J. Am. Chem. Soc. **1993,** *115,* 10925–10937

The Nature of Multiple Bonds. 1. σ,π Bonds *vs* Bent Bonds, a Computational Survey

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 nature of multiple bonds within an independent-particle picture, climbing a hierarchy of approximations to the full generalized valence bond (GVB) description, the most general wave functions for which an independent particle interpretation of the bonding is possible. We begin with a systematic computational survey of molecules with multiple bonds, comparing σ,π and bent bond descriptions, using the strongly orthogonal perfect-pairing (SOPP) approximation to the GVB method. Although in several cases the bent-bond model is energetically favored using SOPP-GVB wave functions, in a number of other cases the usually accepted σ,π bond description is energetically favored. In order to obtain a definitive answer to the long-standing question of the better orbital description of the bonding, we conclude that the full GVB theory must be employed without restrictions. We outline a procedure by which generalized valence bond wave functions can be rigorously obtained without spin coupling or orbital orthogonality constraints and apply it to a sequence of molecules directed toward finding the best qualitative description of the bonding in multiple bonds: σ,π bonds or bent bonds? Our calculations lend support to Slater's and Pauling's sixty-year-old conjectures, finding the bent bond description *energetically* superior to the symmetry-restricted σ,π bond representation in the theoretical limit of wave functions able to meaningfully address this question.

Introduction

Much of our understanding of the electronic ground states of molecules and solids is couched in the language of bonds, lone pairs, and dangling orbitals—useful qualitative concepts deduced by experimentalists over many years. In large measure this is because of the high degree of transferability that the properties which can be associated with these idealized structures have over a wide spectrum of physical environments. For instance, the idealized C–H bond can be associated with an equilibrium internuclear separation of 1.08 Å, an intrinsic bond energy of 4.3 eV, and a force constant of 5×10^5 dyn/cm, and the idealized C–C single bond, with 1.54 Å, 3.6 eV, and 4.5×10^5 dyn/cm, values[1] that can be used to predict to a high degree of accuracy the properties of such diverse systems as methane and the hydrogenated diamond surface. Furthermore, the advantage of structural chemistry—the ability to rationalize and predict geometrical parameters—is readily incorporated into the same context using the principle that hybrid orbitals dictate the bonding. Taken together, these concepts define the valence bond interpretational scheme and offer a wide variety of tools with which to analyze and predict electronic structure and bonding. The utility of these simply physically motivated concepts has been given its most powerful articulation by Pauling in his *The Nature of the Chemical Bond.*[2]

Even in simple covalently bonded systems, however, basic issues have not been resolved within a local bonding context. Adopting the two-electron two-center bond as a basic structural element, J. C. Slater[3] and Linus Pauling[4] pointed out an ambiguity in how to represent multiple bonds. Considering the case of the ethylene molecule, the archetypical double-bonded system, for example, the bond between the carbon atoms is usually described as in Figure 1(a): in terms of a σ bond, with two electrons distributed along the internuclear axis, and a π bond, with two more electrons distributed above and below the molecular plane with a node in that plane. However, Slater and Pauling pointed out that the bonding can be depicted in another fashion. This alternate bonding description, shown in Figure 1(b), consists of two *bent* bonds, with one pair of electrons above and the other pair below the molecular plane. It is this issue, the best qualitative way to describe the multiple bond, that is the subject of this paper.

It is legitimate to ask whether the σ,π bond *vs* bent bond question is even worthwhile, in a practical or even a pedagogical sense, or if instead the four-electron, or six-electron, two-center bond ought not be enshrined as a basic element in the valence bond interpretational scheme without attempting a decomposition into more basic elements. No experiment can possibly distinguish between a σ,π double bond and double bent bonds in any system, and therefore neither can be proven to be "right" in an absolute sense; both are approximate descriptions. The potential value of making any such distinction lies in the utility, general applicability, and economy of the concepts which emerge, and whether one variant is superior to another in describing properties determined by the electronic structure.

Chemists of the previous century devised a very successful structural chemistry based upon interlocking tetrahedra, and in such a representation of the CO_2 molecule, shown in Figure 2(a), double bent bonds between the central carbon atom and the terminal oxygen atoms are readily apparent. Adopting the bonding framework defined by the bent bond idea, Pauling had great success in such semiempirical applications as rationalizing bond lengths and bond angles in molecules containing multiple bonds. When multiple bonds are described as equivalent bent bonds, it is possible to rationalize equilibrium carbon–carbon distances in going from single to double to triple bonds by postulating that the distance for any one bond is constant and that bonds describe arcs between atoms, with the initial directions of the bonds at tetrahedral angles. This simple prescription yields predictions for the ethylene and acetylene C–C separation within 0.02 Å of the experimental values.[2] No analogous prescription for understanding these distances within the σ,π bond context

---

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

® Abstract published in *Advance ACS Abstracts,* October 1, 1993.

[1] Cottrell, T. L. *The Strengths of Chemical Bonds*; Butterworths: London, 1958.

[2] Pauling, L. *The Nature of the Chemical Bond*, 3rd ed.; Cornell University Press: Ithaca, NY, 1960.

[3] Slater, J. C. *Phys. Rev.* **1931**, *37*, 481.

[4] Pauling, L. *J. Am. Chem. Soc.* **1931**, *53*, 1367.

0002-7863/93/1515-10925$04.00/0 © 1993 American Chemical Society

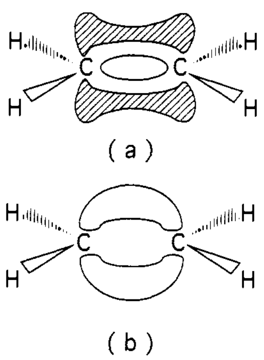

Figure 1. Schematic depictions of qualitative bonding descriptions for the double bond in ethylene: (a) σ,π bond representation; (b) equivalent bent-bond representation.

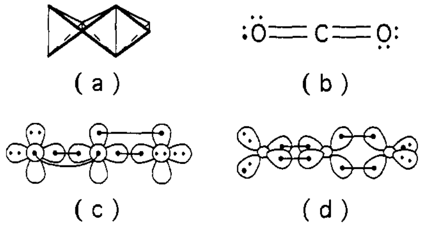

Figure 2. Schematic depictions of the bonding in the carbon dioxide molecule: (a) classical model based on interlocking tetrahedra; (b) Lewis diagram; (c) σ,π bond IP model; (d) bent-bond IP model.

exists. Additionally, the bond angles of ligands on the atoms involved in multiple bonds are frequently well accounted for using similar simple assumptions.[2] For several qualitative applications then, there is a useful decomposition to be made and there is arguably an advantage to be derived from using the perspective of a bent bond framework over a σ,π bond framework. Furthermore, understanding the qualitative character of the important electronic correlation effects can serve as an invaluable aid in constructing effective quantitative calculations. For example, as we shall describe in Part 2,[59] the σ,π bond description cannot even qualitatively describe the dissociation of many multiple-bond systems while the bend-bond description can. Observations such as this can delineate the minimum characteristics of effective approximations for describing potential surfaces.[5,6]

Despite its great conceptual utility, the bent-bond picture has not had much computational support until recently. Using the strongly orthogonal perfect-pairing (SOPP) approximation to the generalized valence bond (GVB) wave function,[7] a method due to Goddard and co-workers,[8] we have found previously that molecules such as carbon dioxide with its double bonds,[9] difluoroacetylene with its triple bond,[10] and the benzene ring, C_6H_6, with its conjugated double bonds[11] are all better described in terms of the equivalent bond or "Ω bond" representation[9] rather than the σ,π bond representation. Other calculations by Palke found bent bonds in ethylene.[12] Together, these studies provided the first quantitative evidence that bent bond descriptions are energetically favored over σ,π bond alternatives, and reopened the question of the better qualitative bonding model. The question is whether bent bonds are a general result or whether these molecules represent isolated exceptions.

In this first paper,[13] we present results of a comprehensive study to systematically examine the relative merits of the σ,π bond and the bent-bond model for a broad selection of molecules with multiple bonds, using correlated *ab initio* wave functions constrained to be rigorously interpretable within an independent-particle (IP) model, *i.e.*, that can be rigorously associated with specific orbital-based bonding descriptions and hence can meaningfully compare the relative merits of different bonding models. For each molecule, we calculate the best wave functions for *both* bonding descriptions and compare the results. The variational principle determines the preferred bonding model: the bonding representation giving the lowest calculated total energy is deemed the better description of the bonding. It is not the purpose of this exercise to describe a more numerically rigorous means to compute molecular properties for molecules with multiple bonds. Much of the electronic correlation energy in multiple bonds is not describable in an IP picture. Approaches such as those using complete active space (CAS) wave functions[14] or the "correlation-consistent" configuration interaction scheme of Carter and Goddard[5] provide more accurate numerical treatments for multiple bonds but *cannot speak to the relative merits of different bonding models*; *only IP wave functions can meaningfully compare different bonding descriptions*. We will discuss the conditions that must be satisfied for a wave function to be IP interpretable and perform calculations for multiple bonds throughout the hierarchy of resultant approximations, culminating in the most general IP wave function: the full generalized valence bond (GVB) wave function.[7]

We begin this paper with a discussion of the hierarchy of IP wave functions with which it is possible to compare different bonding descriptions. The next section describes previous work that has been directed toward elucidating the nature of multiple bonds and presents the results of our systematic calculational survey of multiply-bonded molecules within the SOPP approximation to the GVB wave functions. The outcome of our SOPP calculations is mixed, more often than not in conflict with the bent-bond model. Furthermore, restrictions on the SOPP wave functions have been identified as possible sources of biases in the bonding comparisons.[12,15-17] In order to resolve the question of whether bent bonds or σ,π bonds are the better model to describe multiple bonds, we describe a procedure[13] by which self-consistent full GVB wave functions, without any restrictions, for the electronic structure can be generated, using existing quantum chemistry codes. We take this method and apply it to a sampling of small molecules with multiple bonds, including ethylene and acetylene. Our results yield bent bonds as the favored bonding description, showing that the σ,π bond descriptions of multiple bonds are artifacts of approximations to the full independent-particle equations. A brief discussion and our conclusions are presented in the final section.

Hierarchy of Independent-Particle Interpretable Wave Functions

The question of the "better" bonding model only has meaning within an independent-particle picture. In other words, one must be able to write the total wave function as

$$\Psi_{IP} = \mathcal{A}[\varphi_1(r_1)\varphi_2(r_2)\ldots\varphi_N(r_N)\Theta\{N\}] \qquad (1)$$

where the φ_i are spatial orbitals, each occupied by exactly one

---

(5) Carter, E. A.; Goddard, W. A., III. *J. Chem. Phys.* **1988**, *88*, 3132.

(6) Murphy, R. B.; Messmer, R. P. *J. Chem. Phys.* **1992**, *97*, 4170.

(7) Ladner, R. C.; Goddard, W. A., III. *J. Chem. Phys.* **1969**, *51*, 1073.

(8) (a) 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). (b) See: Bair, R. A. Ph.D. Thesis, Caltech, 1980.

(9) Messmer, R. P.; Schultz, P. A.; Tatar, R. C.; Freund, H.-J. *Chem. Phys. Lett.* **1986**, *126*, 176.

(10) Messmer, R. P.; Schultz, P. A. *Phys. Rev. Lett.* **1986**, *57*, 2653.

(11) Schultz, P. A.; Messmer, R. P. *Phys. Rev. Lett.* **1987**, *58*, 2416.

(12) Palke, W. E. *J. Am. Chem. Soc.* **1986**, *108*, 6543.

(13) A more comprehensive description of the work presented here appears in: Schultz, P. A. Ph.D. Thesis, University of Pennsylvania, 1988.

(14) (a) Ruedenberg, K.; Sundberg, K. R. In *Quantum Science*; Calais, J. L., Goscinski, O., Linderberg, J., Ohrn, Y., Eds.; Plenum Press: New York, 1976; p 505. (b) Roos, B. O.; Taylor, P. R.; Siegbahn, P. E. M. *Chem. Phys.* **1980**, *48*, 157. (c) Siegbahn, P. E. M.; Almlöf, J.; Heiberg, A.; Roos, B. O. *J. Chem. Phys.* **1981**, *74*, 2384. (d) Ruedenberg, K.; Schmidt, M. W.; Gilbert, M. M.; Elbert, S. T. *Chem. Phys.* **1982**, *71*, 41.

(15) Gerratt, J.; Raimondi, M.; Cooper, D. L. *Nature* **1987**, *329*, 492.

(16) Bauschlicher, C. W.; Taylor, P. R. *Phys. Rev. Lett.* **1988**, *60*, 859.

(17) Carter, E. A.; Goddard, W. A., III. *J. Am. Chem. Soc.* **1988**, *110*, 4077.

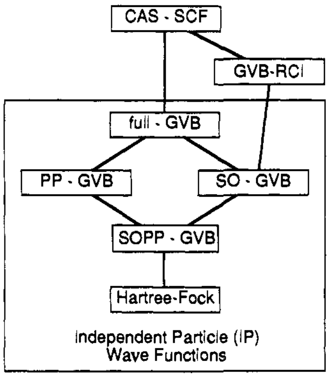

Figure 3. Hierarchy of wave functions. The wave functions within the box can be interpreted within an IP orbital picture. The CAS-SCF and RCI wave functions lie outside an IP interpretation but contain the full-GVB and SO-GVB descriptions as special cases, respectively.

electron, and $\Theta\{N\}$ is an N-electron spin eigenfunction. A wave function that cannot be written in this form *cannot* be rigorously interpreted within an IP picture; hence, it cannot be associated with a simple bonding picture and therefore cannot be used to compare different bonding models. It is in this representation of the wave function, in terms of the interpretational orbitals φ_i, that the physical interpretation of the bonding is made. A schematic depiction of the hierarchy of wave functions used in this series is shown in Figure 3. Those enclosed within the box correspond to the set of approximations interpretable within an IP model.

In the most general wave function within the IP context of eq 1, the spatial forms of each of the singly occupied orbitals φ_i, and the spin couplings among them Θ, are determined variationally without any restrictions on the orbital overlaps or spin couplings. This is the full generalized valence bond (GVB) wave function of Ladner and Goddard.[7] The "spin-coupled" wave function of Gerratt and Lipscomb[18] is identical to this expression. Imposing constraints on this wave function yields a more tractable computational method. First, the spin function Θ is assumed to be well approximated by

$$\Theta\{N\} \approx \Theta_{PP}\{N\} = (\alpha(1)\beta(2) - \beta(1)\alpha(2))(\alpha(3)\beta(4) - \beta(3)\alpha(4)) \ldots \quad (2)$$

where pairs of orbitals are singlet coupled. This constitutes the perfect-pairing (PP) approximation, leading to

$$\Psi_{PP} = \mathcal{A}[\varphi_{1\mu}\varphi_{1\nu}(\alpha\beta - \beta\alpha)\varphi_{2\mu}\varphi_{2\nu}(\alpha\beta - \beta\alpha) \ldots \varphi_{M\mu}\varphi_{M\nu}(\alpha\beta - \beta\alpha)] \quad (3)$$

A second constraint further simplifies the equations. While the orbitals $\varphi_{i\mu}$, $\varphi_{i\nu}$ within each pair continue to be permitted a variationally determined overlap, orbitals in different pairs are constrained to be orthogonal

$$\langle\varphi_{i\mu}|\varphi_{j\nu}\rangle = 0, \quad i \neq j; \quad \text{for arbitrary } \mu \text{ and } \nu \quad (4)$$

the so-called strong orthogonality (SO) condition. The two constraints defined by eq 2 and eq 4, first suggested[19] in 1953 and later implemented by Goddard and co-workers[8,20–22] in the early 1970s, led to a practical computational scheme denoted here as SOPP-GVB.[23] Observe that one final constraint, forcing the orbitals within a pair to be the same

$$\langle\varphi_{i\mu}|\varphi_{i\nu}\rangle = 1 \quad (5)$$

yields a molecular orbital (MO) wave function

$$\Psi = \mathcal{A}[\phi_1\phi_1\alpha\beta\phi_2\phi_2\alpha\beta\ldots\phi_M\phi_M\alpha\beta] \quad (6)$$

Hence MO wave functions are IP wave functions also, the lowest in the IP hierarchy. Yet while the MO wave functions are invariant to changes in the occupied orbitals related by unitary transformations,[24] the same is not true of the more general IP wave functions. Changing the orbitals in any way changes the energy of a GVB wave function. In addition, experience has demonstrated that the interpretational orbitals of the IP wave functions in the GVB family usually take on forms readily associated with the idealized hybrid orbital constructs of the valence bond interpretational scheme. As a consequence, wave functions associated with different bonding models will have variationally distinct energies. These general IP wave functions can, therefore, meaningfully test the more appropriate bonding model, *i.e.* calculate the variationally best wave functions corresponding to the bonding models and compare the computed energies.

In addition, we use calculations incorporating chemical resonance of different valence bond structures, or "structure interaction" (SI)—by analogy to the configuration interaction (CI) that is based on different orbital configurations that are generated from molecular orbital theory. We compute the energetics of the SI wave functions

$$\Psi_{SI} = c_A\Psi_A + c_B\Psi_B + \ldots \quad (7)$$

with IP wave functions Ψ_I corresponding to different bonding descriptions. While not strictly interpretable within an IP picture, the SI wave function is describable in terms of an IP + resonance picture and the bonding is analyzed in terms of the orbitals comprising the components Ψ_I.

All wave functions are expandable in terms of a conventional CI expansion over an orthogonal orbital basis set, including the IP wave functions described above. The converse is not true; in general, a CI expansion cannot be rendered in an IP picture. Complete active space self-consistent field (CAS-SCF) and restricted-CI (RCI) wave functions are commonly used CI expansions that have full-GVB and SO-GVB as special cases if specific relationships among the CI coefficients are satisfied, but in general are not amenable to an orbital interpretation.

Calculational Details

The calculations which follow involve wave functions throughout this hierarchy of IP interpretable wave functions. Hartree–Fock and SOPP-GVB calculations employ the GVB2P5 program.[8] Core electrons do not play a role in the bonding; they are treated as doubly-occupied closed-shell orbitals and ignored in any following discussion. Higher level GVB calculations employ a self-consistent method based on a constrained CI approach maintaining interpretability within an IP picture,[13] to be described in more detail below. In these calculations only the orbitals associated with the multiple bonds are explicitly correlated. The remainder of the electrons are treated in doubly-occupied orbitals. For PP-GVB and full-GVB wave functions, the calculations were further simplified by limiting the 1s core orbitals to the spatial forms computed in the lower level SOPP-GVB calculations.[25]

---

[18] Gerratt, J.; Lipscomb, W. N. *Proc. Natl. Acad. Sci. U.S.A.* **1968**, *59*, 332.

[19] Hurley, A. C.; Lennard-Jones, J. E.; Pople, J. A. *Proc. R. Soc. London* **1953**, *A220*, 446.

[20] Goddard, W. A., III; Dunning, T. H., Jr.; Hunt, W. J.; Hay, P. J. *Acc. Chem. Res.* **1973**, *6*, 368.

[21] 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.

[22] Hunt, W. J.; Hay, P. J.; Goddard, W. A., III. *J. Chem. Phys.* **1972**, *57*, 738.

[23] This method was originally christened with the unfortunate nomenclature of "GVP-PP"—unfortunate in the sense that it fails to make the SO condition explicit. For our purpose, this is a critical distinction and we will use the more precise nomenclature. In addition, the general case will usually be referred to as full-GVB to differentiate it from its various approximations.

[24] Fock, V. *Z. Phys.* **1930**, *61*, 126.

[25] In test calculations, allowing the spatial forms of the core orbitals to optimize in the SCF calculations was found to have little effect on the results.

The structure interaction calculations use our implementation of the resonating-GVB method of Voter and Goddard.[26] To the extent possible, the experimental geometry was used in the molecular calculations, data for diatomics being obtained from Huber and Herzberg[27] and those for polyatomics from Herzberg.[28] Unless otherwise noted, valence double-ζ basis sets, *e.g.*, 9s5p contracted to 3s2p for first-row atoms and 4s contracted to 2s for hydrogen,[29] plus polarization d-functions on first-row atoms [ζ = 0.75 (C), 0.80 (N), 0.85 (O), and 0 (F)] were used. The silicon calculations used an effective potential.[30]

Theoretical Background: Bent Bonds *vs* σ,π Bonds

Many early computational investigations took advantage of the invariance of the mean-field wave function to unitary transformations among the occupied orbitals[24] to examine the relative merits of different bonding descriptions for multiple bonds. Perhaps the most successful variant of the many localized molecular orbital (LMO) methods is the orbital procedure first suggested by Lennard-Jones and Hall[31] and later implemented by Edmiston and Ruedenberg (ER).[32] The first application of LMOs directed toward multiple bonds was the calculation of Foster and Boys on the formaldehyde molecule[33] using their principle of exclusive orbitals. Their results were in accord with the ideas of Slater and Pauling, and this general result of bent bonds or "banana bonds", as they are colloquially referred to,[34] was to be repeatedly obtained throughout the next decade. Using the ER procedure, Kaldor found bent bonds in the double bond of ethylene and in the triple bond of acetylene.[35] This result was confirmed later in a more comprehensive study,[36] in which the concept of $\sigma-\pi$ separability was examined in a variety of molecules and found to be lacking.

The same orbital invariance which made localized molecular orbital procedures possible, however, also rendered them rather arbitrary, a problem most forcefully demonstrated by von Niessen.[37] The results of different localization procedures for C_2, N_2, and CO were qualitatively inconsistent with one another, one prescription might yield bent bonds, another, σ,π bonds, and a third, orbitals not compatible with any classical bonding description. The "better" description is primarily a matter of taste—the σ,π bond and bent-bond MO descriptions have identical energies.

Until recently, few calculations incorporating electronic correlation effects were directed toward the question of bent bonds. Perhaps the first was a crude valence bond calculation for ethylene by Penney[38] in 1934, in which it was estimated that σ,π bonds would be favored over bent bonds by a large margin. Using σ,π and bent-bond orbital bases in correlated calculations, Klessinger concluded a σ,π orbital basis was better for describing the multiple bonds than an equivalent bent-bond orbital basis for CO and N_2,[39] and ethylene and acetylene.[40] These calculations, however, were not self-consistent and, furthermore, did not use IP wave functions. The first correlated study to satisfy both these conditions was SOPP-GVB calculations for ethylene and acetylene[41] in 1972, yielding σ,π bonds for both molecules. Bent-bond solutions were not obtained for comparison, but a significant lowering with respect to the SOPP energy obtained upon doing a CI among the six orbitals describing the triple bond in acetylene was cited as indicative that "some sort of banana-like description may be appropriate" in that case.[41] Nonetheless, while a majority of LMO studies found that the aesthetically and intuitively appealing sp^3-derived bent-bond description was obtained for most multiple bonds, the few studies introducing electronic correlation into the wave function found the opposite, leading to σ,π bond descriptions. These results were interpreted as an affirmation of the σ,π bond model, and a systematic investigation of the question was not undertaken.

SOPP-GVB Calculations: Bent Bonds *vs* σ,π Bonds

In 1986, two independent studies emerged simultaneously that reopened the question of the viability of the bent-bond model. SOPP-GVB calculations for CO_2 found the bent-bond model strongly preferred to the σ,π model,[9] and an approximately variational calculation for ethylene relaxing the SO condition[12] found bent bonds. Since this "discovery" of bent bonds, they have also been found to be the favored bonding mode for CO_2^-, CO_3^-, and CO_3^{2-} at the SOPP level of approximation,[42] for the double bonds in $H_2Si{=}SiH_2$ and $F_2C{=}CF_2$,[43] and for some hypervalent molecules.[44] Previously, only a few molecules had been looked at with an eye toward testing the bent-bond hypothesis, and with the exception of Penney's crude estimates for ethylene,[38] none had compared IP wave functions for *both* bonding models. A more systematic approach to this question now seems appropriate. Hence, we have performed SOPP-GVB calculations for a broad selection of small molecules containing multiple bonds, obtaining wave functions corresponding to both bonding models. Table I catalogs the results.

The first results yielding a bent-bond description as the variational solution were for the CO_2 molecule.[9] The essence of the classical description is captured in the Lewis diagram of Figure 2(b): double bonds between the carbon and the oxygen atoms, and two lone pairs on each oxygen. Within the σ,π bond model, each double bond is made up of a σ bond and a π bond, as schematically illustrated in Figure 2(c). When orbital symmetry restrictions are relaxed, however, SOPP calculations with eight perfect pairs among the 16 valence electrons yield a wave function with an energy 0.31 eV lower, whose interpretational orbitals φ_i take on forms described in the schematic illustration of Figure 2(d). Both double bonds become equivalent bent-bond pairs, with two sets of lone-pair orbitals on each oxygen atom, also bent. That a single-bonding structure lacks the full symmetry of the electronic ground state is remedied classically by invoking the concept of chemical resonance. A total description consisting of (at least) two bonding structures, I + I′, has the correct symmetry where the bonding structure, denoted I, is taken together with a second structure, denoted I′, obtained by a 90° rotation about the molecular axis. Quantum mechanically, the SOPP-

---

(26) (a) Voter, A. F.; Goddard, W. A., III. *Chem. Phys.* **1981**, *57*, 253. (b) Voter, A. F. Ph.D. Thesis, Caltech, 1982.

(27) Huber, K. P.; Herzberg, G. *Constants of Diatomic Molecules*; Molecular Spectra and Molecular Structure, Vol. 4; Van Nostrand: New York, 1979.

(28) Herzberg, G. In *Electronic Spectra of Polyatomic Molecules*; Van Nostrand: Princeton, 1966.

(29) Dunning, T. H., Jr.; Hay, P. J. In *Methods in Electronic Structure Theory*; Schaefer, H. F., III, Ed.; Modern Theoretical Chemistry, Vol. 3; Plenum Press: New York, 1977.

(30) Rappé, A. K.; Smedley, T. A.; Goddard, W. A., III. *J. Phys. Chem.* **1981**, *85*, 1662.

(31) Lennard-Jones, J. E.; Pople, J. A. *Proc. R. Soc. London* **1950**, *A202*, 166.

(32) Edmiston, C.; Ruedenberg, K. *Rev. Mod. Phys.* **1963**, *35*, 457.

(33) (a) Boys, S. F. *Rev. Mod. Phys.* **1960**, *32*, 296. (b) Foster, J. M.; Boys, S. F. *Rev. Mod. Phys.* **1950**, *32*, 300.

(34) Coulson, C. A. *Valence*; Oxford University Press: London, 1961.

(35) Kaldor, U. *J. Chem. Phys.* **1967**, *46*, 1981.

(36) Newton, M. D.; Switkes, E.; Lipscomb, W. N. *J. Chem. Phys.* **1970**, *53*, 2645.

(37) (a) von Niessen, W. *Theor. Chim. Acta (Berlin)* **1972**, *27*, 9; (b) **1973**, *29*, 29.

(38) Penney, W. G. *Proc. R. Soc. London* **1934**, *A144*, 166.

(39) Klessinger, M. *Int. J. Chem. Phys.* **1967**, *46*, 3261.

(40) Klessinger, M. *Int. J. Quantum Chem.* **1970**, *4*, 191.

(41) Hay, P. J.; Hunt, W. J.; Goddard, W. A., III. *J. Am. Chem. Soc.* **1972**, *94*, 8293.

(42) Freund, H.-J.; Messmer, R. P. *Surf. Sci.* **1986**, *172*, 1.

(43) Goddard, W. A., III. As cited in ref 12.

(44) (a) Patterson, C. H.; Messmer, R. P. *J. Am. Chem. Soc.* **1990**, *112*, 4138. (b) Messmer, R. P. *J. Am. Chem. Soc.* **1991**, *113*, 433.

(45) Bieri, G.; Heilbronner, E.; Stadelmann, J.-H.; Vogt, J.; von Niessen, W. *J. Am. Chem. Soc.* **1977**, *99*, 6832.

(46) *Landolt-Boornstein Tables: Numerical Data and Functional Relationships in Science and Technology*; New Series Vol. II/7; Springer-Verlag: Berlin, 1976.

(47) Lischka, H.; Kohler, H. *Chem. Phys. Lett.* **1982**, *85*, 467.

Table I. Energies for σ,π and Bent-Bond Wave Functions for Molecules with Multiple Bonds[a]

molecule	SOPP pairs	σ,π bonds	bent bonds	$E(\Omega) - E(\sigma\pi)$
$O{=}C{=}O$	8	−187.765 05	−187.776 32	−0.31
	+SI	−187.765 10	−187.813 97	−1.33
$FC{\equiv}CF$[b]	3	−274.575 24	−274.584 67	−0.48
	11	−274.658 31	−274.676 08	−0.26
$C{\equiv}O$	5	−112.830 32	−112.825 87	+0.12
$+C{=}O + C{=}O'$	+SI	−112.830 32	−112.847 94	−0.48
$H_2C{=}CH_2$[c]	2	−78.075 36	−78.069 81	0.15
	6	−78.134 51	−78.128 31	0.19
$F_2C{=}CF_2$[d]	2	−473.528 70	−473.528 64	0.00
$H_2Si{=}SiH_2$[e]	2	−580.096 64	−580.098 42	−0.05
$H_2C{=}C{=}CH_2$[f]	8	−115.958 63	−115.946 68	0.33
$H_2C{=}O$[g]	6	−113.993 20	−113.985 15	0.22
$HC{\equiv}CH$	3	−76.875 16	−76.873 68	0.04
	5	−76.902 11	−76.897 09	0.14
$N{\equiv}N$	3	−109.032 55	−109.018 20	0.39
	5	−109.044 80	−109.031 07	0.37
$C{\equiv}N$	4	−92.272 37	−92.261 36	0.30
$N{\equiv}C{-}C{\equiv}N$	9	−184.761 10	−184.749 74	0.31
$C{\equiv}C$	4	−75.532 97	−75.523 52	0.26

[a] Total energies in hartrees, differences in eV. [b] C_2F_2 geometry from ref 45, $\zeta^d = 1.34$ added for F. [c] Ethylene and acetylene carbon $\zeta^d = 0.532$. [d] C_2F_4 geometry from ref 46. [e] Si_2H_4 geometry from ref 47. [f] Valence double-ζ without polarization. [g] Hydrogen basis 5s/2s rather than 4s/2s.

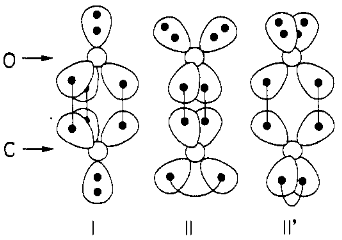

Figure 4. Schematic depiction within a bent-bond model of bonding alternatives for CO.

GVB wave functions Ψ_{I} and $\Psi_{I'}$ corresponding to the bonding structures I and I′ are used to obtain a total SI wave function Ψ_{SI} of the correct symmetry: $\Psi_{SI} = c(\Psi_{I} + \Psi_{I'})$. In these SI calculations, the margin favoring bent bonds widens to 1.33 eV.

Difluoroacetylene is an example of a triple bond that had been demonstrated to be better described with bent bonds.[10] Carbon monoxide is a molecule whose bonding is also usually described in terms of a triple bond. The bent-bond representation is depicted as I in Figure 4. However, Pauling argued that it is also necessary to consider the two symmetrically related (by a 90° rotation about the molecular axis) double-bonded forms in order to describe this molecule properly. The bent-bond models correspond to the double-bond structures denoted as II and II′ in Figure 4. In this formally neutral structure, there are double bent bonds between the carbon and the oxygen, along with two lone pairs on the oxygen (radially separated) and one lone pair on the carbon (angularly separated). Unlike the case for CO_2 or C_2F_2, the single-structure SOPP-GVB calculation for CO does not favor bent bonds; the most stable single-structure five-pair SOPP wave function takes the form of triple σ,π bonds and terminal lone pairs (the triple bent bond SOPP wave function energy is 0.12 eV higher). However, the SI calculation implied by Pauling's resonance model—$\Psi_{SI} = C_{I}\Psi_{I} + C_{II}(\Psi_{II} + \Psi_{II'})$, with Ψ_{I}, Ψ_{II}, and $\Psi_{II'}$ being the many-electron SOPP-GVB wave functions associated with the respective bonding structures in Figure 4—manifests a large contribution from the double-bond structures. The stabilization afforded by this "resonance" yields an energy for the bent-bond representation lower by almost half a volt than the energy in the σ,π bond context.

Outside of the molecules discussed above, however, the results are discouraging for bent bonds. Of five additional double-bonded molecules considered, only one, Si_2H_4, favors bent bonds, and none of the triple-bonded molecules do so. In the nitrogen molecule, σ,π bonds are favored by nearly 0.4 eV. Examination of the archetypical multiply-bonded molecules shows that our results confirm the early SOPP results of Hay *et al.*:[41] we find that the variationally favored representation of the bonding in ethylene and acetylene is constituted of σ and π bonds. We were also able to obtain bent-bond SOPP wave functions despite the fact that they are not the lowest energy solutions. The bent-bond results are disfavored by 0.19 and 0.14 eV, respectively, for these two molecules. Substituting fluorine atoms for hydrogen atoms, however, inverts this order for acetylene; the same substitution nearly do the same for ethylene.

In calculations for ethylene,[12] Palke found that relaxing the orbital overlap constraints among all the orbitals imposed in the strong-orthogonality approximation sufficed to reverse the relative stabilities of the two bonding models given by SOPP calculations. Unfortunately, the magnitude of the bias could not be determined, as only the most stable solution at each level of approximation, SOPP-GVB (σ,π bond) and PP-GVB (bent bond), was calculated. In our SOPP calculations, energy differences between the bonding models tend to be larger for triple-bond molecules than for double-bond molecules. Bent bonds are higher in energy by an average of ~0.1 eV per double bond and ~0.3 eV per triple bond. This behavior is consistent with a bias against the bent-bond representation—were strong orthogonality a serious constraint, double bonds would be less impacted than triple bonds. In a triple bond more orthogonality constraints are imposed among the orbitals (3 pair–pair constraints × 2 orbitals/pair × 2 orbitals/pair = 12) than among orbitals of double bonds (1 pair–pair constraint × 2 × 2 = 4). For σ,π bond wave functions, of course, SO is not a constraint on the oribtals of the multiple bond, as orbitals of different pairs are orthogonal by symmetry.

That this orbital crowding could indeed be a major factor is supported by the impact of changes in the basis set. The better the basis set, the better the bent-bond model wave functions fare in the comparisons. For example, the removal of the carbon d-polarization functions in ethylene impacts the bent-bond result by 0.06 eV more than the σ,π result. With SO imposed, as more orbitals crowd into the bond region, the basis set needs to be more flexible to allow the orbitals of each pair to bond effectively while at the same time maintaining orthogonality to orbitals of other pairs.

Conclusions based on SOPP results that favor bent bonds have also been disputed on the grounds that restrictions on the form of spin coupling among the electrons in the multiple bond (imposed in the PP approximation to GVB wave functions) introduce a bias into the comparisons. On the basis of CI calculations intended to test this possibility, Bauschlicher and Taylor (BT)[16] and Carter and Goddard (CG)[17] had argued that the perfect-pairing restriction on the spin coupling among the orbitals of a multiple bond represented a significant limitation on the wave function and constituted a bias against the conventional σ,π bond description. In particular BT argued that the bent-bond description of C_2F_2 given by SOPP calculations is an artifact of the PP constraint of the SOPP approach and that the σ,π bond model is the correct one once PP limitations are lifted. Although the above criticism is flawed (see Part 2), the bias nonetheless is certainly plausible and does exist; π bond orbitals have smaller overlaps and hence are more disposed to alternate spin couplings (besides singlet perfect pairing) than bent bond orbitals. The question is the magnitude of this effect and its weight with respect to bias incorporated in the SO approximation. Clearly, to do a definitive analysis, it is necessary to relax both conditions simultaneously, in a self-consistent calculation. Preliminary results for difluoroacetylene[48] and tetrafluoroethylene[49] have shown variational GVB calculations to produce bent-bond

---

(48) Messmer, R. P.; Schultz, P. A. *Phys. Rev. Lett.* **1988**, *60*, 860.

(49) Schultz, P. A.; Messmer, R. P. *J. Am. Chem. Soc.* **1988**, *110*, 8258.

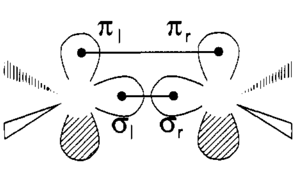

Figure 5. Schematic depiction of the orbitals of a σ,π bond model description of the double bond in ethylene.

solutions, resolving the debate over the better bonding model for those specific molecules. In the next section we describe how to eliminate the restrictions to the full-GVB wave functions and extend the analysis of the nature of the bonding in multiple bonds to the limit of the most general wave functions possible within an IP model.

GVB and Constrained Configuration Interaction

To explore the limits of the IP model for multiple bonds, we need to compute GVB wave functions, eq 1, at the top of the IP hierarchy. Except for a few early applications, however, the method has not found great use, as the nonorthogonality intrinsic to the interpretational orbitals that make up the GVB wave function makes the full method difficult to implement and computationally impractical for more than a very small number of electrons due to the $N!$ scaling required for the computations. As a consequence of this daunting property, studies using the full power of the GVB method are scarce, mostly restricted to small molecules[7,22,48-50] or operating on only a small subset of the electrons of a larger molecule, typically π electron systems in organic molecules such as the allyl radical, butadiene, and benzene.[51]

The SOPP-GVB method was fashioned into a practical computational scheme[8,21] by taking advantage of the fact that a simple relation transforms the nonorthogonal interpretational orbital set $\{\varphi_i\}$ into an orthogonal basis set $\{\phi_i\}$ via

$$\varphi_{il} = \phi_{i\mathrm{b}} + \lambda_i\phi_i a; \ \varphi_{i\mathrm{r}} = \phi_{i\mathrm{b}} - \lambda_i\phi_{i\mathrm{a}} \qquad (8)$$

where, neglecting normalization throughout, $\phi_{i\mathrm{b}}$ and $\phi_{i\mathrm{a}}$ are bonding and antibonding "natural orbitals" and λ_i is trivially related to the orbital overlap. Therefore, the SOPP wave function (cf. eqs 3 and 4) can be recast in a standard multideterminant configuration interaction (CI) expansion of 2^N terms:

$$\Psi_{\mathrm{SOPP}} = \mathcal{A}[(\phi_{1\mathrm{b}}^2 - \lambda_1^2\phi_{1\mathrm{a}}^2)\alpha\beta(\phi_{2\mathrm{b}}^2 - \lambda_2^2\phi_{2\mathrm{a}}^2)\alpha\beta\ldots(\phi_{M\mathrm{b}}^2 - \lambda_M^2\phi_{M\mathrm{a}}^2)\alpha\beta] \qquad (9)$$

The SCF calculations are done in the multiconfiguration SCF (MCSCF) context of eq 9 using an orthogonal basis, although the interpretation of the bonding is made using the overlapping orbitals of the IP representation of the wave function.

We use the same basic strategy to investigate the effects of relaxing the restrictions of the SOPP-GVB wave function. We rewrite the more general IP wave functions such as the GVB wave function of eq 1 in terms of conventional CI expansions over orthogonal orbitals and apply existing MCSCF procedures to optimize the wave functions. The general CI wave functions defined by the configuration list required to describe the GVB wave functions will not, in general, be interpretable in the IP context. It is necessary to place constraints upon the coefficients of the terms making up the configuration list, in an IP constrained-CI (CCI) that serves as the basis for the MCSCF calculation.

CCI Expansion of the GVB Wave Function for Double (σ,π) Bonds. We restrict our attention to those molecules possessing a plane of symmetry through the plane bisecting the bond axis, such as C_2H_4. The full-GVB wave function for the double bond within the σ,π bond model described in Figure 5 can be written

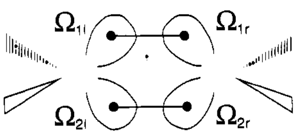

Figure 6. Schematic depiction of the orbitals of a bent-bond model description of the double bond of ethylene.

$$\Psi_{\mathrm{GVB}}^{\sigma\pi} = \mathcal{A}[\Phi\sigma_l\sigma_r\pi_l\pi_r\{c_{\theta1}\Theta_1 + c_{\theta2}\Theta_2\}] \qquad (10)$$

where Θ_1 denotes the PP spin coupling, and Θ_2 denotes the orthogonal four-electron singlet, and Φ describes all the electrons outside of those involved in describing the double bond. Perfect pairing is the only operative restriction on the σ,π bond GVB wave function, as orthogonality between bond pairs is dictated by symmetry. To transform from the GVB wave function of eq 10 to the CCI representation of the GVB wave function, one uses the orbital substitutions of eq 8, making the association of $\phi_{1\mathrm{b}}$ with the bonding σ_b, $\phi_{1\mathrm{a}}$ with the antibonding σ_a, $\phi_{2\mathrm{b}}$ with the bonding π_b, and $\phi_{2\mathrm{a}}$ with the antibonding π_a, to obtain

$$\Psi_{\mathrm{GVB}}^{\sigma\pi} \equiv \Psi_{\mathrm{SO}}^{\sigma\pi} = \mathcal{A}[\Phi(c_{\theta1}\{\sigma_\mathrm{b}^2\pi_\mathrm{b}^2 - \lambda_\sigma^2\sigma_\mathrm{a}^2\pi_\mathrm{b}^2 - \lambda_\pi^2\sigma_\mathrm{b}^2\pi_\mathrm{a}^2 + \lambda_\sigma^2\lambda_\pi^2\sigma_\mathrm{a}^2\pi_\mathrm{a}^2\}\alpha\beta\alpha\beta + c_{\theta2}\{\sigma_\mathrm{b}^1\sigma_\mathrm{a}^1\pi_\mathrm{b}^1\pi_\mathrm{a}^1\}\Theta_2)] \qquad (11)$$

The CCI expansion contains five terms but has only three degrees of freedom in the coefficients corresponding to the two degrees of freedom provided by the overlaps in the σ and π bonds plus the degree of freedom offered by the spin function. The variables λ_σ, λ_π, and $c_{\theta2}$ describe the degrees of freedom in the coefficients of the configuration state functions (CSF)—configurations associated with specific spin eigenfunctions—in the CCI expansion of the GVB wave function. The properties of this SO-GVB wave function will be discussed in greater detail in Part 2.

CCI Expansion of the GVB Wave Function for Double Bent Bonds. The natural starting point for expanding the bent-bond wave function schematically depicted in Figure 6 is to use the same strategy described above for the σ,π bond wave function, *i.e.*, use the orbital relationships of eq 8 to transform the IP representation of the bent-bond wave function into a CI form. First we define the SO-GVB wave function as

$$\Psi_{\mathrm{SO}}^{\Omega} = c_{\theta1}^{\Omega}\Psi_{\theta1}^{\Omega} + c_{\theta2}^{\Omega}\Psi_{\theta2}^{\Omega} \qquad (12)$$

where Θ_1 is the perfect-pairing spin coupling. The expansion for the PP component is

$$\Psi_{\theta1}^{\Omega} = \mathcal{A}[\Phi\Omega_{1l}\Omega_{1r}\Omega_{2l}\Omega_{2r}\Theta_{\mathrm{PP}}(4)] \qquad (13a)$$

$$\rightarrow \mathcal{A}[\Phi\{\Omega_{1\mathrm{b}}^2\Omega_{2\mathrm{b}}^2 - \lambda_\Omega^2\Omega_{1\mathrm{a}}^2\Omega_{2\mathrm{b}}^2 - \lambda_\Omega^2\Omega_{1\mathrm{b}}^2\Omega_{2\mathrm{a}}^2 + \lambda_\Omega^4\Omega_{1\mathrm{a}}^2\Omega_{2\mathrm{a}}^2\}\alpha\beta\alpha\beta] \qquad (13b)$$

and the second component is

$$\Psi_{\theta2}^{\Omega} = \mathcal{A}[\Phi\Omega_{1l}\Omega_{1r}\Omega_{2l}\Omega_{2r}\Theta_2(4)] \qquad (13c)$$

$$= \mathcal{A}[\Phi\Omega_{1\mathrm{b}}^1\Omega_{1\mathrm{a}}^1\Omega_{2\mathrm{b}}^1\Omega_{2\mathrm{a}}^1\Theta_2(4)] \qquad (13d)$$

where $\Omega_{i\mathrm{b}}$ and $\Omega_{i\mathrm{a}}$ are bonding and antibonding bent-bond natural orbitals, respectively, of the two bent bonds. We take advantage of the equivalence of the bent-bond pairs and set $\lambda_1 = \lambda_2 = \lambda_\Omega$. In the GVB wave function, IP orbitals of different pairs overlap, and natural orbitals thus obtained no longer form an orthogonal set. Hence, this procedure no longer generates an orthogonal CI expansion. It is possible to use an orthogonalized bent-bond orbital basis to generate an orthogonal expansion, but this expansion will no longer be compact and, furthermore, does not take full advantage of the symmetry intrinsic to the bonding description.

Instead of a bent-bond computational orbital basis, it proves more convenient to expand the wave function in a σ,π orbital basis, defined as follows:

---

(50) Cooper, D. L.; Gerratt, J.; Raimondi, M. In *Ab Initio Methods in Quantum Chemistry*; Lawley, K. P., Ed.; Wiley Publishing: New York, 1987.

(51) Benjamin, L. G. Ph.D. Thesis, Caltech, 1974.

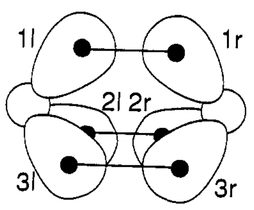

Figure 7. Schematic depiction of the orbitals of a bent-bond model description of a triple bond.

$$\sigma_b = c_{\sigma b}(\Omega_{1l} + \Omega_{1r} + \Omega_{2l} + \Omega_{2r}) \quad (14a)$$

$$\sigma_a = c_{\sigma a}(\Omega_{1l} - \Omega_{1r} + \Omega_{2l} - \Omega_{2r}) \quad (14b)$$

$$\pi_b = c_{\pi b}(\Omega_{1l} + \Omega_{1r} - \Omega_{2l} - \Omega_{2r}) \quad (14c)$$

$$\pi_a = c_{\pi a}(\Omega_{1l} - \Omega_{1r} - \Omega_{2l} + \Omega_{2r}) \quad (14d)$$

where the normalization coefficients are related to the overlaps of the IP orbitals. Within this basis, the SO-GVB bent-bond wave function alternatively may be expanded as

$$\Psi^{\Omega}_{\theta 1} = \mathcal{A}\Big[\Phi\Big\{\sigma_b^2\pi_b^2\alpha\beta\alpha\beta - \frac{1}{2}\lambda_{\Omega}^2(\sigma_b^2\sigma_a^2 + \pi_b^2\sigma_a^2 + \sigma_b^2\pi_a^2 + \pi_b^2\pi_a^2)\alpha\beta\alpha\beta + \lambda_{\Omega}^2\sigma_b^1\pi_b^1\sigma_a^1\pi_a^1\Theta_1(4) + \lambda_{\Omega}^4\sigma_a^2\pi_a^2\alpha\beta\alpha\beta\Big\}\Big] \quad (15)$$

in terms of symmetry orbitals. Doing the same for the non-PP spin coupling of the orbitals yields

$$\Psi^{\Omega}_{\theta 2} = \mathcal{A}[\Phi\Omega_{1l}\Omega_{1r}\Omega_{2l}\Omega_{2r}\Theta_2(4)] = \mathcal{A}[\Phi\Omega^1_{1b}\Omega^1_{1a}\Omega^1_{2b}\Omega^1_{2a}\Theta_2(4)] \rightarrow \mathcal{A}[\Phi(\sigma_b + \pi_b)^1(\sigma_a + \pi_a)^1(\sigma_b - \pi_b)^1(\sigma_a - \pi_a)^1\Theta_2(4)] \rightarrow \mathcal{A}\Big[\Phi\Big\{(\sigma_b^2\sigma_a^2 - \pi_b^2\sigma_a^2 - \sigma_b^2\pi_a^2 + \pi_b^2\pi_a^2)\alpha\beta\alpha\beta + \frac{2}{\sqrt{3}}\sigma_b^1\pi_b^1\sigma_a^1\pi_a^1\Theta_2(4)\Big\}\Big] \quad (16)$$

A total of eight CSFs (seven configurations) describes the general bent-bond SO-GVB wave function. The equivalent orbital basis expansion of eq 13 requires only five CSFs. The advantage of the symmetry orbital basis expansion is that relaxing strong orthogonality requires no extra terms; it merely alters the relative weights of the CSFs already used in this CCI expansion of the SO-GVB wave function.[13] Note the distinction between the σ,π symmetry imposed on the basis set orbitals used in the computations and the IP interpretation in terms of bent bonds.

Among these eight terms, the full-GVB CCI expansion has four degrees of freedom, corresponding to three unique overlaps—$S_{lr} = \langle\Omega_{il}|\Omega_{ir}\rangle$, $S_{ll'} = \langle\Omega_{1l}|\Omega_{2l}\rangle$, and $S_{lr'} = \langle\Omega_{1l}|\Omega_{2r}\rangle$—and the spin coupling. It is worth noting that $\{\sigma_b^1\sigma_a^1\pi_b^1\pi_a^1\} - \Theta_1$ CSF, found to be important in describing the double bond in Part 2 and yet inconsistent with an IP interpretation within the σ,π bond context, is consistent with an IP interpretation within a bent-bond model; it appears in the bent-bond CCI expansion of eq 16.

CCI Expansion of the GVB Wave Function for Triple Bent Bonds. As above with double bonds, the triple-bond molecules we will consider all have a reflection plane bisecting the bond axis. The general form of a triple-bond GVB wave function is

$$\Psi_{GVB} = \mathcal{A}[\Phi\varphi_{1l}\varphi_{1r}\varphi_{2l}\varphi_{2r}\varphi_{3l}\varphi_{3r}\Theta] \quad (17)$$

where Θ is a general six-electron spin singlet (there are five independent six-electron singlets). The σ,π bond GVB wave function is identical to the SO-GVB wave functions for N_2 described in Part 2, and as above, the CCI expansion is straightforward. For the CCI expansion of the triple bent bond GVB wave function schematically depicted in Figure 7, it again proves more convenient to expand the bent-bond orbitals $\Omega_{i(l,r)}$ in terms of an orthogonal symmetry orbital basis

$$\Omega_{i(l,r)} = c_{\sigma b}\sigma_b + c_{\pi b}\Big[\cos\Big(\frac{i-1}{3}2\pi\Big)\pi_{xb} + \sin\Big(\frac{i-1}{3}2\pi\Big)\pi_{yb}\Big] \pm \Big\{c_{\sigma a}\sigma_a + c_{\pi a}\Big[\cos\Big(\frac{i-1}{3}2\pi\Big)\pi_{xa} + \sin\Big(\frac{i-1}{3}2\pi\Big)\pi_{ya}\Big]\Big\} \quad (18)$$

where the coefficients are related to the three unique (same as for the double bond—S_{lr}, $S_{ll'}$, and $S_{lr'}$) overlaps among the bent-bond IP orbitals. The equivalence of the three bonds is immediately apparent; they are related by 120° rotations about the internuclear axis. Inserting these relations into the GVB wave function of eq 17 and expanding for each independent spin coupling results in a conventional CI expansion of 38 configurations (44 CSFs) that can be computed using existing MCSCF codes.[13]

GVB Computational Procedure

The prescription for computing full-GVB wave functions then is as follows. The wave function is rewritten as a conventional CI expansion

$$\Psi = \sum_i c_i(\{S\},\{\Theta\})\Psi_i(\{\phi^{sym}\}) \quad (19)$$

over symmetry orbitals where the Ψ_i are CSFs and the expansion coefficients c_i are determined variationally by the IP overlaps $\{S\}$ and the optimal spin coupling $\{\Theta\}$. The initial guesses for the orthogonal symmetry orbital basis set $\{\phi^{sym}\}$ are taken from SOPP-GVB calculations. In the case of the bent-bond wave functions, the orthogonal symmetry orbital set is generated by a unitary transformation of the equivalent orbital orthogonal basis.

The first step is accomplished by calculating the CI Hamiltonian matrix elements

$$H_{ij} = \langle\Psi_i|H|\Psi_j\rangle$$

over the CSFs using a fixed orbital basis set and then minimizing the following energy expression

$$E_{GVB} = \langle\Psi_{GVB}|H|\Psi_{GVB}\rangle = \sum_{i,j} c_i(\{S\},\{\Theta\})c_j(\{S\},\{\Theta\})H_{ij} \quad (20)$$

as a function of the orbital overlaps and spin couplings. A simple direct minimization procedure suffices for this step. The generated CCI expansion coefficients serve as input into a general MCSCF procedure[52] to generate a new optimized orthogonal symmetry orbital basis set. The CCI and MCSCF steps are then alternately repeated until convergence, typically a <0.000 005-hartree change in energy between macrocycles. The IP orbitals from which the bonding interpretation is made can be reconstituted from the optimized parameters and orbital basis. The advantage of the above procedure is that it is general enough to generate all levels of IP wave functions and makes use of existing highly developed technology. The disadvantage is that CCI expansions must be specifically generated for each general class of system.

The energetic convergence of the SCF calculations is rapid, typically within three or four macrocycles. The overlaps of bond pair orbitals stabilize rapidly, with changes <0.0001 between macrocycles at energetic convergence. Nonbonding overlaps in the bent-bond calculations coverge more slowly. Changes between macrocycles would be ~0.001.

GVB Results: Ethylene

Table II summarizes the computed energies for ethylene of the hierarchy of IP wave functions for the two models. With respect to the HF result, the energetic stabilization of the SOPP-GVB wave function correlating the two pairs associated with the double bond is ~1 eV, with the σ,π bond description favored by 0.15 eV over the bent-bond description. Allowing a general spin coupling among the orbitals in the σ,π bond description, *cf.* eq 11, results in an additional 0.07-eV stabilization in a self-consistent

---

(52) Ruedenberg, K.; Cheung, L. M.; Elbert, S. T. *Int. J. Quantum Chem.* **1979**, *15*, 1069.

Table II. Calculated Energies for C_2H_4 Using IP Wave Functions[a]

wave function	total E	ΔE_{tot}	ΔE_T	ΔE_{NA}	ΔE_{ee}
Hartree–Fock	−78.037 24	+0.000	0.000	0.000	0.000
		σ,π bonds			
SOPP-GVB	−78.075 36	−1.037	3.448	−5.631	1.145
full-GVB	−78.078 00	−1.109	3.907	−6.193	1.177
		bent bonds			
SOPP-GVB	−78.069 81	−0.886	2.780	−3.956	0.291
PP-GVB	−78.079 00	−1.136	3.747	−6.129	1.246
full-GVB	−78.079 25	−1.143	3.832	−6.196	1.221
		non-IP			
CASSCF	−78.090 91	−1.460	4.439	−7.222	1.322

[a] Total energies in hartrees, differences in eV; ΔE_T, ΔE_{NA}, and ΔE_{ee} are the differences in kinetic energy, nuclear attraction energy, and electron–electron interaction energy, respectively.

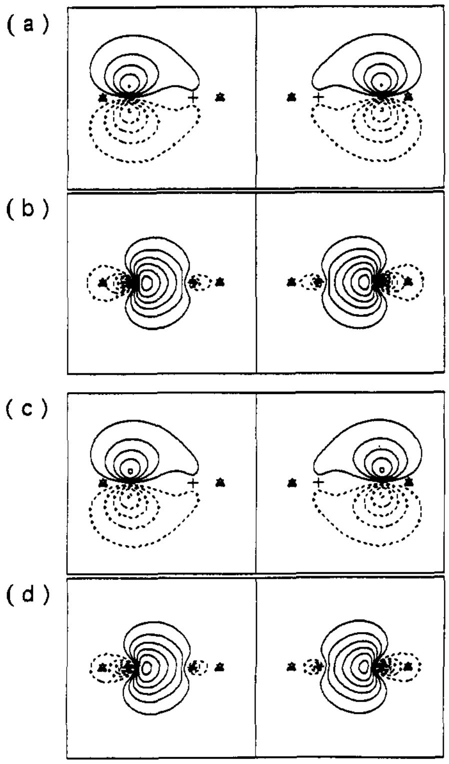

Figure 8. Orbital amplitude contour plots of IP bond pairs in σ,π bond wave functions for C_2H_4: (a) SOPP-GVB π bond pair; (b) SOPP-GVB σ bond pair; (c) full-GVB π bond pair; (d) full-GVB σ bond pair.

Table III. Overlaps among Double-Bond Orbitals for IP Wave Functions for C_2H_4

	σ,π bonds		bent bonds		
wave function	S_σ	S_π	S_{lr}	$S_{ll'}$	$S_{lr'}$
SOPP-GVB	0.883	0.648	0.814	0.000	0.000
PP-GVB	0.883[a]	0.648[a]	0.845	0.548	0.641
full-GVB	0.881	0.643	0.834	0.479	0.564

[a] Same as SOPP, as SO is not a restriction.

calculation. As strong orthogonality is not a constraint, this is the full-GVB limit of the σ,π bond model. The small change in energy upon relaxing the PP restriction on the wave function suggests only small changes in the spatial forms of the orbitals. A glance at the orbital amplitude contour plots confirms this inference. The σ and π bond orbitals of the SOPP-GVB wave function displayed in Figure 8(a,b) are very similar to those of the full-GVB wave function shown in Figure 8(c,d). The change in orbital overlaps, presented in Table III, is small and slightly (~1%) reduced from the SOPP values, reflecting the added triplet character in the bond pairs brought about by the partial non-PP coupling.

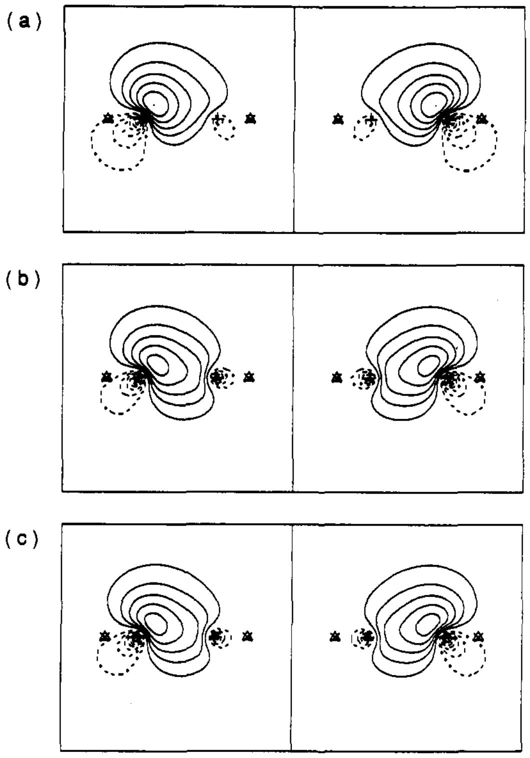

Figure 9. Orbital amplitude contour plots of IP bond pairs in bent-bond wave functions for C_2H_4: (a) SOPP-GVB bent-bond pair; (b) PP-GVB bent-bond pair, (c) full-GVB bent-bond pair.

For the bent-bond description, allowing the bond orbitals of the SOPP-GVB wave function to take on a general spin coupling yields an energy lowering of only 0.02 eV, indicating that the PP restriction is of negligible consequence for the bent-bond representation of the bond. On the other hand, relaxing the SO restriction, keeping the PP spin coupling, is more energetically significant, yielding a 0.25-eV stabilization with respect to the SOPP-GVB calculation. The magnitude of the change in the energy is accompanied by large changes in the forms of the bond orbitals, as seen in the contour plots of Figure 9 and in the computed overlaps presented in Table III. The bond pair overlap (S_{lr}) increases from 0.814 to 0.845 for the self-consistent PP-GVB wave function. More significantly, the nonbonding overlaps, restricted to be zero in the SOPP result, grow to 0.548 between orbitals on the same atom ($S_{ll'}$) and as large as 0.641 for the orbitals involved in different bond pairs and on different carbon atoms ($S_{lr'}$). In an approximately variational PP-GVB procedure, Palke[12] obtained an on-site overlap of 0.516, in good agreement with the present, fully variational result.

Simultaneously relaxing the PP constraint in addition to the SO contraints, yielding the full GVB bent-bond wave function, is worth an additional 0.01 eV. Relative to the SOPP-GVB wave function, the optimal bent-bond full-GVB wave function captures 0.26 eV in correlation energy. Though the energy gain in this final step is small, the changes in the orbitals, shown in Figure 9(c), are more substantial. The bonding overlaps decrease 1.5% from those of the PP-GVB model, again reflecting added triplet character in the bond pairs. The nonbonding overlaps decrease by 12%, a more significant change. With respect to the PP coupling, the optimal coupling augments the already existing triplet character between the hybrids on a single site and hence tends to make them overlap less.

Using configurations involving all possible occupations of the four basis orbitals by the four electrons (as in the bent-bond GVB wave function) but removing the IP constraints on the CI coefficients results in a further lowering of the energy. This CAS wave function[14] nets 1.46 eV in correlation energy with respect to the HF reference and ~0.3 eV with respect to either

Table IV. Calculated Energies for C_2H_2 Using IP Wave Functions[a]

wave function	total E	ΔE_{tot}	ΔE_{T}	ΔE_{NA}	ΔE_{ee}
Hartree–Fock	−76.820 78	+0.000	0.000	0.000	0.000
		σ,π bonds			
SOPP-GVB	−76.875 17	−1.480	4.919	−7.974	+1.575
full-GVB	−76.885 12	−1.751	6.060	−9.375	+1.564
		bent bonds			
SOPP-GVB	−76.873 68	−1.439	3.339	−5.630	−0.192
PP-GVB	−76.884 05	−1.717	5.635	−9.013	+1.662
full-GVB	−76.888 87	−1.845	6.476	−10.080	+1.759
		non-IP			
CASSCF	−76.923 03	−2.782	7.160	−11.768	+1.826

[a] Total energies in hartrees, ΔE values given in eV.

of the GVB wave functions. The best IP wave functions capture roughly three-quarters of the correlation energy of the CASSCF wave function.

In the IP limit of the full-GVB wave functions, the bent-bond results are favored by 0.03 eV. The magnitude of the SOPP bias against a bent-bond model is 0.25 eV with respect to PP-GVB and 0.19 eV with respect to the full-GVB limit. Hence, if one adopts the variational principle as the criterion by which to measure the relative merit of the two bonding models, the bent-bond model is superior.

Analysis of the orbitals leads to some interesting observations. The angles found between bent-bond orbitals on a single site involved in separate bonds are much smaller than the 109.47° that would be expected on the basis of the idealized sp^3 tetrahedral hybrids of Pauling. In fact, the largest angle (between maxima in amplitude of orbitals on the same site) is 92°, between SOPP bent-bond orbitals. The PP-GVB wave function is characterized by strong overlaps of orbitals between the pairs, and the angle decreases to 71°. Attendant with the decrease of overlap between them as a result of the enhanced triplet character, the angle between the on-site orbitals increases slightly to 73° in the full-GVB wave function.

This may not be the best measure of the angle between hybrids on a single site, and we have also examined the results of a projection onto a single site, using a standard Mulliken analysis (ignoring d-character) of the IP orbitals over the atomic basis functions. Using the ratio of the p_π *vs* p_σ character in the orbital, the angle between the on-site projected hybrids h and h′ can be defined:

$$\angle_{\mathrm{hh'}} = 2\tan^{-1}(p_\pi/p_\sigma) \tag{21}$$

Using this analysis, the results of the SOPP calculations are more in line with expectations. This projection of the SOPP orbitals yields $sp^{3.38}$ hybrids calculated to be 111° apart. The PP-GVB and full-GVB orbitals, however, still emphasize the s-character and yield angles smaller than expected, $sp^{1.74}$ and 78°, $sp^{1.84}$ and 85°, respectively. That nonorthogonal orbitals have an excess of s-character had been noted previously in the studies of Palke *et al.*[12,53]

Results: Acetylene

Table IV summarizes the results of calculations for acetylene. The stabilization offered by the SOPP-GVB wave function (with three correlated pairs) with respect to the HF reference is ~50% larger than the same stabilization for the double bond in ethylene. The σ,π bond model is favored by 0.04 eV. The full-GVB calculation for the σ,π bond wave function lowers the energy by another 0.27 eV. Here, the σ,π bond orbitals do exhibit a more discernible change. In Figure 10, the contour plots of the SOPP and full-GVB orbitals are displayed. The σ bond orbitals localize more strongly in the bonding region with inclusion of alternate spin couplings. Delocalization onto the hydrogen atoms, present in the SOPP orbitals, is no longer evident in the full-GVB orbitals. The bond overlaps, given in Table V, show the decrease that is the hallmark of the inclusion of non-PP couplings into the wave function.

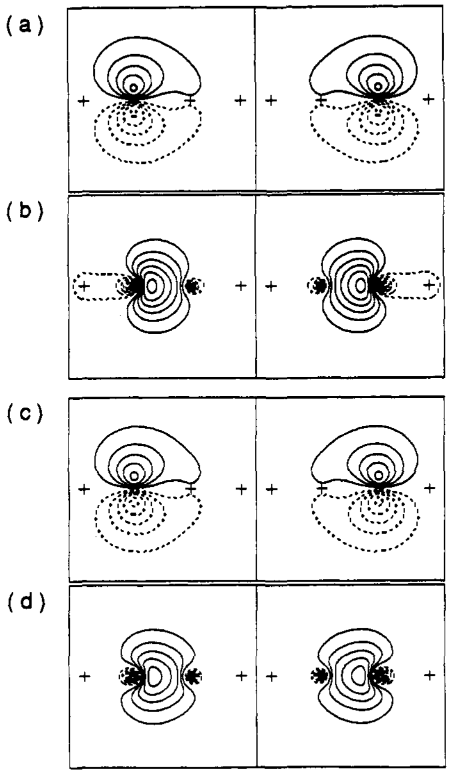

Figure 10. Orbital amplitude contour plots of IP bond pairs in σ,π bond wave functions for C_2H_2: (a) SOPP-GVB π bond pair; (b) SOPP-GVB σ bond pair; (c) full-GVB π bond pair; (d) full-GVB σ bond pair.

Table V. Overlaps among Triple-Bond Orbitals for IP Wave Functions for C_2H_2

	σ,π bonds		bent bonds		
wave function	S_σ	S_π	S_{lr}	$S_{\mathrm{ll'}}$	$S_{\mathrm{lr'}}$
SOPP-GVB	0.912	0.700	0.799	0.000	0.000
PP-GVB	0.912[a]	0.700[a]	0.849	0.526	0.577
full-GVB	0.910	0.687	0.800	0.316	0.359

[a] Same as SOPP, as SO is not a restriction.

Our calculations reveal that the PP constraint on the bent-bond wave function is of small energetic importance and that the SO constraint is again much more significant. The orbital contour plots of Figure 11 graphically depict, as one climbs the IP hierarchy of wave functions, the changes suggested from the values presented in Table V. The PP-GVB orbitals, Figure 11(b), overlap more strongly and clearly take on more s-character than the SOPP orbitals, Figure 11(a). The nonbonding overlaps are 0.526 between on-site orbitals and 0.577 between sites, only slightly less than those found for ethylene. Allowing the orbitals of different bond pairs to overlap yields 0.28 eV. The energy per SO restriction is much reduced from that for ethylene, despite the fact that the overlaps become just as large. The full-GVB bent-bond orbitals obtained when the PP restriction is also relaxed are displayed in Figure 11(c). The overlaps are all reduced from the PP-GVB case, and the orbitals lose s-character. The bonding overlap decreases 6% to 0.800, and the on-site and off-site nonbonding overlaps are reduced to 0.316 and 0.359. The relatively large change in the energy of the full-GVB wave function is to 0.41 eV below the SOPP reference and 0.13 eV lower than the PP-GVB value.

The CASSCF wave function shows almost 1 eV of correlation energy not describable in an IP context. The GVB wave function

---

(53) Kirtman, B.; Chipman, D. M.; Palke, W. E. *J. Am. Chem. Soc.* **1977**, *99*, 1305.

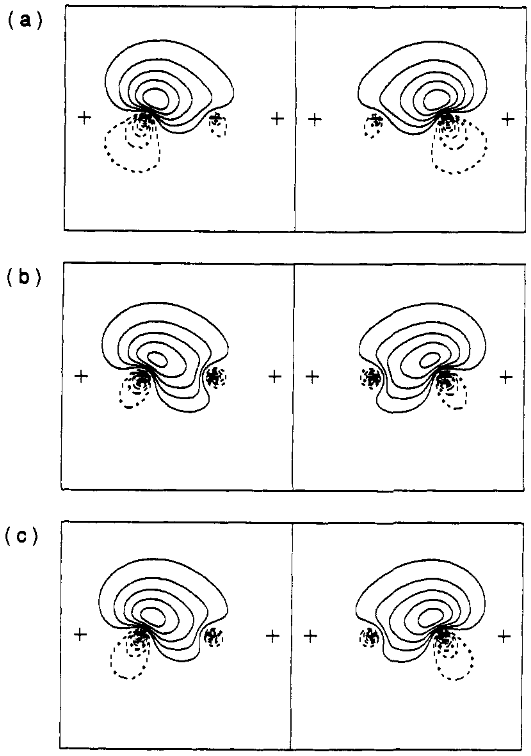

Figure 11. Orbital amplitude contour plots of IP bond pairs in bent-bond wave functions for C_2H_2: (a) SOPP-GVB bent-bond pair; (b) PP-GVB bent-bond pair; (c) full-GVB bent-bond pair.

Table VI. Calculated Total Energies (in hartrees) of IP Wave Functions for Several Multiple-Bond Molecules

wave function	C_2F_4	C_2F_2	N_2	C_2
Hartree–Fock	–473.488 80	–274.526 18	–108.957 63	–75.389 40
		σ,π bonds		
SOPP-GVB	–473.528 70	–274.575 26	–109.032 54	–75.532 97
full-GVB	–473.533 84	–274.588 58	–109.039 35	–75.542 35
		bent bonds		
SOPP-GVB	–473.528 64	–274.584 67	–109.018 20	–75.523 52
PP-GVB	–473.539 19	–274.590 53	–109.037 03	–75.541 95
full-GVB	–473.539 40	–274.595 66	–109.038 81	–75.544 41

Table VII. Orbital Analyses for Bent-Bond IP Wave Functions

system	S_{lr}	$S_{ll'}$	$S_{lr'}$	$\angle_{ll'}$ (deg)	sp^x	$\angle_{hh'}$ (deg)
			SOPP-GVB			
C_2H_4	0.814	0.000	0.000	92	3.38	111
C_2F_4	0.799	0.000	0.000	102	2.26	124
C_2H_2	0.799	0.000	0.000	101	2.95	117
C_2F_2	0.791	0.000	0.000	104	2.55	118
C_2	0.816	0.000	0.000	104	2.71	117
N_2	0.811	0.000	0.000	84	10.1	104
			PP-GVB			
C_2H_4	0.845	0.548	0.641	71	1.74	78
C_2F_4	0.833	0.534	0.615	80	1.30	86
C_2H_2	0.849	0.526	0.577	83	1.17	109
C_2F_2	0.813	0.359	0.394	95	1.46	113
C_2	0.904	0.711	0.753	69	0.81	95
N_2	0.916	0.743	0.780	34	4.02	43
			full-GVB			
C_2H_4	0.834	0.479	0.564	73	1.84	85
C_2F_4	0.825	0.492	0.564	86	1.34	90
C_2H_2	0.800	0.316	0.359	94	1.64	115
C_2F_2	0.795	0.284	0.304	96	1.59	114
C_2	0.819	0.381	0.437	93	1.57	112
N_2	0.828	0.397	0.450	72	3.84	90

obtains two-thirds of the 2.78 eV of correlation energy possible from an unconstrained description (CASSCF) using the same configurational space.

The SOPP calculation favors the σ,π bond model by 0.04 eV. The full-GVB calculations find the bent-bond model favored by 0.09 eV. On the basis of the variational principle, the bent-bond model is again superior to the σ,π bond model. The bias against bent bonds in the SOPP approximation, with respect to the GVB wave function, is found to be 0.13 eV. The strong-orthogonality restriction is the most significant element in this bias.

The results of the orbital analyses are very similar to those for ethylene. The angles between the bent-bond orbitals on a single site are again smaller than the tetrahedral angles expected from an idealized sp^3 description. The angles exhibited for the C_2H_2 orbitals shown in Figure 7 are 101° between SOPP orbitals, as small as 83° between $sp^{1.17}$ PP-GVB orbitals, and 94° between full-GVB orbitals. Projecting onto a single site *via* a Mulliken analysis as described above finds angles between atomic hybrids more in line with expectations: 117° and $sp^{2.95}$ for SOPP, 109° and $sp^{1.17}$ for PP-GVB, and 115° and $sp^{1.64}$ for full-GVB orbitals. As for ethylene, the hybrids show a significant excess of s-character.

Results: Other Molecules

The IP calculations were also applied to a sampling of other molecules. Computed energetics for C_2F_4, C_2F_2, N_2, and C_2 are summarized in Table VI. Orbital analyses for bent-bond wave functions for all molecules considered are presented in Table VII.

C_2F_4. The description of the carbon–carbon double bond does not change much upon substitution of the hydrogen atoms of ethylene with fluorine atoms. The results for C_2F_4 presented in Table VI paint a picture similar to that found for C_2H_4. The PP restriction is somewhat more significant for the σ,π bond wave functions and less significant for the bent-bond wave functions, and the SO constraint proves to be the more serious restriction on the general wave function. The two bonding models are essentially equal in energy at the SOPP level of approximation for C_2F_4, while the full-GVB-SCF result finds the bent-bond representation of the bonding to be favored by 0.15 eV. The overlap and character of the GVB orbitals of the two molecules are also very similar, as seen in Table VII. The bent-bond IP orbitals are presented in Figure 12.

An interesting observation is that even though the ground state of the CF_2 fragments is a singlet (as opposed to the triplet ground state for CH_2), the effect of relaxing the PP spin restriction for both bonding models is to accentuate the on-site triplet rather than on-site singlet character. For the σ,π bond GVB wave function, this is not surprising—the orbitals on a single site are orthogonal by symmetry and hence will favor a triplet coupling over a singlet coupling. In fact, the σ,π bond representation of the bonding *cannot* dissociate formally into the ground-state $^1A_1$ CF_2 fragments (the two states possible are $^3B_1$ and $^1B_1$). For the bent-bond model, this would not be a problem, as the $^1A_1$ ground-state fragments are accessible from the bent-bond IP description. Hence, that the general spin coupling accentuates on-site *triplet* character is somewhat surprising, especially in light of the fact that the computed GVB on-site orbital overlap is 0.49, which should facilitate a singlet interaction. This suggests that the spin coupling in the dissociation of the double bond does not necessarily progress monotonically from the spin coupling of the molecule to that of the fragments. Although the contribution of the non-PP spin coupling is quite small in the bent-bond GVB wave function, it is possible that a better basis set could alter this outcome, *i.e.*, any inadequacy in the basis set would be biased against the on-site singlet description, as all four orbitals, mutually overlapping, compete for the same basis functions.

C_2F_2. The results for the triple bond in C_2F_2 parallel the results in C_2H_2. Relaxation of PP for the σ,π bond wave function yields a substantial 0.36 eV in additional correlation energy, but the change in the orbitals (not shown) is small. Relaxation of the

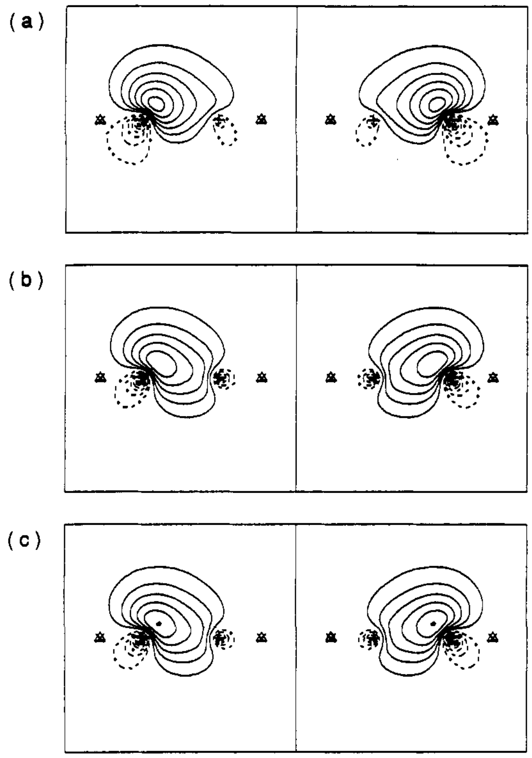

Figure 12. Orbital amplitude contour plots of IP bond pairs in bent-bond wave functions for C_2F_4: (a) SOPP-GVB bent-bond pair; (b) PP-GVB bent-bond pair; (c) full-GVB bent-bond pair.

PP spin-coupling restriction in the bent-bond wave functions is more significant than it is in acetylene, but the SO restriction remains the primary constraint on the SOPP wave function. The PP-GVB energy is 0.16 eV below the SOPP energy, and simultaneous relaxation of the PP restriction gives a full-GVB wave function that is 0.14 eV below the PP-GVB energy. The bent-bond IP orbitals are shown in Figure 13. This marks the only case considered in which relaxation of all the constraints of the SOPP wave function benefits the σ,π bond wave function more than the bent-bond wave function. Nonetheless, the final full-GVB results favor the bent-bond description by 0.19 eV.

N_2. The simplest molecule that contains a triple bond, the nitrogen molecule, has SOPP results that favor the σ,π bond model the strongest, 0.39 eV for calculations correlating the orbitals of the triple bond. Relaxing the PP constraint on the σ,π bond wave function to obtain the full GVB result lowers the energy by 0.19 eV. Turning to the bent-bond wave functions, relaxing the strong-orthogonality restrictions is worth 0.51 eV, almost twice that for any molecule considered to this point, and hence this constraint is a major restriction on the form of the IP wave function for N_2. The magnitude of the nonbonding overlaps in the PP-GVB wave function reflects this, $S_{1l'}$ and $S_{1r'}$ being 0.74 and 0.78—these *nonbonding* overlaps are larger than the *bonding* overlaps typical for carbon–carbon π bonds in the molecules considered above! Relaxing the PP constraint to obtain the full-GVB bent-bond wave function yields only 0.05 eV more, but the orbitals undergo major changes, $S_{1l'}$ and $S_{1r'}$ being reduced to 0.40 and 0.45. The relaxation of the constraints of the SOPP approximation to the general IP wave function for the bent-bond representation of the bond is worth a total of 0.56 eV. This value is large and demonstrates an SOPP bias against bent bonds of $0.56 - 0.19 = 0.37$ eV, but the σ,π bond model is still favored for the full-GVB wave function, but by only 0.01 eV. This is a case where a better basis set may be needed for the bent-bond description to be adequately represented.

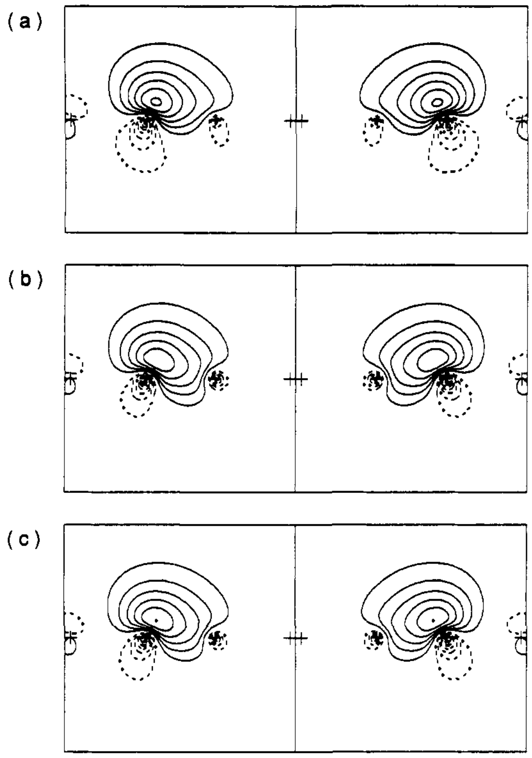

Figure 13. Orbital amplitude contour plots of IP bond pairs in bent-bond wave functions for C_2F_2: (a) SOPP-GVB bent-bond pair; (b) PP-GVB bent-bond pair; (c) full-GVB bent-bond pair.

Analysis and Discussion

The restrictions of the SOPP-GVB approach have significant impact on the results of calculations for multiple bonds. The relaxation of the SO and PP constraints on the wave function shows a consistent pattern in the molecules we have considered. The PP constraint is the less important of the two restrictions on the wave function, and non-PP spin couplings are more important in describing triple bonds than they are in describing double bonds. The PP restriction constitutes the entire limitation on the σ,π bond representation of the wave function and tends to be more important in that case than for the bent-bond representation of the wave function. The bonding interaction embodied by the PP spin coupling is clearly better described using the bent-bond model. This observation is confirmed by the quantitative calculations which show that once the strictures of the SOPP approximation are released, the bent-bond model is found to be the energetically preferred description of the bond.

The only molecule for which our full-GVB calculations did not favor outright the bent-bond representation of the bond is N_2. This is probably an artifact, partially of the basis set but probably also because the IP treatment is only applied to the orbitals of the triple bond. If the correlated treatment is extended, the lone pairs will impact the comparison, especially as the final margin is small. The bent-bond representation is likely to be more strongly affected than the σ,π bond representation. A simple illustration of the merit in this claim is the observation that the five-pair SOPP calculation favors the σ,π bond result by 0.02 eV less than the three-pair calculation; this is large enough to reverse the judgment rendered by the three-pair GVB calculations. There are additional arguments to be made however.

The same counting arguments invoked to rationalize why relaxing SO constraints among orbitals of a multiple bond would benefit bent bonds more than σ,π bonds[10] are also valid here. There are six sets of orthogonality constraints between the three bent-bond pairs and the two lone pairs, while there are only two such constraints in considering the σ,π bond description of the molecule. Analysis of the orbitals obtained in the calculations provides some evidence that these constraints are important. The nitrogen atom ground state is ^4S with a doubly occupied 2s and three singly occupied, quartet-coupled p orbitals. The N≡N bond is formed as p orbitals pairwise couple into bond pairs and the s orbitals become lone pairs. The atoms retain, to a large degree, this character in the molecule. The bond orbitals of the bent-bond SOPP wave function exhibit a hybridization of $sp^{10.1}$—almost pure p. Correspondingly, the lone pair orbitals are $sp^{0.26}$, mostly s. The relaxation of SO restrictions has already been noted to induce great changes in the oribitals; its effect on the hybridization of the IP orbitals is to increase the s-character greatly. The PP-GVB hybridization is $sp^{4.02}$. The full-GVB orbitals, with a hybridization of $sp^{3.84}$, continue this trend. This increased s-character in the bond orbitals is accompanied by a corresponding decrease of the s-character in the lone-pair orbitals, to $sp^{0.35}$ in PP-GVB and $sp^{0.46}$ in full-GVB. This indicates a strong competition for the same basis orbitals and suggests that relaxing the SO constraint between the lone-pair and bent-bond orbitals could be energetically very significant. This competition further implies that bent-bond GVB results will be highly dependent on the quality of the basis set, with any deficiency likely to bias against a bent-bond picture.

The origin of the energy stabilization from including alternate spin coupling is obvious. The large stabilization that results from relaxing strong orthogonality comes about from a very simple effect: orthogonal orbitals do not form attractive bonding interactions.[54] Allowing orbitals of different bond pairs to overlap allows them to form more favorable interactions and lower the energy. That the overlap of orbitals in different bonds localized on *different* atoms is larger than that of the orbitals located on the same site is consistent with this picture. The "bonding" interaction between ostensibly "nonbonding" orbitals can be rather substantial, as seen particularly in the large nonbonding overlaps for the bent-bond GVB wave functions for N_2 and C_2.

An analysis of how the energy changes as more general wave functions are applied yields some interesting observations. A detailed energy breakdown for ethylene is presented in Table II and for acetylene in Table IV; similar behavior is seen for the other molecules. In general, as one climbs the hierarchy of approximations and obtains a lower total energy, the kinetic energy increases, the electron–electron repulsion energy also increases, and the improvement in total energy comes about entirely because of a large compensating increase in the nuclear attraction energy. As the nuclear attraction energy is the only attractive energy in the problem, it is understandable that this energy should improve with improvements in the wave function.

Imposing orthogonality constraints between orbitals in the bent-bond wave functions creates increased nodal character in the orbitals in order to make them orthogonal, and eliminating these artificial nodes will act to reduce the kinetic energy. That the kinetic energy actually *increases* as SO is relaxed might as first be unexpected. However, reduction in nodal character allows the orbitals to localize more effectively about the nuclei, and the more strongly localized orbitals have higher kinetic energy and electron–electron repulsion energy which is, however, more than compensated for by the much improved electron–nuclear attraction. Ruedenberg describes a similar balance in the various energetic contributions to the formation of a single bond.[55]

There is a rough transferability of bond orbital characteristics between systems, as the compilation in Table VII illustrates. Displayed are the overlaps among the bent-bond orbitals (S_{lr}, $S_{ll'}$, $S_{lr'}$), angles between the orbitals on the same site ($\angle_{ll'}$), atomic hybridizations as derived from Mulliken analyses (sp^x), and the angles between atomic hybrids composing the orbitals ($\angle_{hh'}$) as determined from Mulliken populations. Though there is some variation, the constancy of the bonding overlaps, particularly those at the SOPP and full-GVB levels of approximation, testifies to how transferable the two-electron bond unit is from system to system.

Despite the fact that the energy is relatively insensitive to the values of the nonbonding overlaps—the convergence of the nonbonding overlaps was much slower than the convergence of the energy with a very flat potential surface—the same transferability exists among the nonbonding overlaps among orbitals in the same class of multiple bonds. With only minor deviations, the results for C_2F_4 reproduce those for C_2H_4. The angles between orbitals are also very similar. The hybridization changes can be attributed to the electron-withdrawing nature of the fluorine ligands. The C–F bond orbitals will be highly polarized away from the carbon and toward the fluorine due to the difference in electronegativities. Hence, the carbon contribution to the C–F bond will be more p_σ and less s—removing an electron from a p orbital incurs a smaller energetic cost than removing an electron from an s orbital—and the orbitals of the C≡C multiple bond take on more s and less p_σ character. Hence the angle, *cf.* eq 21, between the orbitals narrows.

The properties of the C≡C triple bond are also very similar if one examines SOPP and full-GVB results. The SOPP orbitals overlap ~0.80, are at angles ~103° with respect to one another, and have hybridization of $sp^{2.75\pm0.2}$ with those hybrids at 117°. As seen in Table VII, the full-GVB orbitals exhibit a similar congruence. The three molecules with a carbon–carbon triple bond, despite the very different environments of the triple bonds, have similar overlaps among bonding orbitals, angles within 3° of one another, and hybridizations within 0.04 of $sp^{1.6}$. The PP-GVB results show a much greater variation in the orbitals between different C≡C triple bonds.

The transferability of bond orbitals between different systems is an encouraging manifestation of the unchanging intrinsic nature of the bonds. This had been empirically established for C═C double bonds[56] and is seen here in the similar nature of the IP descriptions of double bonds in C_2H_4 and C_2F_4. Our results, however, suggest that the same transferability may also apply to C≡C triple bonds.

Conclusions

The calculations presented in this paper represent the first rigorous investigation of the nature of multiple bonds in the most general IP context possible. The application of the constrained-CI procedure to do the GVB calculations leads to the following conclusions:

(1) Imposing the perfect-pairing spin restriction is not a significant restriction on the full IP wave function in considering typical covalent systems near their equilibrium geometries. If alternate spin couplings are not important in the description of multiple bonds as the above results appear to demonstrate, then they will certainly not be important in describing the electronic structure of systems made up of simple single covalent bonds in which separate pairs of electrons are not in such close proximity as in the multiple bonds. Indeed, this conclusion could be expected; otherwise Hartree–Fock and other mean-field theories, or SOPP-GVB, would not work as well as they do—they mandate a single spin coupling of the electrons and would incur drastic errors if PP was not closely obeyed.

(2) The strong-orthogonality restriction is found to be a significant restriction on the wave function in describing the orbitals of multiple bonds. Relaxing SO restrictions is found to yield stabilizations of up to 0.5 eV, in treating N_2 and C_2 within the bent-bond representation, and result in overlaps between nonpaired orbitals within multiple bonds as large as 0.7.

(3) The bent-bond model for the bonding is found to be preferred by the results of the calculations using the more general wave functions, in contrast to the opposite results frequently produced

---

(54) Slater, J. C. *J. Chem. Phys.* **1951**, *19*, 220.

(55) Ruedenberg, K. *Rev. Mod. Phys.* **1962**, *34*, 326.

(56) Carter, E. A.; Goddard, W. A., III. *J. Phys. Chem.* **1986**, *90*, 998.

by the SOPP wave functions. By considering the criterion of better total energy, the bent-bond model for multiple bonds is found to be preferred to the σ,π bond model. The only exception to this is N_2, for which qualitative considerations suggest that confining the correlated treatment to the multiple bond preferentially favors the σ,π bond model and that a more expanded IP treatment would yield bent bonds as the preferred description. This then serves as a renewed affirmation of the bent-bond concepts of Slater[3] and Pauling.[4]

(4) A large amount of correlation within the bond is not interpretable within an independent particle model. Using the same orbital basis as that for the GVB calculations, the unconstrained CASSCF calculations obtain up to an additional 1 eV in correlation energy. The IP calculations do obtain better than two-thirds of the correlation energy of the CASSCF calculations, however.

(5) Full-GVB orbitals contain a greater degree of s-character, $\sim sp^{1.7\pm.1}$ for the carbon orbitals involved in multiple bonds, than that presumed by Pauling's tetrahedral hybrids. This serves to reinforce conclusions found in previous calculations regarding excess s-occupancy of nonorthogonal IP orbitals.[12,53] Furthermore, angles between the bonding IP orbitals measured directly from orbital amplitudes are uniformly less than the tetrahedral ideal. However, projections onto single-site hybrids *via* Mulliken charge analyses produce angles more in line with expectations, being tetrahedral for carbon and at right angles for the orbitals of nitrogen. Nonetheless, these results indicate that the notion of tetrahedral hybrids on atoms as the basis of bonding must be regarded as qualitative rather than quantitative.

(6) Improved treatment of electronic correlation is accompanied by an improved electron–nuclear interaction and a worsened kinetic energy. This reflects a competition between the two energies in developing the wave functions: the effect of correlation is to obtain better access to the nuclei for the electrons while the less correlated approach emphasizes the kinetic energy. As the nuclear attraction term is the sole attractive energy in the problem, this must be the case. The analysis of the energy parallels that describing the formation of single bonds.[55]

A question one might ask about the whole issue of bent bonds *vs* σ,π bonds is, does this distinction really matter considering the fact that the GVB wave function captures only $^2/_3$ or $^3/_4$ of the correlation energy obtained from the corresponding CASSCF wave function? This is certainly a relevant query, but recent work[57] concludes that CASSCF wave functions for multiple bonds are interpretable in terms of resonating valence bond structures which have bent bonds. Thus the relevance of the bent-bond discussion is not limited to the GVB wave function; it also provides a compact interpretation of more complex and accurate wave functions. Furthermore, since a generalized Møller–Plesset approach based on a CASSCF wave function can yield quite accurate results,[6] the relevance of the bent-bond GVB-like description to interpret very general wave functions also seems to be in evidence.

The principal conclusion of this paper is, *within an independent particle interpretable model, the most appropriate bonding model for multiple bonds is in terms of bent bonds rather than σ,π bonds*. As the full-GVB wave functions used in arriving at this conclusion are the most general independent-particle interpretable wave functions possible, this verdict is definitive for molecules for which a single classical valence bond structure is sufficient to characterize the bonding. Hence, there may be an element of truth in Pauling's conjecture of 1958 that the σ,π bond description may be a "passing fad".[58] For molecules in which classically one bonding structure is *not* sufficient to describe the bonding, the situation, in principle, could be different. We examine that question of bent bonds and resonance in Part 3 of this series.

Acknowledgment. We thank Prof. Klaus Ruedenberg for generously providing the ALIS suite of programs with which all the MCSCF calculations were done. 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.

---

(57) Recent work (described in: Murphy, R. B.; Messmer, R. P. *J. Chem. Phys.* **1993**, *98*, 7958) shows that the CASSCF wave function can be interpreted as a resonating valence bond wave function to a very high degree of accuracy.

(58) Pauling, L. *Theoretical Organic Chemistry*, Proceedings of the Kekulé Symposium, 1958, Chemical Society; Butterworths: London, 1959.

(59) Schultz, P. A.; Messmer, R. P. *J. Am. Chem. Soc.*, following paper in this issue.