10938 J. Am. Chem. Soc. 1993, 115, 10938-10942

The Nature of Multiple Bonds. 2. Significance of the Perfect-Pairing Approximation

Peter A. Schultz† **and Richard P. Messmer***

Contribution from the Department of Physics, University of Pennsylvania, Philadelphia, Pennsylvania 19104, and General Electric Corporate Research and Development, Schenectady, New York 12301

Received December 17, 1992⊗

Abstract: We examine the importance in describing a multiple bond of including non-perfect-pairing spin couplings among the electrons. We describe how to relax the perfect-pairing restriction of the usual strongly orthogonal perfect-pairing approximation to the generalized valence bond method, while rigorously remaining within an independent-particle model that allows an orbital interpretation of the bonding. In calculations on ethylene and the nitrogen molecule, we find that the contribution of non-perfect-pairing spin couplings to the description of multiple bonds is remarkably small and that the perfect-pairing spin restriction is a relatively benign limitation on the wave function, for molecular geometries near the equilibrium geometry.

Introduction

In covalent systems, the strongly orthogonal perfect-pairing (SOPP) generalized valence bond (GVB) method[1] is a natural starting point to discuss the bonding. Unlike the Hartree–Fock method, it provides the flexibility in the wave function necessary to properly dissociate a bond, and further, it maps very closely onto the valence bond interpretational scheme on which so much of our understanding of bonding is based. In systems with two-electron/two-center bonds, coupling of pairs of electrons into singlets is usually a very good approximation; otherwise the Hartree–Fock method, with its closed-shell singlets, would not work as well as it does. For molecules with multiple bonds, however, the case is not so clear. The purpose of this paper is to critically examine the nature of spin coupling in multiple bonds.

One need only consider the simple case of the ethylene molecule illustrated in Figure 1 to appreciate that the PP spin coupling restriction can be a very serious constraint. While coupling of the electrons of the double bond into two perfect-pair singlet bonds may be a reasonable approximation near the equilibrium geometry, it cannot describe the spin coupling in C_2H_4 dissociated into two triplet ground-state CH_2 fragments. There is no reason *a priori* to believe that the contribution of the alternate coupling represented by the fragment limit is not energetically significant near equilibrium, and it must be investigated explicitly via computation.

In this paper[2] we examine the impact of the perfect-pairing approximation in describing multiple bonds, while rigorously retaining an independent-particle (IP) interpretation, the only context in which this question has meaning. We discuss results of two case studies. First we consider the archetypical double-bond molecule, ethylene. In our results, the PP constraint is found to be of little energetic consequence near the equilibrium geometry. This is true whether one adopts a σ,π bond or bent-bond picture. To determine whether this is more generally true for multiple bonds or unique to ethylene, we consider the triple bond in the nitrogen molecule. We obtain a similar outcome and conclude that PP is not a significant restriction on the description of multiple bonds, *near the equilibrium geometry.* This result contradicts conclusions regarding the severity of the PP approximation in describing multiple bonds derived from configuration interaction (CI) studies.[3-5] A misunderstanding of how properly to introduce alternate spin couplings into the treatment of a multiple bond without also introducing elements that make the wave function incompatible with an IP interpretation is the source of this discrepancy. Hence, we begin our presentation with a discussion of this issue. We describe a method for incorporating alternate spin couplings into SOPP-GVB descriptions and compute SO-GVB wave functions.[6] The approach hinges on expanding IP wave functions in terms of conventional CI expansions. To retain the orbital interpretation of the bonding, this expansion must be done carefully. The critical terms leading to confusion are isolated and analyzed.

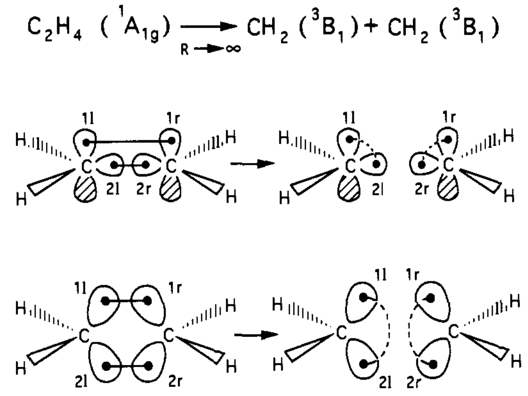

Figure 1. Schematic depiction of the spin state for the IP orbitals of ethylene in the molecular and dissociated limits. Solid line denotes singlet coupling, and dashed line, triplet coupling.

Relaxing the Perfect-Pairing Restriction

To illustrate the need to generalize beyond a perfect-pairing description to treat dissociation of multiple bonds, we begin with ethylene. As illustrated in Figure 1, the perfect-pairing IP description of the bonding near equilibrium consists of two singlet-

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† Present address: Sandia National Laboratories, Division 1421, Albuquerque, NM 87185.

⊗ Abstract published in *Advance ACS Abstracts*, September 15, 1993.

(1) (a) Bobrowicz, F. W.; Goddard, W. A., III. In *Methods in Electronic Structure Theory*; Schaefer, H. F., III, Ed.; Modern Theoretical Chemistry, Vol. 3; Plenum Press: New York, 1977. (b) Bair, R. A.; Goddard, W. A., III; Voter, A. F.; Rappé, A. K.; Yaffe, L. G.; Bobrowicz, F. W.; Wadt, W. R.; Hay, P. J.; Hunt, W. J. GVB2P5 Program (unpublished). (c) See: Bair, R. A. Ph.D. Thesis, Caltech, 1980.

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0002-7863/93/1515-10938$04.00/0

coupled pairs, φ_{1l} and φ_{1r}, and φ_{2l} and φ_{2r}, one orbital of each pair localized on the right and one on the left. Focusing on the double-bond orbitals, this wave function can be written as

$$\Psi(C_2H_4) = \mathcal{A}[\Phi\varphi_{1l}\varphi_{1r}\varphi_{2l}\varphi_{2r}\Theta_1(4)] \qquad (1)$$

where Φ accounts for all electron orbitals outside of those associated with the carbon–carbon double bond and $\Theta_1(4)$ is a four-particle singlet spin eigenfunction corresponding to the perfect pairing of two pairs. The form of the φ_i—σ,π orbitals or bent-bond "Ω" orbitals—is purposely not specified, as the same arguments apply to both, for dissociation into triplet fragments. If the fragments had singlet ground states, however, *e.g.*, $F_2C{=}CF_2 \rightarrow F_2C + CF_2$, one could not describe even qualitatively the dissociation of the molecule within a σ,π bond context. In the dissociated limit of triplet ground-state CH_2 fragments, the two orbitals on the left carbon, σ_{1l} and φ_{2l}, are triplet coupled, as are φ_{1r} and φ_{2r} on the right carbon. The overall spin state remains a singlet, as these two triplets couple to $S = 0$. The wave function for the fragments can be written as

$$\Psi(CH_2 + CH_2) = \mathcal{A}[\Phi\varphi_{1l}\varphi_{2l}\varphi_{1r}\varphi_{2r}\Theta_2(4)] \qquad (2)$$

where $\Theta_2(4)$ is a four-electron singlet spin eigenfunction, distinct from, and orthogonal to, the singlet $\Theta_1(4)$. The forms of these singlet spin eigenfunctions are given explicitly below:

$$\Theta_1(4) = \frac{1}{2}(\alpha\beta - \beta\alpha)(\alpha\beta - \beta\alpha) = \frac{1}{2}(\alpha\beta\alpha\beta - \alpha\beta\beta\alpha - \beta\alpha\alpha\beta + \beta\alpha\beta\alpha) \qquad (3a)$$

$$\Theta_2(4) = \frac{1}{2\sqrt{3}}(\alpha\beta\alpha\beta + \alpha\beta\beta\alpha + \beta\alpha\alpha\beta + \beta\alpha\beta\alpha - 2\alpha\alpha\beta\beta - 2\beta\beta\alpha\alpha) \qquad (3b)$$

These two singlets span the two-dimensional four-electron singlet spin space.

To describe dissociation of the molecule, from near equilibrium as described by the wave function of eq 1, into CH_2 fragments, as described by eq 2, it is convenient to put the orbitals in the same order, exchanging φ_{2l} and φ_{1r} in eq 2, along with the spins associated with them, to arrive at an alternate equivalent representation of the fragment wave function:

$$\Psi(CH_2 + CH_2) = \mathcal{A}\left[\Phi\varphi_{1l}\varphi_{1r}\varphi_{2l}\varphi_{2r}\left\{\frac{\sqrt{3}}{2}\Theta_1 + \frac{1}{2}\Theta_2\right\}\right] \qquad (4)$$

In this representation it can be seen that the alternate, nonbonding spin coupling Θ_2 of the four electrons must be explicitly added to the perfect-pairing coupling

$$\Psi = \mathcal{A}[\Phi\varphi_{1l}\varphi_{1r}\varphi_{2l}\varphi_{2r}\{c_{\theta1}\Theta_1 + c_{\theta2}\Theta_2\}] = c_{\theta1}\Psi_{\theta1} + c_{\theta2}\Psi_{\theta2} \qquad (5)$$

to describe dissociation from the molecular wave function of eq 1 to the fragment wave function of eq 4. At dissociation ($R \rightarrow \infty$), $c_{\theta1}$ and $c_{\theta2}$ will be as given in eq 4. Near equilibrium ($R \approx R_e$), the PP term, $\Psi_{\theta1}$, will presumably dominate.

The SOPP-GVB method is a practical computational scheme because of the fact that there exists a simple transformation from the nonorthogonal interpretational orbital set $\{\varphi_i\}$ into an orthogonal basis set $\{\phi_i\}$, and the SOPP wave function

$$\Psi_{SOPP} = \mathcal{A}[\varphi_{1l}\varphi_{1r}(\alpha\beta - \beta\alpha)\varphi_{2l}\varphi_{2r}(\alpha\beta - \beta\alpha)...\varphi_{Ml}\varphi_{Mr}(\alpha\beta - \beta\alpha)] \qquad (6)$$

can be expanded in a standard multideterminant expansion over an orthogonal basis of 2^N terms:

$$\Psi_{SOPP} = \mathcal{A}[(d_{1b}\phi_{1b}^2 - d_{1a}\phi_{1a}^2)\alpha\beta(d_{2b}\phi_{2b}^2 - d_{2a}\phi_{2a}^2)\alpha\beta...(d_{Mb}\phi_{Mb}^2 - d_{Ma}\phi_{Ma}^2)\alpha\beta] \qquad (7)$$

The d_i's are coefficients trivially related to the singlet pair orbital overlaps, $S_i = \langle\varphi_{il}|\varphi_{ir}\rangle$, and ϕ_{ib} and ϕ_{ia} are bonding and antibonding basis orbitals for each bond. The overlapping interpretational orbitals φ_i are related to the orthogonal basis set orbitals by (neglecting normalization throughout the following discussion)

$$\phi_{ib} = \frac{1}{[2(1 + S_i)]^{1/2}}(\varphi_{il} + \varphi_{ir});\ \phi_{ia} = \frac{1}{[2(1 - S_i)]^{1/2}}(\varphi_{il} - \varphi_{ir}) \qquad (8a)$$

or, conversely,

$$\varphi_{il} = \phi_{ib} + \lambda_i\phi_{ia};\ \varphi_{ir} = \phi_{ib} - \lambda_i\phi_{ia} \qquad (8b)$$

To treat the spin recoupling, the SOPP wave function must be augmented. For the example of C_2H_4, the perfect-pairing term of eq 5, $c_{\theta1}\Psi_{\theta1}$, can be expanded as follows:

$$\Psi_{\theta1} = \mathcal{A}[\Phi\{\phi_{1b}^2\phi_{2b}^2 - \lambda_1^2\phi_{1a}^2\phi_{2b}^2 - \lambda_2^2\phi_{1b}^2\phi_{2a}^2 + \lambda_1^2\lambda_2^2\phi_{1a}^2\phi_{2a}^2\}\alpha\beta\alpha\beta] \qquad (9)$$

The term associated with the alternate coupling, $\Psi_{\theta2}$, is similarly expanded, performing the substitutions of eq 8 to get

$$\Psi_{\theta2} = \mathcal{A}[\Phi\varphi_{1l}\varphi_{1r}\varphi_{2l}\varphi_{2r}\Theta_2] \rightarrow \mathcal{A}[\Phi(\varphi_{1b} + \lambda_1\phi_{1a})(\phi_{1b} - \lambda_1\phi_{1a})(\phi_{2b} + \lambda_2\phi_{2a})(\phi_{2b} - \lambda_2\phi_{2a})\Theta_2] \rightarrow \mathcal{A}[\Phi\phi_{1b}^1\phi_{1a}^1\phi_{2b}^1\phi_{2a}^1\Theta_2] \qquad (10)$$

where the last step is obvious when we note that the character of Θ_2 is to triplet couple the first two, and also the last two orbitals, hence requiring occupation of pairwise orthogonal orbitals.

Adopting the notation $(n_{1b}n_{1a}n_{2b}n_{2a})$ to describe each of the configurations in the CI expansion, n_μ describing the occupation of orbital ϕ_μ in the configuration

$$(n_{1b}n_{1a}n_{2b}n_{2a}) \leftrightarrow \phi_{1b}^{n_{1b}}\phi_{1a}^{n_{1a}}\phi_{2b}^{n_{2b}}\phi_{2a}^{n_{2a}}$$

the CI representation of the SOPP wave function for ethylene, eq 9, is described using four configurations: (2020), (0220), (2002), and (0202). Inspection of eq 10 shows treating the alternate spin coupling requires the term with a (1111) occupation and a Θ_2 spin coupling.

Restricted Configuration Interaction (RCI)

To construct a GVB-RCI wave function[7] for a general molecule, all terms accessible by single excitations [(20) → (11)] within pairs, in addition to the double excitations [(20) → (02)] that describe the SOPP pairs, are added to the SOPP expansion. Given three possible occupations within each pair—(20), (02) from the SOPP, and the new (11)—and M pairs, an RCI expansion consists of 3^M configurations, along with all permissible spin couplings within each spatial configuration, as opposed to the 2^M configurations given by the SOPP expansion.

GVB-RCI expansions contain all the terms necessary to allow for the spin recoupling described above among the orbitals of multiple bonds. It was on the basis of calculations using expansions of this kind[3-5] that it was concluded that PP is a profound restriction on the description of multiple bonds. Looking at C_2F_2, Bauschlicher and Taylor[4] found that self-consistent RCI calculations yield greater than 1 eV in energy lowering with respect to SOPP-GVB calculations. Incidentally, the impact was found to be strongly dependent on the bonding representation. While SOPP-GVB calculations for C_2F_2 favor bent bonds[8] (unlike the case for C_2H_4, *cf.* Table I), the RCI calculation using a σ,π orbital basis is favored by 0.22 eV, amounting to a reversal of 0.47 eV in the comparison of the bonding models. This observation is inconsistent with results in Part 1,[15] which suggest a much smaller importance for the spin coupling. In the discussion below,

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Table I. Total Energies for C_2H_4 and N_2 Using SOPP + RCI Wave Functions[a]

	C_2H_4 (2 pairs)		N_2 (5 pairs)	
wave function	σ,π	Ω	σ,π	Ω
SOPP-GVB	−78.075 36 (0.00)	−78.069 81 (+0.15)	−108.044 80 (0.00)	−108.031 11 (+0.37)
GVB-RCI	−78.089 18 (−0.38)	−78.081 76 (−0.17)	−108.097 95 (−1.45)	−108.079 62 (−0.95)
SO-GVB	−78.077 59 (−0.06)	−78.070 55 (+0.13)	−108.052 40 (−0.21)	−108.034 78 (+0.27)
POL-RCI	−78.087 36 (−0.33)	−78.081 16 (−0.16)	−108.092 24 (−1.29)	−108.076 50 (−0.86)

[a] Total energies in hartree. For explanation of wave functions, see text. Numbers in parentheses are relative energies in eV.

calculations were performed using the geometries and basis sets described in Part 1.

Ethylene Molecule

Applied to the problem of the double bond in the ethylene molecule, the GVB-RCI calculation adds only the (1111) configuration to the SOPP expansion; the (1120)-like configurations generated by the general RCI being excluded by spatial symmetry. The results are listed in Table I. The RCI calculations yield an energy lowering with respect to SOPP results of 0.38 eV for the σ,π description and 0.33 eV for the description using the bent-bond orbital basis. This appears to validate the arguments of Bauschlicher and Taylor,[4] and Carter and Goddard[3,5] with respect to the importance of non-PP spin couplings.

However, examining each of the terms that comprise the GVB-RCI wave function more carefully, we find that the GVB-RCI wave function, in general, *cannot* be rigorously interpreted in a simple bonding context, and the reason relates to the nature of the open-shell term (1111). With four singly occupied orbitals, two distinct singlet spin functions are possible (listed in eq 3), and hence the (1111) configuration contributes two independent components. An independent component, defined by an orbital occupation with a specific spin state, is referred to as a configuration state function (CSF). The term of eq 10 that relaxes the PP restriction of the two-pair SOPP wave function, however, *uses only one of the two spin couplings possible. The perfect-pairing singlet spin coupling,* Θ_1, *of these open-shell orbitals included in the GVB-RCI is incompatible with an independent-particle picture.*

That the (1111)-Θ_1 term included in the GVB-RCI calculations is incompatible with an IP interpretation does not necessarily invalidate the arguments[3-5] regarding the importance of alternate spin couplings. Although in general the SO-GVB wave function requires only a limited subset of the CSFs of the full-GVB-RCI wave function, it may be the case that the RCI does not take advantage of the extra flexibility and, hence, remains a good approximation to an SO-GVB wave function.[9]

To address this question, the RCI calculation for ethylene was repeated, with the modification that the CSF incompatible with an IP interpretation, (1111)-Θ_1, was excluded from the expansion. The results are presented in Table I. The new spin coupling flexibility offered by this wave function, as compared to SOPP-GVB, produces a lowering of less than 0.1 eV for both the σ,π bond model and bent-bond model, demonstrating that non-PP spin coupling has little importance in ethylene.

If not spin recoupling, what is the role of the (1111)-Θ_1 term? This term, $\phi_{1b}\phi_{1a}\phi_{2b}\phi_{2a}\Theta_1$, has a form reminiscent of two SOPP-GVB pairs. Applying formally the same transformation (eq 8) used to generate the orthogonal orbitals from SOPP orbitals yields

$$\phi_{1b}\phi_{1a}\phi_{2b}\phi_{2a}\Theta_1 = \{(\phi_{1b}+\phi_{1a})^2-(\phi_{1b}-\phi_{1a})^2\}\alpha\beta\{(\phi_{2b}+\phi_{2a})^2-(\phi_{2b}-\phi_{2a})^2\}\alpha\beta = \{\varphi_{1l}^2-\varphi_{1r}^2\}\alpha\beta\{\varphi_{2l}^2-\varphi_{2r}^2\}\alpha\beta = \{\varphi_{1l}^2\varphi_{2l}^2-\varphi_{1r}^2\varphi_{2l}^2-\varphi_{1l}^2\varphi_{2r}^2+\varphi_{1r}^2\varphi_{2r}^2\}\alpha\beta\alpha\beta \quad (11)$$

This CSF corresponds to interpair correlation—the polarization of the two electrons of one pair from one side of the bond to the other, while the electrons of the other pair do the same[7]—and cannot be directly interpreted in an IP framework. Incorporating this non-IP term and excluding the (1111)-Θ_2 term that corresponds to the recoupling of the electron spins recovers most of the stabilization (POL-RCI of Table I) of the full-GVB-RCI, and hence *almost the entire stabilization of the GVB-RCI is* attributable *to the non-IP augmentation of the wave function.*

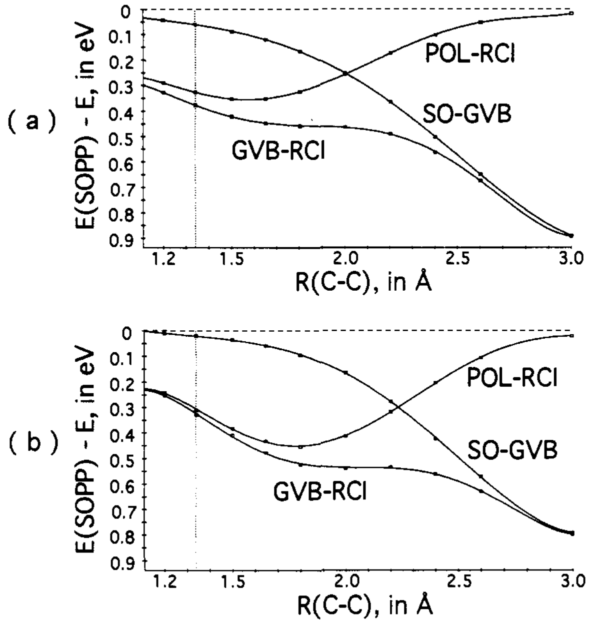

Figure 2. Plots of the energetic stabilization yielded by various extensions (discussed in the text) to the SOPP-GVB wave functions as a function of carbon–carbon separation in ethylene. The plots show the energy lowering with respect to the SOPP-GVB result, in eV, starting with (a) the σ,π bond SOPP-GVB wave function and (b) the bent-bond SOPP-GVB wave function.

As the carbon–carbon distance increases, importance of non-PP spin couplings must also increase in order for dissociation into CH_2 fragments to occur. A series of SOPP and RCI calculations, varying the carbon–carbon distance and keeping hydrogen atoms fixed in relation to the carbons to which they are coordinated, were performed for bent-bond and σ,π bond descriptions. The energetic stabilization with respect to the SOPP-GVB results is plotted in Figure 2. For both bend-bond and σ,π bond references, it is not until a ~50% increase in carbon–carbon bond length that spin recoupling becomes as important as the polarization term. Transition from a polarization-dominated regime to a recoupling-dominated regime occurs over a narrow range of internuclear separation. At greater separation, roughly twice equilibrium, the recoupling is responsible for the entire stabilization given by the RCI wave function. Crossover in the bent-bond calculations occurs at greater separation than in the σ,π bond calculations, and energetic significance of the recoupling lags behind the σ,π bond case. In either, however, at any distance near equilibrium (marked by the vertical line in the plot) non-PP spin pairing in the double bond is not important.

There are a variety of possible reasons for this result: (i) The PP spin coupling is intrinsically dominant at equilibrium geom-

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(9) Just such a situation occurs for the unconstrained CI calculation using the SOPP configurations, with 2^{M-1} degrees of freedom in the CI coefficients, as it results in a wave fucntion that is a close approximation to the SOPP wave function, with only M degrees of freedom among those same coefficients.

etries for multiple bonds. (ii) C_2H_4 is a special case. The splitting between the triplet and singlet states for the CH_2 fragments is relatively small (0.39 eV),[10] and hence preference for a specific fragment state is weak, allowing the PP bonding term to dominate. (iii) Spin recoupling among four electrons constitutes a "forbidden reaction",[11] and hence the lack of alternate couplings is natural for double-bonded systems. Theoretical evidence refutes reason ii. Carter and Goddard established empirically that intrinsic bond energies of carbon—carbon double bonds in XYC=CX′Y′ are independent of the substituents.[12,13] The dissociation fragments CXY they considered have a wide range of carbon on-site singlet–triplet splittings. If reason ii were true, this variation would be reflected in varying contributions of alternate spin couplings to the equilibrium molecular wave function and lead to different intrinsic bond energies. Hence, the question reduces to whether double bonds are specially resistant to alternate couplings or whether the PP spin coupling is intrinsically dominant in all multiple bonds.

Nitrogen Molecule

The N_2 molecule is an ideal system to resolve this issue. It has a triple bond, and the splitting among the states of the dissociated fragments is much larger than that for ethylene. The first excited state of the nitrogen atom is 2.4 eV above the ^4S ground state.[14] The approach used to include alternate spin couplings in the triple bond is analogous to the approach used in the double bond. The difference is that one has six electrons rather than four and hence has five singlet eigenfunctions rather than two.

All five valence pairs were correlated in the SOPP calculations, resulting in three N–N bond pairs and a lone pair on each of the nitrogen atoms. The results of the RCI calculations for the triple bond are presented in Table I. The energetic stabilization offered by this RCI calculation is seen to be many times larger than that found in ethylene, amounting to 1.45 eV using the σ,π bond SOPP orbitals and 1.32 eV using the bent-bond SOPP orbitals.

There are five independent singlets among the six bonding electrons. The SOPP wave functions for the description of the triple bond can be written

$$\Psi_{\mathrm{SOPP}}^{\sigma\pi} = \Psi_{\theta1}^{\sigma\pi} = \mathcal{A}[\Phi\sigma_{\mathrm{l}}\sigma_{\mathrm{r}}\pi_{x\mathrm{l}}\pi_{x\mathrm{r}}\pi_{y\mathrm{l}}\pi_{y\mathrm{r}}\Theta_{\mathrm{PP}}(6)] \quad (12a)$$

$$\Psi_{\mathrm{SOPP}}^{\Omega} = \Psi_{\theta1}^{\Omega} = \mathcal{A}[\Phi\Omega_{1\mathrm{l}}\Omega_{1\mathrm{r}}\Omega_{2\mathrm{l}}\Omega_{2\mathrm{r}}\Omega_{3\mathrm{l}}\Omega_{3\mathrm{r}}\Theta_{\mathrm{PP}}(6)] \quad (12b)$$

describing one spin coupling of the valence bond (VB) orbitals for σ,π bonds and bent-bond (Ω) orbitals. Non-PP spin couplings can be generated by recoupling the electrons taken four at a time, as in eq 5, leaving the remaining pair singlet coupled. This generates three new singlets for each

$$\begin{aligned} \Psi_{\theta2}^{\sigma\pi} &= \mathcal{A}[\Phi\sigma_{\mathrm{l}}\sigma_{\mathrm{r}}\Theta_{\mathrm{PP}}(2)\pi_{x\mathrm{l}}\pi_{x\mathrm{r}}\pi_{y\mathrm{l}}\pi_{y\mathrm{r}}\Theta_2(4)] \\ \Psi_{\theta3}^{\sigma\pi} &= \mathcal{A}[\Phi\pi_{x\mathrm{l}}\pi_{x\mathrm{r}}\Theta_{\mathrm{PP}}(2)\sigma_{\mathrm{l}}\sigma_{\mathrm{r}}\pi_{y\mathrm{l}}\pi_{y\mathrm{r}}\Theta_2(4)] \\ \Psi_{\theta4}^{\sigma\pi} &= \mathcal{A}[\Phi\pi_{y\mathrm{l}}\pi_{y\mathrm{r}}\Theta_{\mathrm{PP}}(2)\sigma_{\mathrm{l}}\sigma_{\mathrm{r}}\pi_{x\mathrm{l}}\pi_{x\mathrm{r}}\Theta_2(4)] \quad (13a) \end{aligned}$$

$$\begin{aligned} \Psi_{\theta2}^{\Omega} &= \mathcal{A}[\Phi\Omega_{1\mathrm{l}}\Omega_{1\mathrm{r}}\Theta_{\mathrm{PP}}(2)\Omega_{2\mathrm{l}}\Omega_{2\mathrm{r}}\Omega_{3\mathrm{l}}\Omega_{3\mathrm{r}}\Theta_2(4)] \\ \Psi_{\theta3}^{\Omega} &= \mathcal{A}[\Phi\Omega_{2\mathrm{l}}\Omega_{2\mathrm{r}}\Theta_{\mathrm{PP}}(2)\Omega_{1\mathrm{l}}\Omega_{1\mathrm{r}}\Omega_{3\mathrm{l}}\Omega_{3\mathrm{r}}\Theta_2(4)] \\ \Psi_{\theta4}^{\Omega} &= \mathcal{A}[\Phi\Omega_{3\mathrm{l}}\Omega_{3\mathrm{r}}\Theta_{\mathrm{PP}}(2)\Omega_{1\mathrm{l}}\Omega_{1\mathrm{r}}\Omega_{2\mathrm{l}}\Omega_{2\mathrm{r}}\Theta_2(4)] \quad (13b) \end{aligned}$$

for a total of four singlets for each bonding representation. In both cases, the fifth and final spin singlet results in a spatial symmetry for the total wave function incompatible with the ground state.

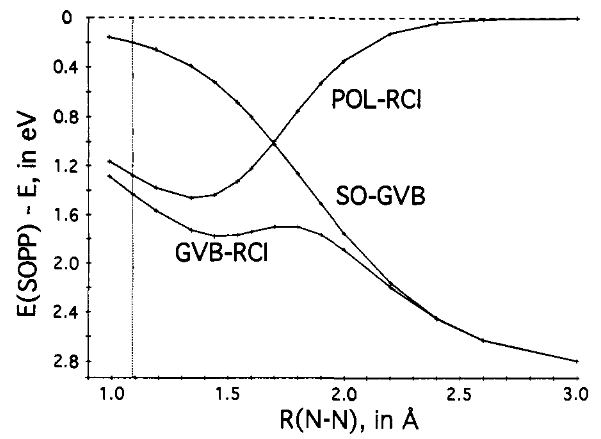

Figure 3. Plot of the energetic stabilization yielded by various extensions (discussed in the text) to the σ,π bond SOPP-GVB wave function as a function of nitrogen–nitrogen separation. The plot shows the energy lowering with respect to the SOPP-GVB calculation, in eV.

In relaxing the PP spin restriction, the wave function can be written as a sum of four terms:

$$\Psi_{\mathrm{SOGVB}} = c_{\theta1}\Psi_{\theta1} + c_{\theta2}\Psi_{\theta2} + c_{\theta3}\Psi_{\theta3} + c_{\theta4}\Psi_{\theta4} \quad (14)$$

Examining the non-PP terms, we find that, just as in the case of the double bond, the recoupling involves (1111)-like configurations, using only the $\Theta_2(4)$ spin eigenfunction (*cf.* eq 10). These SO-GVB results, presented in Table I, show that only a small fraction of the total RCI energy lowering is due to lifting the PP spin coupling restriction. The additional spin freedom results in only 0.21-eV stabilization for the σ,π bond wave function and 0.10 eV for the bent-bond wave function.

The majority of the stabilization of the RCI, just as for the double-bond case, results from the simultaneous polarization of electrons in different bonds. The calculations (POL-RCI) which include the IP-incompatible CSFs but exclude the CSFs required to accomplish the SO-GVB recoupling yield 89% of the total GVB-RCI($\sigma\pi$) and 94% of the GVB-RCI(Ω) stabilization.

The dependence of the stabilization of the various wave functions with respect to the SOPP-GVB reference as a function of internuclear separation is plotted in Figure 3. Only the σ,π bond case is considered; the contribution of the recoupling is maximized in this description, and hence it represents the bound of its importance. As for ethylene, the bonding is well within the polarization-dominated regime near the equilibrium distance (denoted by the vertical line). Spin flexibility becomes more important as the distance increases. With an ~50% increase in internuclear separation, it is energetically more important than the polarization. At roughly twice the equilibrium length, the stabilization of the RCI is almost entirely attributable to spin recoupling. In its general features, the functional dependence of the RCI stabilization is the same as that observed for ethylene.

Discussion and Conclusions

In application to multiple bonds, it is found that the non-PP spin flexibility is unimportant at near equilibrium geometries; the perfect-pairing spin coupling describes the ground state very well. Given that the strong-orthogonality restriction between pairs was imposed throughout, the fragment high-spin couplings had the greatest possible opportunity to be expressed in the ground-state wave function; the on-site atomic-like orbitals are automatically orthogonal by construction and therefore ideally suited to multiplet pairing. That this did not occur indicates that the perfect-pairing constraint is not significant. This constitutes the principal conclusion to be derived from the above results: *in*

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examining the ground-state electronic structure, non-PP spin-coupling terms only become important well beyond the region of the equilibrium geometry.

In hindsight, that perfect pairing is a good approximation is not surprising. The inclusion of alternate pairings involves building triplet character into the bond pairs of the SOPP-GVB wave function. Near equilibrium, however, these bond pair orbitals have large overlaps, and to triplet couple them requires making them orthogonal in order to satisfy Pauli's principle, with a correspondingly high energy cost. For C_2H_4, the overlaps are 0.88 and 0.65 for the σ and π bond pair orbitals, respectively, and 0.81 for the bent-bond pair orbitals. Similar values result for N_2. As the molecule dissociates, the bonding overlaps become smaller, this cost decreases, and the spin coupling among the bond orbitals changes toward the spin coupling of the fragments.

The GVB-RCI wave function is clearly a poor approximation to an SO-GVB wave function. While the configurations added in the RCI expansion do include those necessary to allow the relaxation of the PP restriction on the SOPP wave function, the principal correlation effect added cannot be interpreted with an IP framework but instead involves interpair correlation effects. Thus the use of full-GVB-RCI wave functions, as in the study by Bauschlicher and Taylor[4] on C_2F_2, renders any conclusions regarding qualitative bonding description impossible. The incompatibility with an IP picture, however, can easily be corrected by restricting the RCI expansion to only those CSFs necessary to describe the spin recoupling of SO-GVB. In essence, the approach we describe reproduces the spin-optimized-GVB method described by Bobrowicz.[6]

Acknowledgment. This work was supported in part by the National Science Foundation MRL Program under Grant DMR-8519059 at the Laboratory for Research on the Structure of Matter, University of Pennsylvania.