analytic ones to within 0.05 kcal/mol, and the relative energies to within 0.008 kcal/mol. For GVB wave functions the similar results are 0.05 and 0.007 kcal/mol.

For singlet-triplet excitation energies (same geometry), the PS-1C calculations lead to errors of 0.01 to 0.20 kcal/mol for HF and 0.00 to 0.09 kcal/mol for GVB. These errors are quite acceptable. With PS-2C the error drops to a maximum of 0.009 kcal/mol, which is negligible.

In general, for ethylene, the PS method does a better job at reproducing the results for GVB wave functions than it does for HF wave functions. We presume this to be an artifact to the particular grids and dealiasing sets used, since we see no physical reason for this effect.

V. DISCUSSION

We find that the PS method with 1C corrections leads to an accurate description of the GVB-PP wave functions and that the energy differences for singlet-triplet excitations and bond dissociation are well described. In addition, we find that with use of the effective potential (ECP) on Si, the uncorrected PS results are quite accurate. This suggests that PS approaches will be useful in calculations of chemically interesting phenomena, such as excitation energies and bond dissociation processes.

The code used to carry out the calculations reported above was obtained by interfacing the standard GVB2PS program¹⁸ with the original PS HF program. The combined code has not yet been optimized for efficiency, so we do not present timing results in this paper. An optimized implementation is now nearing completion so that timing tests should be available soon. Preliminary results indicate that substantial reductions in CPU time and disk storage similar to those obtained for HF studies of large systems can be achieved for GVB calculations.

With regard to higher levels of electron correlation, the PS method can be applied to general CI calculations if the CI matrix can be expressed in terms of Coulomb and exchange operators (the integrals are evaluated each iteration, a direct method). In these cases, a factor of M (as in the HF and GVB algorithms) can be gained in formulating the action of the CI matrix on a trial vector. Of course, the actual performance of the method for such purposes is best tested with calculations.

A particularly attractive application would be to some of the less computationally demanding forms of CI that could be implemented for very large systems. Among these are restricted CI, which properly spin couples the GVB-PP wave function, and correlation-consistent CI, in which only a few electron pairs are allowed to enter the virtual space.^{17,19} We plan to begin implementation of these methods in the near future.

It is straightforward to incorporate analytic first and second derivatives into PS calculations and such work is in progress.

These studies have given us some additional insight into the role of the grids in determining accuracy, and we believe that it will be possible to develop similar sized grids with even higher accuracy.

The 2C corrections give results that are more accurate than the 1C corrections by a factor of about three or more. However, 2C corrections require greater computation time than is required for 1C corrections, and we have not determined whether adding diatomic corrections is faster than simply increasing the grid size.

VI. CONCLUSIONS

We find that the PS algorithm for the direct evaluation of Coulomb and exchange operators leads to accurate results for GVB wave functions, suggesting a wide range of applications in quantum chemistry. The PS method provides uniform accuracy for a range of basis sets (including diffuse functions of s , p , and d with various exponents), for systems with effective core potentials, and for a wide range of geometric conformations (including bond dissociation). Additional studies are underway using the PS algorithm for transition-metals complexes. In summary, we believe that the PS algorithm has a future in *ab initio* quality studies of molecular systems.

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