The Pairwise Correlated Generalized Valence Bond Model of Electronic Structure I; The Estimation of Pair Energies from Orbital Overlaps

(electron correlation/potential energy surfaces/excited states/molecular orbital theory/many electron theory)

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ABSTRACT A new method for the accurate a priori calculation of atomic and molecular energies is proposed. The new method agrees with experiment to within less than 1 kcal/mole in all cases examined thus far, and is applicable to excited states and to transition states for chemical reactions. Since the new method corrects the results of generalized valence bond calculations for the effects of electron pair correlations, we call the new method the pairwise correlated generalized valence bond method. The description of the electronic structure of atoms and molecules in terms of one electron orbitals provides a simple and therefore useful starting point for any more detailed theory. The energy obtained from calculations based upon orbitals is generally in error by about 0.015 au (10 kcal/mole)* for each electron. Although these errors comprise a small fraction of the total energy, they are quite large by chemical standards. It is, therefore, necessary to go beyond an orbital picture to obtain a chemically adequate description of electronic structure.

The errors inherent in an orbital model can be accounted for in terms of the correlated motion of the electron pairs (1). The novel feature of the new method is that the correlation correction is determined in an a priori fashion directly from the orbitals. This allows us to treat much larger systems than we could by calculating correlation energies using an ab initio variational approach, but maintains our ability to predict these correlation energies as functions of molecular geometry. The latter is absolutely necessary if we are to examine potential energy surfaces for chemical reactions. It is with an eye towards the study of transition states and reaction pathways that the new method has been developed.

GENERALIZED VALENCE BOND PAIR ENERGIES

If we introduce electron correlation into the wavefunction explicitly (2), our calculation becomes much more difficult. If we use configuration interaction (3), the wavefunction is no longer easy to interpret. We shall, therefore, follow Sin-anoğlu (1), and express the total energy as the sum of the energy resulting from an orbital calculation, plus a sum of pair energies. Since we want the orbital pair energies to include only the effects of real electron correlation, (4) so that we can describe the dissociation of chemical bonds, we select the generalized valence bond (GVB) orbitals developed by Ladner and Goddard (5) as our starting point:

\[
E_{PCGVB} = E_{GVB} + \sum_{i<j} \epsilon_{ij},
\]

and refer to the corrected result as the pairwise correlated generalized valence bond (PCGVB) method.

In order to picture the general behavior of GVB electron pair correlation energies, let us consider two hydrogen atoms, A and B, at large separation (Fig. 1a). The electron repulsion is \(R_{AB}^{-1}\) and is not altered by electron correlation (if we ignore the small Van Der Waals attraction). As we bring the two atoms closer together, the charge distributions begin to overlap (Fig. 1b). The electron repulsion is now \(R_{AB}^{-1}\) plus an additional term arising from the overlapping of the two charge distributions where \(r_{AB}\) is very small. It is this additional term that is removed by electron correlation. In the correlated wavefunction, only one electron will occupy this region at a time. Hence, the correlation energy is determined by the overlapping of the two charge distributions, rather than by the total electron repulsion. This is true not only for the large bond lengths we have considered above, but also for the

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Abbreviations: PCGVB, pairwise correlated generalized valence bond; GVB, generalized valence bond; HF, Hartree-Fock; Re, equilibrium bond length; R, internuclear distance; au, atomic unit.

* The atomic unit of energy used is the Hartree (1 Hartree = 27.21 eV = 627.5 kcal/mole).

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Fig. 1. The overlapping of GVB orbitals when: \(R_{AB}\) is large (a); \(R_{AB}\) is small (b); \(R_{AB}\) is zero, \(z\) is small (c); and \(R_{AB}\) is zero, \(z\) is large (d).
### Table 1. Exponents (effective nuclear charges) of minimum basis set GVB and HF orbitals for two electron atoms

<table>
<thead>
<tr>
<th>Atom</th>
<th>( z_1 )</th>
<th>( z_2 )</th>
<th>( \tilde{z} ) Exp.</th>
<th>HF Exp.</th>
</tr>
</thead>
<tbody>
<tr>
<td>H(^+)</td>
<td>0.28323</td>
<td>1.03923</td>
<td>0.68123</td>
<td>0.88750</td>
</tr>
<tr>
<td>He(^+)</td>
<td>1.18853</td>
<td>2.18317</td>
<td>1.68585</td>
<td>1.68750</td>
</tr>
<tr>
<td>Li(^+)</td>
<td>2.07898</td>
<td>3.29490</td>
<td>2.68694</td>
<td>2.68750</td>
</tr>
<tr>
<td>Be(^{2+})</td>
<td>3.98471</td>
<td>4.38973</td>
<td>3.68722</td>
<td>3.68750</td>
</tr>
<tr>
<td>Ne(^{4+})</td>
<td>8.57308</td>
<td>10.90164</td>
<td>9.68746</td>
<td>9.68750</td>
</tr>
</tbody>
</table>

\( z = a b \) \( z - \frac{5}{16} \) \( z - \frac{5}{16} + \) \( z - \frac{5}{16} \) \( z - \frac{5}{16} \)

\( \sqrt{z - \frac{5}{16}} \) \( \sqrt{z - \frac{5}{16}} \) \( \sqrt{z - \frac{5}{16}} \) \( \sqrt{z - \frac{5}{16}} \)

* The results we obtained are virtually identical to those in ref. 16.
* Asymptotic forms.
* Eq. 3.

The united atom limit when \( R_{AB} \) is zero (Fig. 1c). If we increase the nuclear charge, the size of the orbitals decreases (Fig. 1d) and the total electron repulsion increases. Hence, as \( z \) approaches infinity, so does the total electron repulsion. However, the correlation energy has a finite limit, and therefore cannot be proportional to the total electron repulsion. We now examine the GVB expression for the energy and obtain a functional form for the overlap dependence of the correlation energy.

We shall not attempt to rigorously derive an exact relationship between pair energies and orbital overlaps (which is probably impossible), but instead we shall use the form of the GVB energy expression as a guide to help us to discover an approximate but useful relationship. Since the GVB wavefunction and the exact wavefunction both satisfy the virial theorem, we can restrict our discussion to the GVB error in the potential energy. The error in the potential energy obtained from a GVB wavefunction (5) for two electrons can be expressed as a coulomb term plus or minus an exchange term:

\[
(V)_{GBV} - (V)_{EXACT} = V_{11} + V_{12} + J_{12} - (V)_{EXACT}
\]

\[
\pm \frac{2S_{12}V_{12} + K_{12} - (V)_{EXACT}}{1 \pm S_{12}}^2.
\]  

where \( V, J, K, \) and \( S \) refer to nuclear attraction, coulomb, exchange, and overlap integrals respectively. The plus and minus signs refer to singlet and triplet states and we have assumed normalization of the orbitals.

We shall find it convenient to define the orbital, \( \tilde{\rho} \), as the geometric mean of the orbitals \( \rho_1 \) and \( \rho_2 \):

\[
\tilde{\rho} = \left( \frac{\rho_1 \rho_2}{S_{12}} \right)^{1/2},
\]  

where the denominator is necessary to preserve normalization. The motivation for considering this geometric mean is that the Hartree-Fock (HF) orbital is very nearly the geometric mean of the two GVB orbitals it splits into (Table 1). This geometric mean approximation is equivalent to the physically reasonable assumption that the average nuclear charge seen by two electrons is independent of the orbital splitting. The approximation is clearly excellent for low values of the nuclear charge, and is exact in the limit of infinite nuclear charge (Table 1).

Making use of this geometric mean orbital, the exchange term of the GVB potential energy error can now be expressed as:

\[
2S_{12}V_{12} + K_{12} - (V)_{EXACT}^2 \frac{1 \pm S_{12}^2}{1 \pm 12^2} = \frac{S_{12}^2}{1 \pm S_{12}^2}
\]

\[
\times (2V_{\phi \phi} + J_{\phi \phi} - (V)_{EXACT})^2 = \frac{S_{12}^2}{1 \pm S_{12}^2}((V)_{\phi \phi} - (V)_{EXACT})
\]

where \( (V)_{\phi \phi} \) is the HF potential energy for the doubly occupied orbital \( \phi \). Hence, the exchange term is related in a simple way to the overlap and the HF potential energy error.

Unfortunately, the coulomb portion of the GVB potential energy error cannot be disposed of as neatly as the exchange term. However, if we make an additional approximation, we can obtain an expression for the coulomb term that is reasonably accurate and extremely useful. If we examine the coulomb and exchange terms we find that:

\[
S_{12}^2((V)_{\phi \phi} - (V)_{EXACT}) = \int \varphi_1(1)\varphi_1(1)
\]

\[
\times \left[ V_1 + V_2 + \frac{1}{r_{12}} - (V)_{EXACT} \right] \varphi_2(2)\varphi_2(2)dr,
\]

and

\[
V_{11} + V_{22} + J_{12} - (V)_{EXACT} = \int \varphi_1(1)\varphi_1(1)
\]

\[
\times \left[ V_1 + V_2 + \frac{1}{r_{12}} - (V)_{EXACT} \right] \varphi_2(2)\varphi_2(2)dr.
\]

We recall from the above that the portion of the electron repulsion that is removed by electron correlation arises from the region where the two charge distributions overlap and \( r_{12} \) is very small (1). Therefore, \( r_1 \) is similar to \( r_2 \) and:

\[
\varphi_1(1)\varphi_1(1)\varphi_2(2)\varphi_2(2) \sim |\varphi_1(1)\varphi_2(1)||\varphi_2(2)\varphi_2(2)|,
\]

in the region where electron correlation is important. The absolute values are necessary to preserve the sign of the two electron distribution. The change in the coulomb term when we introduce electron correlation is therefore roughly given by:

\[
V_{11} + V_{22} + J_{12} - (V)_{EXACT} \sim |S_{12}((V)_{\phi \phi} - (V)_{EXACT})
\]

where the absolute overlap integral, \( |S_{12}| \) is defined as:

\[
|S_{12}| = \int |\varphi_1(1)\varphi_1(1)|dr.
\]

Substituting Eq. 4 and Eq. 8 in Eq. 2 we arrive at the approximation:

\[
(V)_{GBV} - (V)_{EXACT} \approx \left[ \frac{|S_{12}|^2 + S_{12}^2}{1 \pm S_{12}^2} \right]
\]

\[
\times ((V)_{\phi \phi} - (V)_{EXACT}),
\]

where \( x \) is an adjustable parameter to compensate for the crudeness of Equation 8. Since the HF, GVB, and exact wavefunctions all satisfy the virial theorem, we can approximate the GVB pair correlation energy as:
for two electron systems in their equilibrium geometry.

For systems with three or more electrons, we encounter orbitals that are neither singlet nor triplet coupled (5). The pair energies of these "doublet coupled" pairs can be analyzed in the same way to obtain the approximation:

\[ \epsilon_{ij}^{GVB} \approx \frac{1}{2} \chi |S_{ij}|^2 \epsilon_{pp} \]

If we use the value of \( \epsilon_{pp} \) from the molecule of interest, the exclusion effects suggested by Sinanoğlu (1) are automatically taken into account. We shall discuss refinements in a later paper. Of far greater immediate interest is the question of whether or not the simple approximations given above are useful.

The above equations can always be made exact by an appropriate choice of \( \chi \). However, we shall have a useful approximation only if \( \chi \) is reasonably independent of the particular atom or molecule under study. Examination of Eq. 7 indicates that \( \chi \) should depend upon the type of orbitals involved (e.g., 1s, 2s, 2p, etc.) but should be independent of the scale (nuclear charge), since this is the same for all orbitals involved.

If we consider the limiting situation of strongly overlapping GVB orbitals:

\[ \lim_{S_{ii} \to 1} \frac{\epsilon_{ij}^{GVB}}{S_{ij}} = \frac{1 + \chi \epsilon_{pp}}{2} \]

we see that \( \chi \) should equal 1 whenever the GVB and HF pair energies involve the same kind of correlation. For example, the \((2s,2s')\) pair in the beryllium atom involves almost exclusively an angular correlation whether we begin with the HF or the GVB wavefunction. However, although HF (1s,1s') pair energies include both angular and radial correlation, the GVB (1s,1s') pair energies include only angular correlation (4), and \( \chi_{1s,1s'} \) should, therefore, be less than 1. Examination of the asymptotic forms of HF, GVB, and exact solutions of two electron atoms as the nuclear charge becomes infinitely large (so that \( S_{ii} \) approaches 1), indicates that an appropriate choice of \( \chi_{1s,1s'} \) would be approximately \((\sqrt{2} - 1)\). The value of \( \chi \) that will make Eq. 11 exact is compiled in Table 2 for a variety of atomic and molecular states. These values fall quite nicely into the two categories we have predicted, and indicate that the appropriate value of \( \chi \) is easily decided upon from the types of orbitals involved in the pair interaction.

### EXAMPLES

The closed shell ground states of two-electron atoms and molecules provide an unambiguous test of whether we can accurately predict individual GVB pair energies, since they have only one pair energy and we know the exact total energies (6, 7). For these systems whose orbitals are everywhere positive, Eq. 11 reduces to the relationship:

\[ \epsilon_{ij}^{GVB} \approx \frac{\sqrt{2S_{ii}^2} \epsilon_{pp}}{1 + S_{ii}} \]

between the HF and GVB pair energies. This overlap dependence of the ratio of the GVB and HF pair energies is easily tested and turns out to be remarkably accurate (Fig. 2). There can be little question of the importance of GVB overlap overlaps in the determination of GVB pair energies for these systems.

We can rearrange Eq. 14 to obtain the total energy estimate:

\[ E_{PCGVB} = E_{GVB} - \frac{\sqrt{2S_{ii}^2} \epsilon_{pp}}{1 - (\sqrt{2} - 1)S_{ii}} (E_{HF} - E_{GVB}), \]

### Table 2. The parameter, \( \chi \), in Eq. 11 remains reasonably constant regardless of the charge in an atomic ground state, the internuclear distance in a chemical bond, or the particular molecule we examine. It depends only upon the type of orbitals involved

<table>
<thead>
<tr>
<th>Two-electron state</th>
<th>(-\epsilon_{HF})</th>
<th>(-\epsilon_{GVB})</th>
<th>(S_{ij})</th>
<th>(\chi)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. H(^{-}); 1S</td>
<td>24.97 (^b)</td>
<td>8.78 (^b)</td>
<td>0.56572 (^a)</td>
<td>0.45</td>
</tr>
<tr>
<td>2. He; 1S</td>
<td>26.36 (^b)</td>
<td>16.12 (^b)</td>
<td>0.87893 (^a)</td>
<td>0.403</td>
</tr>
<tr>
<td>3. Li(^+); 1S</td>
<td>27.28 (^b)</td>
<td>17.87 (^b)</td>
<td>0.92807 (^a)</td>
<td>0.416</td>
</tr>
<tr>
<td>4. Be(^{2+}); 1S</td>
<td>27.77 (^b)</td>
<td>18.69 (^b)</td>
<td>0.94879 (^a)</td>
<td>0.421</td>
</tr>
<tr>
<td>5. z = \infty; 1S</td>
<td>29.25</td>
<td>20.96</td>
<td>1.00000</td>
<td>0.433</td>
</tr>
<tr>
<td>6. H(_2); R = \infty</td>
<td>—</td>
<td>0.000</td>
<td>0.00000</td>
<td>—</td>
</tr>
<tr>
<td>7. H(_2); 5 au</td>
<td>25.65 (^c)</td>
<td>0.575 (^c)</td>
<td>0.12396 (^f)</td>
<td>0.45</td>
</tr>
<tr>
<td>8. H(_2); 3.5</td>
<td>25.65 (^c)</td>
<td>3.54 (^c)</td>
<td>0.35684 (^f)</td>
<td>0.22</td>
</tr>
<tr>
<td>9. H(_2); 2.25</td>
<td>25.65 (^c)</td>
<td>9.60 (^c)</td>
<td>0.64294 (^f)</td>
<td>0.27</td>
</tr>
<tr>
<td>10. H(_2); 1.8</td>
<td>25.65 (^c)</td>
<td>11.85 (^c)</td>
<td>0.73415 (^f)</td>
<td>0.32</td>
</tr>
<tr>
<td>11. H(_2); 1.425</td>
<td>25.65 (^c)</td>
<td>14.00 (^c)</td>
<td>0.79870 (^f)</td>
<td>0.401</td>
</tr>
<tr>
<td>12. C(_2)H(_6); C—C(_w)</td>
<td>46.61 (^d)</td>
<td>26.74 (^d)</td>
<td>0.631 (^e)</td>
<td>1.01</td>
</tr>
<tr>
<td>13. C(_2)H(_6); C—C(_w)</td>
<td>46.61 (^d)</td>
<td>30.31 (^d)</td>
<td>0.691 (^e)</td>
<td>1.01</td>
</tr>
<tr>
<td>14. C(_2)H(_6); C—C(_w)</td>
<td>46.61 (^d)</td>
<td>33.15 (^d)</td>
<td>0.790 (^e)</td>
<td>0.96</td>
</tr>
<tr>
<td>15. C(_2)H(_6); C—C(_w)</td>
<td>46.61 (^d)</td>
<td>36.97 (^d)</td>
<td>0.822 (^e)</td>
<td>0.97</td>
</tr>
<tr>
<td>16. C(_2)H(_6); C—C(_w)</td>
<td>46.61 (^d)</td>
<td>40.33 (^d)</td>
<td>0.873 (^e)</td>
<td>1.00</td>
</tr>
<tr>
<td>17. C(_2)H(_6); C—C(_w)</td>
<td>46.61 (^d)</td>
<td>42.24 (^d)</td>
<td>0.909 (^e)</td>
<td>1.01</td>
</tr>
</tbody>
</table>

\(^a\) kcal/mole.
\(^b\) Ref. 2.
\(^c\) The value at \( R_{0} \) (ref. 9) is used for all \( R \).
\(^d\) The value for C\(^{2+}\) is used from ref. 14.
\(^e\) Ref. 4.
\(^f\) Ref. 15.
\(^g\) \( \epsilon_{ij}^{GVB} = \epsilon_{ij}^{HF} - \Delta \epsilon_{ij} \), where \( \Delta \epsilon_{ij} \) is the drop in energy when orbitals \( i \) and \( j \) are allowed to split. See ref. 13.
\(^h\) W. A. Goddard, III, personal communication.

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\[
\left( S_{ii} = 1 - \chi \frac{\epsilon_{pp}}{2} \right)
\]
so that the PCGVB method can be viewed as an extrapolation of the HF and GVB calculations. Total energies calculated using Eq. 15 are presented in Table 3 for two-electron atoms and in Table 4 for the hydrogen molecule. Our extrapolation is clearly successful; we have reduced the errors in our energy estimates by two orders of magnitude.

A more critical test case for our ability to examine reaction pathways is provided by the hydrogen molecule at geometries other than the equilibrium bond length, \( R_e \). We arrived at Eq. 14 by using the geometric mean approximation and the form of the virial theorem appropriate to equilibrium geometries, and hence this relationship is not necessarily a good approximation at other geometries. However, if our original argument that the GVB pair energies are primarily determined by orbital overlaps is valid, then \( \epsilon_{pp}^{\text{GVB}} \) is simply a scale factor depending upon the nuclear charges and types of orbitals, but not the geometry of the nuclei. Hence, we are tempted to extend the overlap approximation to non-equilibrium geometries through the expression:

\[
\epsilon_{12}^{\text{GVB}}(R) = \frac{\sqrt{2S_{12}(R)}}{1 + S_{12}^{+}(R)} \epsilon_{pp}^{\text{HF}}(R),
\]

for \( R \) not equal to \( R_e \), since Eq. 14 is valid when \( R \) equals \( R_e \). This nicely approximates the observed behavior of the GVB pair energy of \( \text{H}_2 \) as we vary the bondlength (Fig. 3). At large internuclear distances the error in the HF energy becomes very large (3) (Fig. 3). Since this arises from a basic flaw in the HF wavefunction that has nothing to do with dynamic electron correlation (4), it would not be appropriate to use values of \( \epsilon_{pp}^{\text{HF}} \) obtained for large internuclear distances. However, since the HF correlation energy is relatively constant at small \( R \), we could use the value of \( \epsilon_{pp}^{\text{HF}} \) for any value of \( R \) for which the \( \text{H}_2 \) ground state is a closed shell (Fig. 3). We shall use the value of \( \epsilon_{pp}^{\text{HF}} \) at the equilibrium distance, since \( \text{EHF}(R_e) \) will also be available for the polyatomic systems we shall examine later and this value is consistent with our derivation of the overlap approximation. This approximation reproduces the potential energy curve obtained by Kolos and Wolniewicz using lengthy expansions for the wave-function (7), to within 0.4 kcal/mole for all values of \( R \) (Fig. 4).

The observed behavior of this equation suggests that we shall use the value of \( \epsilon_{pp}^{\text{HF}} \) at the equilibrium distance, since it will be available for all the systems we shall examine later and this value is consistent with our derivation of the overlap approximation. This approximation reproduces the potential energy curve obtained by Kolos and Wolniewicz using lengthy expansions for the wave-function (7), to within 0.4 kcal/mole for all values of \( R \) (Fig. 4).

### Table 3. Calculated ground state energies of two electron atoms

<table>
<thead>
<tr>
<th>Method</th>
<th>Atom</th>
<th>( \text{H}^- )</th>
<th>( \text{He} )</th>
<th>( \text{Li}^+ )</th>
<th>( \text{Be}^{++} )</th>
<th>RMS(^2 ) error</th>
</tr>
</thead>
<tbody>
<tr>
<td>HF(^a)</td>
<td>-0.48793</td>
<td>-2.86168</td>
<td>-7.23641</td>
<td>-13.61130</td>
<td>-13.61130</td>
<td>0.02444</td>
</tr>
<tr>
<td>GVB(^b)</td>
<td>-0.513839</td>
<td>-2.87796</td>
<td>-7.251415</td>
<td>-13.62577</td>
<td>-13.62577</td>
<td>0.02528</td>
</tr>
<tr>
<td>PCGVB(^c)</td>
<td>-0.52736</td>
<td>-2.90421</td>
<td>-7.27983</td>
<td>-13.65514</td>
<td>-13.65514</td>
<td>0.00040</td>
</tr>
<tr>
<td>Exact(^d)</td>
<td>-0.527751</td>
<td>-2.903724</td>
<td>-7.279913</td>
<td>-13.65566</td>
<td>-13.65566</td>
<td>—</td>
</tr>
</tbody>
</table>

\(^a\) Ref. 2.
\(^b\) Ref. 4.
\(^c\) Eq. 15.
\(^d\) Ref. 6.

RMS, root mean square.

### Table 4. Calculated and experimental parameters for the hydrogen molecule

<table>
<thead>
<tr>
<th>Property</th>
<th>Method</th>
<th>( R_e ) (au)</th>
<th>E(Re) (au)</th>
<th>Force constant (au)</th>
<th>( D_e ) (kcal/mole)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>HF</td>
<td>1.392(^e)</td>
<td>-1.13357(^b)</td>
<td>0.411(^a)</td>
<td>83.32(^a)</td>
</tr>
<tr>
<td></td>
<td>GVB</td>
<td>1.430(^b)</td>
<td>-1.152319(^b)</td>
<td>0.3447(^c)</td>
<td>95.58(^c)</td>
</tr>
<tr>
<td></td>
<td>Best Ab initio</td>
<td>1.401(^d)</td>
<td>-1.174475(^d)</td>
<td>0.3714(^d)</td>
<td>109.49(^d)</td>
</tr>
<tr>
<td></td>
<td>PCGVB</td>
<td>1.416</td>
<td>-1.17479</td>
<td>0.3691(^e)</td>
<td>109.68</td>
</tr>
<tr>
<td></td>
<td>Experimental</td>
<td>1.400(^e)</td>
<td>-1.174474(^e)</td>
<td>0.37113(^e)</td>
<td>109.49(^e)</td>
</tr>
</tbody>
</table>

\(^a\) Ref. 8.
\(^b\) Ref. 9.
\(^c\) Ref. 10.
\(^d\) Ref. 7.
\(^e\) Using Eq. 16.
\(^f\) Obtained by fitting a parabola to three points.

![Fig. 3](image-url)
Fig. 4. The energy of the hydrogen molecule as a function of the internuclear distance, R. The curves represent the results of Hartree–Fock (8), Generalized Valence Bond (10), and Exact (i.e., converged to within 0.00001 au) (7) calculations. The points represent the results of Pairwise Correlated Generalized Valence Bond Calculations using Eq. 16.

We cannot test the accuracy of the detailed potential energy surface that the PCGVB method gives for molecules with four or more electrons, since no ab initio calculations of comparable accuracy have been performed on even four electron molecules. However, we can compare the drop in energy that is observed when a pair of orbitals is allowed to split (13) with the drop predicted by the overlap approximation for a series of carbon–carbon σ and π bonds (Fig. 5). The dominant role of overlap in the determination of GVB pair energies is again evident. The suggestion that the overlap approximation for GVB pair energies may apply to carbon–carbon bonds at nonequilibrium geometries with the accuracy we have observed for the hydrogen molecule is indeed encouraging.

CONCLUSIONS
The PCGVB method looks very promising as a method for the accurate description of potential energy surfaces for chemical reactions. Calculations on trial systems indicate that the method will provide accurate estimates for excitation energies and for activation energies for chemical reactions.

I am grateful to William A. Goddard, III for providing values of overlap integrals and other parameters from his calculations, and for the many helpful discussions we have had. I am also grateful to Wesleyan University for the support of this research.