Bent Versus σ–π Bonds in Ethene and Ethyne: The Spin-Coupled Point of View

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Received October 22, 1992

Abstract: The bent-bond (equivalent) and σ–π orbital models for the carbon–carbon double and triple bonds in ethene and ethyne are compared for a whole hierarchy of one-configuration wave functions, starting from the Hartree–Fock wave function, passing through the generalized valence-bond wave function with perfect-pairing and strong-orthogonality constraints, and finishing with the most general wave function based on a single orbital product: the spin-coupled (SC) wave function. The results are also compared with those from complete-active-space self-consistent field (CAS SCF) calculations performed using equivalent divisions of the electrons into core and valence subsets. Equivalent orbitals have been found to yield lower-energy discriptions of the carbon–carbon multiple bonds when applied in the SC framework, where the full spin space is utilized for the valence electrons and *no* orthognality constraints are imposed. However, the energy differences between this model and that using σ and π orbitals are found to be much smaller than the differences between the energies of the corresponding SC and CAS SCF wave functions. Thus, from an energetical point of view, both constructions provide an equally good starting point for the treatment of correlation effects beyond the one-configuration approximation.

1. Introduction

For several decades, the orbital description of carbon–carbon double and triple bonds has been one of the controversial points in quantum chemistry. In fact, the first ideas about the shape of the simplest molecules involving multiple carbon–carbon bonds—ethene and ethyne can be traced back to as early as 1874 when van't Hoff and Le Bel[1] independently advanced the hypothesis of tetrahedral carbon. In their preception, the form of these molecules can be explained by stacking together two tetrahedra in two different ways—either edge-to-edge (for ethene) or face-to-face (for ethyne). Later on, this pre-quantum-chemical model was given a clearer mechanical interpretation in Baeyer's strain theory.[2] It can be regarded as a direct precursor to Pauling's concept of hybridization[3] where the bonding between the two carbon atoms in $H_2C{=}CH_2$ and $HC{\equiv}CH$ is considered to involve either two or three equivalent bent bonds, respectively, formed between pairs of carbon sp^3 hybrid orbitals. The second, alternative description of the multiple carbon–carbon bonds follows from Hückel's molecular orbital approach:[4] the double bond in ethene is supposed to comprise one σ and one π bond and the triple bond in ethyne to comprise one σ and two mutually perpendicular π bonds.

The problem of choosing one of the available quantum-chemical models for the central bonds in $H_2C{=}CH_2$ and $HC{\equiv}CH$ has two separate aspects related to the intended use of the orbitals. If the orbitals are to be employed for the construction of a one-configuration wave function, the better model is usually considered to be the one yielding a lower energy. In the limit of full configuration interaction (CI), the bent-bond and σ–π descriptions are indistinguishable. It is, however, to be expected that the rates of convergence of the corresponding two CI expansions will be different. Clearly, in this case the preferred model should be the one yielding more compact limited CI approximations to the full CI.

The form of the orbitals is physically significant only as long as each orbital is either singly or doubly occupied, i.e., in a one-configuration wave function. In the context of a multiconfiguration (or CI) wave function, the individual orbitals lose their physical relevance, especially with the increase of the number of configurations, and should be regarded as mathematical entities. Therefore, in the general chemical context, it is most interesting to compare the performance of the bent-bond and σ–π models for multiple carbon–carbon bonds within the framework of one-configuration wave functions.

The main types of one-configuration wave functions which are in wide use nowadays are the Hartree–Fock (HF), the generalized valence-bond (GVB),[5] and the spin-coupled (SC) wave functions.[6]

As is well-known, the canonical doubly occupied HF orbitals for ethene and ethyne incorporate the σ–π separation. However, the invariance of the closed-shell HF wave function with respect to any nonsingular linear transformation of the occupied orbitals implies that their form is nonunique. Localization of the canonical doubly occupied HF orbitals can be achieved by subjecting them to an appropriate unitary transformation and may lead to descriptions involving two or three equivalent bent (or, figuratively, "banana") doubly occupied localized orbitals spreading over the carbon–carbon double and triple bonds, respectively.[7] Thus, from an energetical point of view, the HF method does not distinguish between the σ–π and bent-bond models for the central bonds in

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(1) Cohen, E. In *Jacobus Henricus van't Hoff. Sein Leben und Wirken*; Akademische Verlagsgesellschaft: Leipzig, 1912; p 73 *Van't Hoff-Le Bell Centennial*; Ramsay, O. B., Ed.; ACS Symposium Series 12; American Chemical Society: Washington, DC, 1975.

(2) Baeyer, A. *Ber. Dtsch. Chem. Ges.* **1885**, *18*, 2269, 2277.

(3) Pauling, L. *J. Am. Chem. Soc.* **1931**, *53*, 1367.

(4) Hückel, E. *Z. Phys.* **1930**, *60*, 423.

(5) See, e.g.: Bobrowicz, F. M.; Goddard, W. A. In *Modern Theoretical Chemistry, Vol. 3. Methods of Electronic Structure Theory*; Schaefer, H. F., III, Plenum Press: New York, 1977; p 79.

(6) For recent reviews, see, e.g.: Cooper, D. L.; Gerratt, J.; Raimondi, M. *Adv. Chem. Phys.* **1986**, *69*, 319; *Int. Rev. Phys. Chem.* **1988**, *7*, 59; Advances in the Theory of Benzenoid Hydrocarbons, Gutman, I., Cyvin, S. J., Eds. In *Top Curr. Chem.* **1990**, *153*, 41. Gerratt, J.; Cooper, D. L.; Raimondi, M. In *Valence Bond Theory and Chemical Structure*; Klein, D. J., Trinajstić, N., Eds.; Elsevier: Amsterdam, 1990; p 287. Cooper, D. L.; Gerratt, J.; Raimondi, M. *Chem. Rev.* **1991**, *91*, 929.

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

0002-7863/93/1515-6863$04.00/0

$H_2C{=}CH_2$ and $HC{\equiv}CH$. In practice, the availability of orbital energies for the canonical (σ–π) description makes it the preferred one, as it offers certain interpretational advantages.

There are several applications of the most common variant of the GVB approach, incorporating perfect-pairing (PP) and strong-orthogonality (SO) restrictions, to systems involving carbon–carbon double and triple bonds (see, e.g., refs 8–11) which indicate that within the framework of the GVB-PP-SO approximation the σ–π model is invariably lower in energy (except for C_2F_2[10] and C_2F_4,[11] where the ordering is reversed). In fact, as it has been pointed out by Palke[12] and discussed by Messmer and Schultz,[10,13,14] the GVB-PP-SO approach can be considered to have an inherent bias toward σ–π orbitals which form strongly orthogonal pairs by symmetry. On the contrary, the bent-bond model has to adapt additionally to the SO constraints, i.e., they *do* actively limit its variational freedom. Indeed, when no strong orthogonality is assumed, the bent-bond description for ethene becomes the more stable one.[12] A minor drawback of Palke's calculations[12] is that they have been performed by means of an approximate optimization technique[15] which does not provide a completely variational wave function. "Full" GVB calculations on C_2F_2 and C_2F_4 reported in refs 13 and 14, respectively, favor the bent-bond model. In principle, the SC and the "full" GVB wave function (without SO and PP constraints) are identical by definition (see, e.g., their earliest formulations in refs 16a and 16b, respectively). However, a direct comparison between our current "active-space" SC approach[17] and the "full" GVB scheme employed by Messmer and Schultz is hindered by the absence of sufficient detail in their brief initial communications.[13,14] While the interpretation of the electronic structure of halogenated ethenes and ethynes is an interesting problem in itself, it seems more appropriate to study the nature of the carbon–carbon double and triple bonds using C_2H_4 and C_2H_2 as examples, where side effects, such as possible conjugation between the electrons involved in the central bond and the halogen lone pairs, are absent.

The primary aim of the present paper is to provide a comparative study of the bent-bond and σ–π descriptions of multiple carbon–carbon bonds in ethene and ethyne by means of the most general one-configuration wave function available currently: the SC wave function. The recent introduction[17] of a very flexible second-order constrained optimization approach for the completely variational determination of the SC wave function incorporating a doubly occupied core allows the performance of a series of calculations in which the wave function can be subjected, in turn, to all possible combinations of PP and SO constraints. As a consequence, we are in a position to present here treatments of the bent-bond and σ–π models for the central bonds in $H_2C{=}CH_2$ and $HC{\equiv}CH$ within the whole hierarchy of the most common one-configuration approaches. The results are compared with those from complete-active-space self-consistent field (CAS SCF) calculations performed at equivalent divisions of the electrons into core and valence subsets. This allows us to estimate the percentage of the total correlation energy for the particular core–valence partitioning which can be recovered by methods based on a single orbital product.

2. The Spin-Coupled Wave Function

The spin-coupled wave function for a system of N active (or valence) and $2n$ inactive (or core) electrons can be written as[17,18]

$$\Psi_{SM} = \hat{A}(\varphi_1\alpha\varphi_1\beta\varphi_2\alpha\varphi_2\beta\ldots\varphi_n\alpha\varphi_n\beta\psi_1\psi_2\ldots\psi_N\,\Theta_{SM}^N) \quad (1)$$

where $\hat{A}$ stands for the antisymmetrizer, φ_i and ψ_μ denote the core and valence (or SC) orbitals, respectively, and Θ_{SM}^N is the spin function for the valence electrons

$$\Theta_{SM}^N = \sum_{k=1}^{f_S^N} C_{Sk}\Theta_{SM;k}^N \quad (2)$$

Θ_{SM}^N represents a linear combination of *all* linearly independent spin eigenfunctions $\Theta_{SM;k}^N$ for a system of N electrons with total spin S and z-projection of the total spin M. The number of these eigenfunctions is given by

$$f_S^N = \binom{N}{N/2-S} - \binom{N}{N/2-S-1} \quad (3)$$

In the algorithm underlying the code employed in the present calculations, the $\Theta_{SM;k}^N$ terms are constructed in the Kotani basis.[19] If necessary, the spin function for the valence electrons Θ_{SM}^N can be transformed in a straightforward way to another (e.g., Rumer or Serber) spin basis,[20] i.e.,

$$\Theta_{SM}^N = \sum_{k=1}^{f_S^N} {}^{\mathrm{K}}C_{Sk}\,{}^{\mathrm{K}}\Theta_{SM;k}^N = \sum_{k=1}^{f_S^N} {}^{\mathrm{S}}C_{Sk}\,{}^{\mathrm{S}}\Theta_{SM;k}^N = \sum_{k=1}^{f_S^N} {}^{\mathrm{R}}C_{Sk}\,{}^{\mathrm{R}}\Theta_{SM;k}^N \quad (4)$$

where the additional superscripts (cf. eq 2) denote the selected spin basis (K for Kotani, R for Rumer, and S for Serber). Throughout this paper we assume the "standard" ordering of spin bases related to the different paths on the Kotani branching diagram.[19]

The core and SC orbitals are approximated, as in molecular orbital (MO)-based theories, by expansions in a suitable finite basis set of m atomic orbitals (AOs)

$$\varphi_i = \sum_{p=1}^{m} c_{ip}\chi_p; \quad \psi_\mu = \sum_{p=1}^{m} c_{\mu p}\chi_p \quad (5)$$

The orbital coefficients $c_{ip}, c_{\mu p}$ and the spin-coupling coefficients C_{Sk} are considered to form a set of variational parameters determining the energy corresponding to wave function 1. The simultaneous optimization of the energy with respect to *all* variational parameters is achieved through a second-order nonlinear elimination constrained minimization algorithm described in detail in ref 17.

The CAS SCF approach employs $D(N,N,S) = [(N+1)/(2S+1)]\,(f_S^N)^2$ configuration state functions (CSFs) for a system of N active electrons in N orbitals with total spin S. It is invariant with respect to any nonsingular transformation of the active orbitals, and, as a consequence, these last can be chosen to be orthonormal. In contrast, the SC wave function represents a *single* CSF built of singly occupied *nonorthogonal* orbitals. It is, of course, possible to represent the SC wave function as an expansion in terms of more familiar entities, such as Slater determinants. The number of determinants in the expansion is equal to the number of unique products of one-electron spin functions (α and β) defining Θ_{SM}^N, i.e., $\binom{N}{N/2-S}$.

The wave function ansatz used by Palke in his calculations on ethene[12] is a special case of the definition of the SC wave function 1. It corresponds to a restriction of the spin function for the

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

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

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

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

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

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

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

(15) Kirtman, B.; Palke, W. E.; Chipman, D. M. *J. Chem. Phys.* **1976**, *65*, 2556.

(16) (a) Gerratt, J.; Lipscomb, W. N. *Proc. Natl. Acad. Sci. U.S.A.* **1968**, *59*, 332. (b) Ladner, R. C.; Goddard, W. A., III *J. Chem. Phys.* **1969**, *51*, 1073.

(17) Karadakov, P. B.; Gerratt, J.; Cooper, D. L.; Raimondi, M. *J. Chem. Phys.* **1992**, *97*, 7637.

(18) Walters, S. G.; Penotti, F.; Gerratt, J.; Raimondi, M. *Mol. Phys.* **1987**, *61*, 1341. Walters, S. G. Ph.D. Thesis, University of Bristol, 1983.

(19) Pauncz, R. *Spin Eigenfunctions*; Plenum Press: New York, 1979.

(20) Raos, G.; Gerratt, J.; Cooper, D. L.; Raimondi, M. *Mol. Phys.* **1993**, *79*, 197. Karadakov, P. B.; Gerratt, J. *SPINS* (a program for symbolic generation and transformation of spin functions), unpublished.

valence electrons Θ_{SM}^{N} (see eq 2) to its perfect-pairing component only, which for $M = S$ is given by

$$^{\mathrm{K}}\Theta_{SS;\mathfrak{PP}}^{N} \equiv {}^{\mathrm{R}}\Theta_{SS;1}^{N} \equiv {}^{\mathrm{S}}\Theta_{SS;\mathfrak{PP}}^{N} = 2^{-1/2}[\alpha(1)\beta(2) - \alpha(2)\beta(1)]...2^{-1/2}[\alpha(N-2S-1)\beta(N-2S) - \alpha(N-2S)\beta(N-2S-1)]\alpha(N-2S+1)...\alpha(N) \quad (6)$$

The perfect-pairing assumption combined with a further strong-orthogonality requirement reduces wave function 1 to the GVB-PP-SO wave function.[5] The strong-orthogonality concept limits the nonorthogonality between the valence orbitals ψ_μ to within orbital pairs only, i.e.,

$$\langle\psi_{2\mu-1}|\psi_{2\nu-1}\rangle = \langle\psi_{2\mu-1}|\psi_{2\nu}\rangle = \langle\psi_{2\mu}|\psi_{2\nu-1}\rangle = \langle\psi_{2\mu}|\psi_{2\nu}\rangle = \left\langle \begin{Bmatrix}\psi_{2\mu-1}\\ \psi_{2\mu}\end{Bmatrix} \middle| \psi_\rho \right\rangle = 0 \ (\mu \neq \nu = 1,2,...,N/2 - S; \ \rho = N - 2S + 1,...,N) \quad (7)$$

The current version of our SC code[17] is capable of optimizing the energy corresponding to wave function 1 under the additional constraints yielding both the particular case of the wave function employed by Palke,[12,15] as well as the GVB-PP-SO wave function. It is also possible to impose and maintain a predefined set of symmetry constraints which influence the shape of the SC orbitals and determine the overall spatial symmetry of the SC wave function.

As is well-known,[6] the SC orbitals in most cases are obtained in a highly localized form and frequently resemble deformed hybrid atomic orbitals. The SC picture of a particular type of chemical bond, such as C–H, is usually transferable between different systems and is not influenced significantly by structural or even functional changes in the remaining part of the molecule. Therefore, correct SC descriptions of various chemical processes and phenomena can be obtained by considering only a relatively small number of valence electrons occupying SC orbitals localized in the region undergoing the most far-reaching structural changes.[21] This assertion is fully supported by our recent studies of the dissociation of the carbon-oxygen double bond in formaldehyde:[17] the SC description obtained with just four SC orbitals associated with the C=O bond is essentially unaltered by the introduction of four additional SC orbitals which are found to form two C–H bonds. Consequently, for ethene and ethyne it appears justified to restrict the SC part of wave function 1 to the region of the carbon–carbon multiple bond. The corresponding SC wave function for ethene includes four SC orbitals and takes the form (cf. eq 1)

$$\psi_{00} = \hat{A}[\varphi_1\alpha\varphi_1\beta\varphi_2\alpha\varphi_2\beta...\varphi_6\alpha\varphi_6\beta\psi_1\psi_2\psi_3\psi_4(C_{01}\Theta_{00;1}^{4} + C_{02}\Theta_{00;2}^{4})] \quad (8)$$

It is convenient to label the branching diagram (Kotani) spin eigenfunctions $^{\mathrm{K}}\Theta_{00;1}^{4}$ and $^{\mathrm{K}}\Theta_{00;2}^{4}$ (which are used in the SC program) by the series of partial resultant spins obtained after coupling the individual spins of 1, 2, and 3 electrons, namely 1 $\equiv$ ($^1/_2$ 1 $^1/_2$) and 2 $\equiv$ ($^1/_2$ 0 $^1/_2$).

The SC wave function for ethyne incorporates six SC orbitals and can be written as

$$\psi_{00} = \hat{A}(\varphi_1\alpha\varphi_1\beta\varphi_2\alpha\varphi_2\beta...\varphi_4\alpha\varphi_4\beta\psi_1\psi_2...\psi_6 \sum_{k=1}^{5} C_{0k}\Theta_{00;k}^{6}) \quad (9)$$

The Kotani spin functions $^{\mathrm{K}}\Theta_{00;1}^{6}$ – $^{\mathrm{K}}\Theta_{00;5}^{6}$ can be denoted as 1 $\equiv$ ($^1/_2$ 1 $^3/_2$ 1 $^1/_2$), 2 $\equiv$ ($^1/_2$ 1 $^1/_2$ 1 $^1/_2$), 3 $\equiv$ ($^1/_2$ 0 $^1/_2$ 1 $^1/_2$), 4 $\equiv$ ($^1/_2$ 1 $^1/_2$ 0 $^1/_2$), and 5 $\equiv$ ($^1/_2$ 0 $^1/_2$ 0 $^1/_2$). In this case the consecutive numbers give the partial resultant spins for 1, 2, 3, 4, and 5 electrons.

Table I. Total Energies (in hartrees) and Percentages of the Correlation Energy Recovered (values in parentheses) Using the DZ Basis Set

method	orbital type	C_2H_4	C_2H_2
HF	any	–78.011 76 (0.0)	–76.799 54 (0.0)
SC-PP-SO	equivalent	–78.043 96 (57.1)	–76.851 69 (48.5)
SC-SO	equivalent	–78.045 09 (59.1)	–76.856 65 (53.1)
SC-PP[a]	σ–π	–78.051 99 (71.4)	–76.857 86 (54.3)
SC-PP	equivalent	–78.054 57 (76.0)	–76.865 51 (61.4)
SC[a]	σ–π	–78.054 76 (76.3)	–76.868 17 (63.9)
SC	equivalent	–78.054 89 (76.5)	–76.870 74 (66.3)
CAS SCF[b]	any	–78.068 11 (100.0)	–76.907 00 (100.0)

[a] Fulfillment of SO relations ensured by orbital symmetry. [b] "4 in 4" CAS SCF for C_2H_4, "6 in 6" CAS SCF for C_2H_2, simultaneous core and valence space optimization.

3. Results and Discussion

All calculations for ethene and ethyne were carried out at their experimental nuclear geometries[22] [C_2H_4, r(CC) = 1.339 Å, r(CH) = 1.086 Å, ∠HCH = 117.6° (point group D_{2h}); C_2H_2, r(CC) = 1.208 Å, r(CH) = 1.058 Å (point group $D_{\infty h}$)].

We employed two different basis sets: a standard double-ζ basis set[23] of (9s5p/4s) Gaussian functions contracted to [4s2p/2s] and a triple-ζ valence basis set of (10s6p/5s) Gaussian functions contracted to [5s3p/3s] and augmented by polarization functions with exponents d(C) = 0.72 and p(H) = 1.0.[24] For brevity, further in the text we shall refer to the two basis sets as DZ and TZVP, respectively. Unit scaling factors have been used throughout, except for the hydrogen s functions in the DZ basis set (scaling factors of 1.20 and 1.15).

In order to obtain solutions with σ–π separation, we expanded two of the four SC orbitals in the case of C_2H_4 in terms of basis functions symmetric with respect to the molecular plane (yz, the two carbons lie along the z coordinate axis) only and the other two in terms of basis functions antisymmetric with respect to the molecular plane. A similar approach was used for C_2H_2: two of the six SC orbitals were expanded in basis functions symmetric with respect to the xz and yz planes (it is assumed that the molecular axis is aligned along the z coordinate axis), the next two SC orbitals in terms of basis functions antisymmetric with respect to yz, and the remaining two in terms of basis functions antisymmetric with respect to xz.

Another type of symmetry adaptation was employed in the search for bent-bond solutions. For C_2H_4, the four SC orbitals were constrained to transform into one another under the symmetry operations of the point group D_{2h}. In the case of C_2H_2, the SC orbitals were required to reflect into each other in pairs through the symmetry plane ($\hat{\sigma}_{xy}$) perpendicular to the molecular axis; in addition, the coefficients corresponding to basis functions of σ symmetry were constrained to be the same in all three SC orbitals localized primarily on one of the carbon atoms, which was sufficient to ensure equivalence of these three orbitals: upon convergence they are related by $\hat{C}_3$ rotations about the molecular axis.

The total energies obtained with different wave functions based on the two orbital models are collected in Table I for the DZ basis

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[21] It should be mentioned, however, that the *simultaneous* optimization of the core together with the valence orbitals and SC coefficients[16] is a *crucial* point in achieving an unbiased and variationally correct core–valence separation. This is particularly important in cases where the core–valence separation does not follow from orbital symmetry only: for example, the use of a frozen core (see refs 14 and 15) seems to be inappropriate in calculations on halogenated ethenes and ethynes, in which the valence space comprises only the electrons directly involved in the double bond. The number of core orbitals in a calculation on C_2F_4 with four active electrons is 22, and in a calculation on C_2F_2, 12. In each of these cases at least four of the core orbitals utilize to a considerable extent basis functions which are strongly overlapping with the basis functions predominating the active orbitals.

[22] Herzberg, G. *Molecular Spectra and Molecular Structure. III. Electronic Spectra and Electronic Structure of Polyatomic Molecules*; Van Nostrand Reinhold: New York, 1966; pp 629, 611.

[23] Huzinaga, S. *J. Chem. Phys.* **1965**, *42*, 1293. Dunning, T. H. *Ibid.* **1970**, *53*, 2823.

[24] Dunning, T. H. *J. Chem. Phys.* **1971**, *55*, 716.

Table II. Total Energies (in hartrees) and Percentages of the Correlation Energy Recovered (values in parentheses) Using the TZVP Basis Set

method	orbital type	C_2H_4	C_2H_2
HF	any	−78.060 50 (0.0)	−76.846 32 (0.0)
SC[a]	σ–π	−78.101 58 (76.1)	−76.910 50 (62.6)
SC	equivalent	−78.102 46 (77.8)	−76.914 00 (66.0)
CAS SCF[b]	any	−78.114 45 (100.0)	−76.948 86 (100.0)

[a] Fulfillment of SO relations ensured by orbital symmetry. [b] "4 in 4" CAS SCF for C_2H_4, "6 in 6" CAS SCF for C_2H_2, simultaneous core and valence space optimization.

Table III. Selected Overlaps and Weights (${}^{K}P_{02} = {}^{K}C_{02}^2$) of the Perfect-Pairing Spin Function in the Spin Function for the Valence Electrons (C_2H_4, DZ Basis Set, Orbital Ordering as in Figures 4 and 5)

method	orbital type	$\langle\psi_1\vert\psi_2\rangle$	$\langle\psi_3\vert\psi_4\rangle$	$\langle\psi_1\vert\psi_3\rangle$	${}^{K}P_{02} \times 100$
SC-PP-SO	equivalent	0.812	0.812	0.0	100.0
SC-SO	equivalent	0.810	0.810	0.0	98.0
SC-PP	σ–π	0.878	0.636	0.0	100.0
SC-PP	equivalent	0.844	0.844	0.552	100.0
SC	σ–π	0.878	0.629	0.0	96.1
SC	equivalent	0.829	0.829	0.463	98.3

Table IV. Selected Overlaps and Weights (${}^{K}P_{05} = {}^{K}C_{05}^2$) of the Perfect-Pairing Spin Function in the Spin Function for the Valence Electrons (C_2H_2, DZ Basis Set, Orbital Ordering as in Figures 6 and 7)

method	orbital type	$\langle\psi_1\vert\psi_2\rangle$	$\langle\psi_3\vert\psi_4\rangle$	$\langle\psi_1\vert\psi_3\rangle$	${}^{K}P_{05} \times 100$
SC-PP-SO	equivalent	0.799	0.799	0.0	100.0
SC-SO	equivalent	0.794	0.794	0.0	92.0
SC-PP	σ–π	0.908	0.691	0.0	100.0
SC-PP	equivalent	0.874	0.874	0.620	100.0
SC	σ–π	0.906	0.677	0.0	82.9
SC	equivalent	0.800	0.800	0.328	88.2

set and Table II for the TZVP basis set. As the main tendencies observed in the HF, SC, and CAS SCF results obtained with the DZ basis set are preserved in the TZVP basis, we did not repeat all DZ calculations with the larger basis set.

At the SC level, i.e., when no orthogonality constraints are imposed on the valence orbitals and the spin function for the valence electrons is allowed to span the full spin space, for both molecules the wave functions constructed from bent-bond (equivalent) orbitals were found to be lower in energy than those incorporating the σ–π separation. The differences between the energies of the bent-bond and σ–π solutions are very small in the DZ basis and slightly larger, but still insignificant, in the TZVP basis.

The introduction of the strong-orthogonality constraints leads to a reordering of the energies of the wave functions corresponding to the two orbital models. The highest energy solutions from Table I are those with bent-bond orbitals subjected to strong-orthogonality constraints (the SC-PP-SO wave function is identical to the GVB-PP-SO wave function). The comparison between the SC-PP-SO, SC-SO, SC-PP, and SC energies reveals that the strong-orthogonality constraints influence the energies of wave functions built from equivalent orbitals to a much greater extent than the restriction of the spin space to the perfect-pairing spin function only. Indeed, it can be observed in Tables III and IV that overlaps which are forced to be zero by the SO constraints (see the $\langle\psi_1|\psi_3\rangle$ columns for C_2H_4 and C_2H_2, respectively) assume significantly nonzero values when the orbitals are allowed to be nonorthogonal. On the other hand, in all cases when the full spin space was employed, the spin function for the valence electrons was found to be dominated by its perfect-pairing component (see Tables III and IV). This is by no means unexpected, because all calculations were performed at the equilibrium geometries of C_2H_4 and C_2H_2. But should one wish to describe the dissociation of the carbon-carbon double and triple bonds in ethene and ethyne, the correct molecular fragments can be obtained only by employing the full two- or five-dimensional spin spaces, respectively, for the electrons involved in the corresponding multiple bonds, as it has been demonstrated with the SC descriptions of the breaking of the triple carbon–nitrogen bond in HCN[25] and of the double carbon–oxygen bond in formaldehyde.[17]

It is interesting to note that the orbital overlaps calculated using the perfect-pairing spin functions only are larger than those calculated with all spin functions (see Tables III and IV). This can be attributed to the possibility of partial triplet coupling between the spins of pairs of electrons introduced with the full spin space, which tends to reduce the overlaps between the relevant orbitals.

The changes in the shape of the bent-bond orbitals under the influence of the strong-orthogonality and perfect-pairing constraints are more apparent in ethyne, where the triple bond implies a denser "crowding" of the orbitals. One of the six equivalent orbitals from the SC-PP-SO wave function of the bent-bond model is displayed in Figure 1a; its counterparts from the SC-PP and SC wave functions are presented in Figures 1b and 1c, respectively. The orbital stemming from the SC-SO wave function (not shown) is almost indistinguishable from the one taken from the SC-PP-SO wave function. The visual changes in the form of the orbitals included in Figure 1 closely parallel the corresponding changes in the orbital overlaps from Table IV. It should be mentioned that in their overall shape our bent-bond orbitals are very similar to orbitals obtained by other authors (see, e.g., refs 10–12, 14).

Two of the σ and π orbitals from the SC wave function with σ–π separation are shown in Figure 2. The perfect-pairing constraints have little influence on the shape of these orbitals—the orbitals from the SC-PP wave function based on the σ–π model strongly resemble those from Figure 2 (see also ref 8).

The orbitals in ethene look very similar to those in ethyne. They respond in an analogous way to the introduction of SO and PP constraints, but the changes are less obvious.

It is instructive to derive the analogues to the well-known classical VB resonance pictures arising from the SC descriptions of the carbon–carbon multiple bonds in ethene and ethyne. This can be achieved by transforming the spin functions for the valence electrons (eq 2) from the Kotani basis, utilized in the computational algorithm, to the Rumer basis (see eq 4 and refs 19, 20). The results are shown schematically in Figures 4–7. The Rumer spin functions are denoted by indicating the electrons coupled to singlet pairs, i.e., $(\ldots,\mu\text{–}\nu,\ldots)$ corresponds to a factor of $2^{-1/2}[\alpha(\mu)\beta(\nu) - \alpha(\nu)\beta(\mu)]$ in the respective spin function. The weight ${}^{R}P_{Sk}$ of a particular Rumer spin function ${}^{R}\Theta^N_{SM;k}$ in the spin function for the valence electrons Θ^N_{SM} is defined as follows (it is assumed that $\langle\Theta^N_{SM}|\Theta^N_{SM}\rangle = 1$):

$$ {}^{R}P_{Sk} = {}^{R}C_{Sk} \sum_{l=1}^{f_S^N} \langle {}^{R}\Theta^N_{SM;k} | {}^{R}\Theta^N_{SM;l} \rangle \, {}^{R}C_{Sl} \qquad (10) $$

(The orthogonal Kotani and Serber spin bases give rise to much simpler weight expressions, i.e., ${}^{K,S}P_{Sk} = {}^{K,S}C_{Sk}^2$).

The Rumer spin functions for the four electrons involved in the carbon–carbon double bond in ethene (see Figures 4 and 5), just as the Kotani spin functions (Table III) are dominated by their perfect-pairing components. It is interesting to observe that despite the strong overlaps between orbitals ψ_1 and ψ_4, ψ_2 and ψ_3 in the bent-bond case, $\langle\psi_1|\psi_4\rangle = \langle\psi_2|\psi_3\rangle = 0.562$ (TZVP basis, the corresponding value in the DZ basis is 0.555), the pairing scheme 2 ≡ (1–4,2–3) contributes very little to Θ^4_{00} (see Figure 5).

The results for ethyne (Figures 6 and 7) are much more revealing. They suggest a significant "resonance" between the perfect-pairing scheme 1 ≡ (1–2,3–4,5–6) and the three pairing schemes which preserve one of its pairs: 2 ≡ (1–4,2–3,5–6), 3 ≡

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(25) Sironi, M.; Raimondi, M.; Cooper, D. L.; Gerratt, J. *J. Mol. Struct.* (*THEOCHEM*) **1991**, *229*, 279.

(26) Cansdale, J. C.; Karadakov, P. B.; Gerratt, J.; Cooper, D. L.; Raimondi, M., unpublished results.

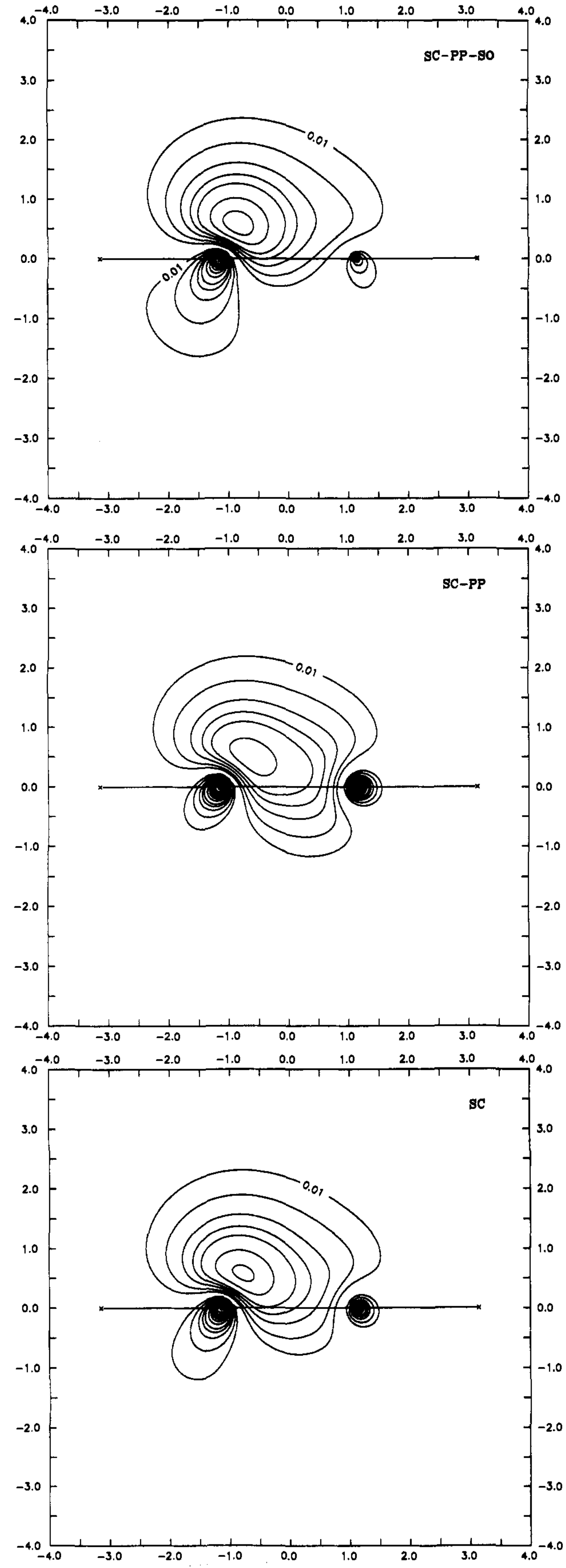


Figure 1. One of the six equivalent spin-coupled orbitals for C_2H_2 in the bent-bond model: (a) from the SC-PP-SO wave function; (b) from the SC-PP wave function; and (c) from the SC wave function. Each orbital is represented by the contours of $|\psi_\mu(\mathbf{r})|^2$ in the plane, with respect to which the orbital is symmetric. Contour levels requested at 0.01, 0.025(0.025)0.1, 0.15(0.05)0.4, 0.5(0.2)1.1, 1.5, 2, 5, 10, 20, and 50. Experimental geometry, DZ basis set, all distances in bohr.

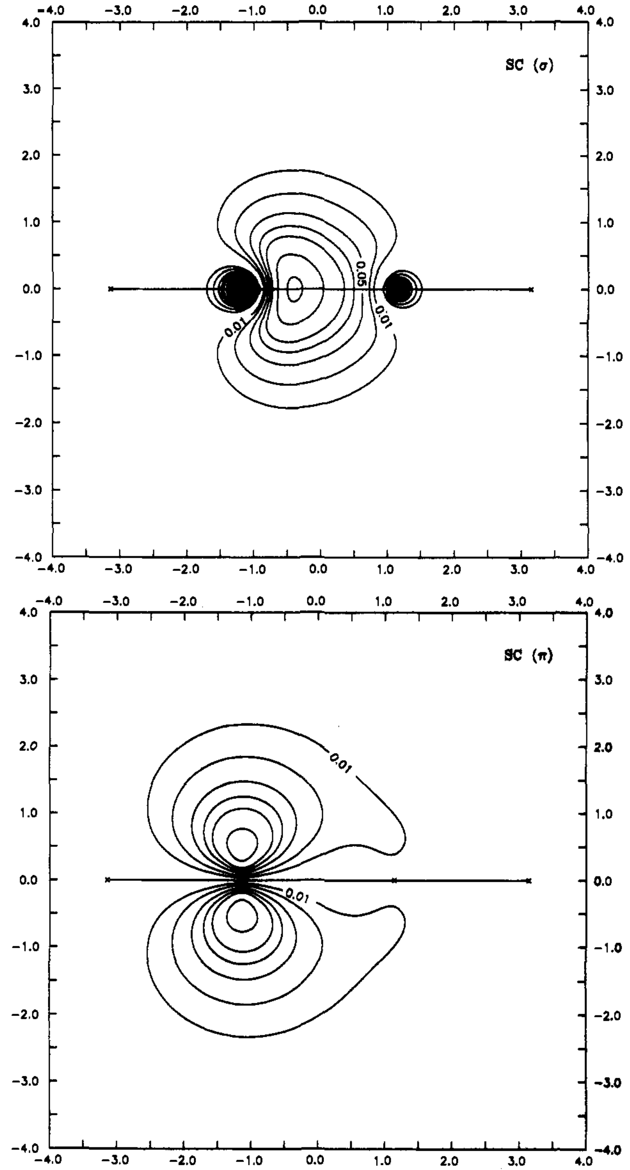


Figure 2. One of the two σ (a) and one of the four π (b) spin-coupled orbitals from the SC wave function for C_2H_2. The orbitals are represented by the contours of $|\psi_\mu(\mathbf{r})|^2$ in planes, with respect to which they are symmetric. Contour levels requested at 0.01, 0.025(0.025)0.1, 0.15(0.05)0.4, 0.5(0.2)1.1, 1.5, 2, 5, 10, 20 and 50. Experimental geometry, DZ basis set, all distances in bohr.

(1–2,3–6,4–5), and 5 ≡ (1–6,2–5,3–4). It is obvious from the figures that spin functions 2 ≡ (1–4,2–3,5–6) and 5 ≡ (1–6,2–5,3–4) in the σ–π model are related by symmetry. The same applies to spin functions 2 ≡ (1–4,2–3,5–6), 3 ≡ (1–2,3–6,4–5), and 5 ≡ (1–6,2–5,3–4) in the bent-bond model. The weight of spin function 4 ≡ (1–6,2–3,4–5) is identically equal to 0 in both cases, as it does not remain invariant under reflection in the $\hat{\sigma}_{xy}$ plane of symmetry. These symmetry considerations indicate that the number of spin-coupling coefficients which can be varied independently, while preserving the overall symmetry of the SC wave function, is *three* for the σ–π model and just *two* for the bent-bond model. Thus, the SC wave function incorporating σ–π separation has *more* spin degrees of freedom than the SC wave function constructed from equivalent orbitals. However, as it can be easily demonstrated, the σ–π construction allows *less* orbital degrees of freedom than its bent-bond counterpart.

It is difficult to compare the relative importance of the spin and orbital degrees of freedom, but the rather close energy values corresponding to the SC wave functions implementing the two orbital models (see Tables I and II) suggest that the balance is rather delicate.

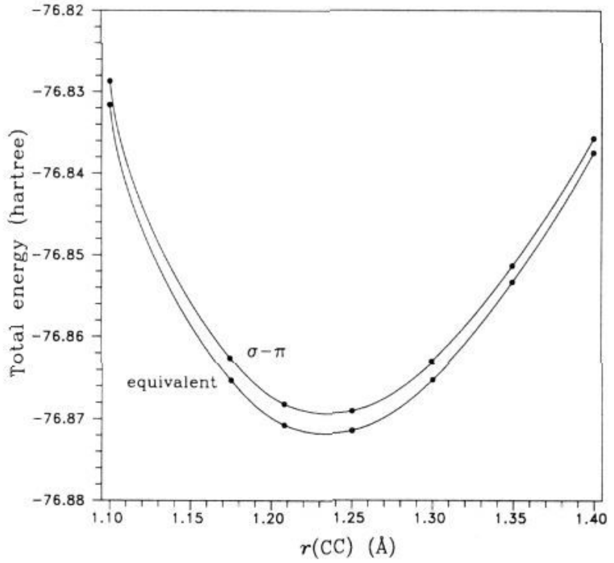
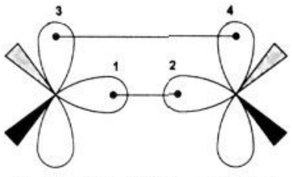
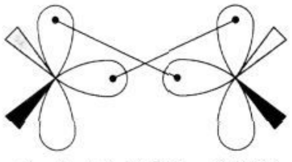


Figure 3. SC potential curves corresponding to variation of the carbon–carbon triple bond length in ethyne close to its equilibrium value for the equivalent and σ–π orbital models.

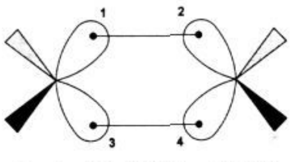


$1 \equiv (1-2, 3-4)$, ${}^{\mathrm{R}}P_{01} = 0.85498$

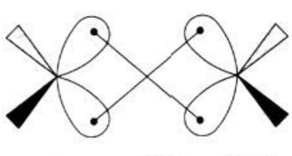


$2 \equiv (1-4, 2-3)$, ${}^{\mathrm{R}}P_{02} = 0.14502$

Figure 4. Rumer spin functions for C_2H_4 (σ–π model), and their weights in the spin function for the valence electrons (TZVP basis).

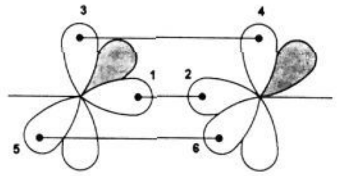


$1 \equiv (1-2, 3-4)$, ${}^{\mathrm{R}}P_{01} = 0.92144$

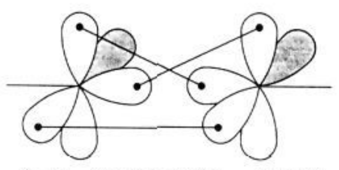


$2 \equiv (1-4, 2-3)$, ${}^{\mathrm{R}}P_{02} = 0.07856$

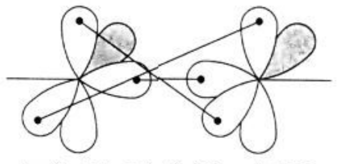
Figure 5. Rumer spin functions for C_2H_4 (bent-bond model), and their weights in the spin function for the valence electrons (TZVP basis).



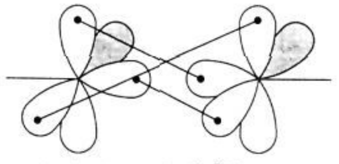
$1 \equiv (1-2, 3-4, 5-6)$, ${}^{\mathrm{R}}P_{01} = 0.44754$



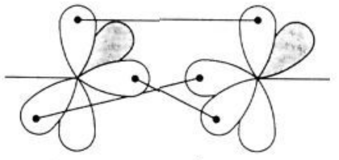
$2 \equiv (1-4, 2-3, 5-6)$, ${}^{\mathrm{R}}P_{02} = 0.21169$



$3 \equiv (1-2, 3-6, 4-5)$, ${}^{\mathrm{R}}P_{03} = 0.12909$



$4 \equiv (1-6, 2-3, 4-5)$, ${}^{\mathrm{R}}P_{04} = 0.0$



$5 \equiv (1-6, 2-5, 3-4)$, ${}^{\mathrm{R}}P_{05} = 0.21169$

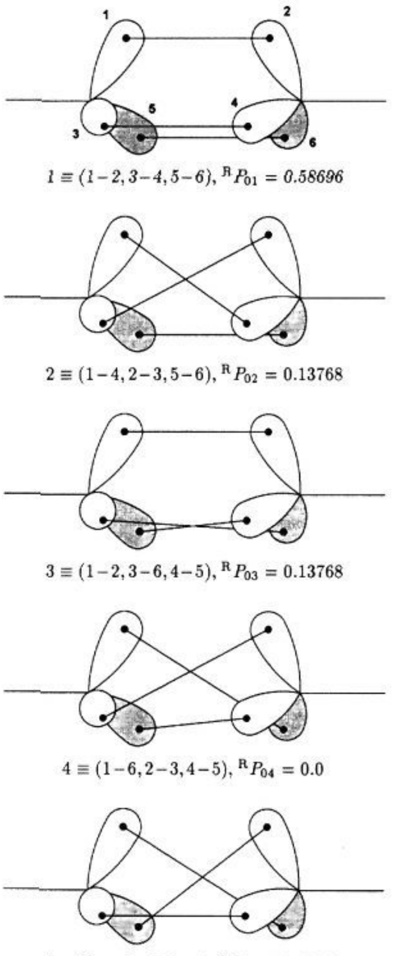
Figure 6. Rumer spin functions for C_2H_2 (σ–π model), and their weights in the spin function for the valence electrons (TZVP basis).

The percentage of the total "N in N" CAS SCF correlation energy recovered by the different correlated one-configuration wave functions we studied varies between 48.5 and 77.8% (see Tables I and II). It should be noted that the largest improvement observed in Table I is due to the removal of the SO constraints in the SC-PP-SO wave function for the bent-bond model in ethene (18.9%) and the smallest, to the extension of the resulting SC-PP wave function to the full spin space for the valence electrons (0.5%). The effect of using all spin functions is more pronounced in ethyne, where the additional correlation introduced can be as large as 9.6% (compare the SC and SC-PP results with σ–π separation in Table I).

Thus, an unbiased assessment of the performance of the bent-bond and σ–π orbital models in the case of a one-configuration wave function is possible only on the basis of calculations free from any SO and PP constraints in the valence subspace.

On the whole, the best correlated wave function based on a single orbital product can recover up to ca. 77–78% of the total "4 in 4" CAS SCF correlation energy for ethene. It is less effective for ethyne, where ca. 66% of the total "6 in 6" CAS SCF correlation energy can be achieved.

We conclude that although the model using equivalent orbitals leads to lower-energy descriptions of the carbon–carbon multiple bonds when applied in the framework of the most general wave function based on a single orbital product, the SC wave function, the energy differences between this model and the model making use of σ and π orbitals are much smaller than the differences between the energies of the corresponding SC and CAS SCF wave functions. Thus, from an energetical point of view, the σ–π construction should provide an equally good starting point for the treatment of correlation effects beyond the one-configuration approximation. Any further improvement of the SC wave function in the direction in the "N in N" CAS SCF wave function is bound to decrease the energy difference between the bent-bond and σ–π models even further because this difference has to disappear entirely in the CAS SCF limit. The orthogonality between the σ and π orbitals could turn out to be an important advantage when handling multiconfigurational VB or CI wave functions,



$1 \equiv (1-2, 3-4, 5-6),\ {}^{R}P_{01} = 0.58696$

$2 \equiv (1-4, 2-3, 5-6),\ {}^{R}P_{02} = 0.13768$

$3 \equiv (1-2, 3-6, 4-5),\ {}^{R}P_{03} = 0.13768$

$4 \equiv (1-6, 2-3, 4-5),\ {}^{R}P_{04} = 0.0$

$5 \equiv (1-6, 2-5, 3-4),\ {}^{R}P_{05} = 0.13768$

Figure 7. Rumer spin functions for C_2H_2 (bent-bond model), and their weights in the spin function for the valence electrons (TZVP basis).

which may easily outweigh the slightly lower energy of the single-configuration reference provided by the bent-bond model.

The SC potential energy curves for the dissociation of the carbon–carbon double and triple bonds in the two cases (equivalent and σ–π orbitals) are very close at all carbon–carbon distances. Figure 3 (results taken from ref 26) shows the two curves for ethyne near the equilibrium r(CC) on an enlarged scale [r(CH) is kept fixed]. In the $r(\mathrm{CC}) \rightarrow \infty$ limit, both orbital models give rise to two CH fragments in the $^4\Sigma^-$ state.[27] A small SC VB calculation (see ref 6) would be necessary to produce the correct $^2\Pi$ states of the radicals.

In our calculations the bent-bond SC wave function is obtained to be lower in energy than its σ–π counterpart just by 0.000 13 (0.000 88) hartree for C_2H_4 and by 0.002 57 (0.003 50) hartree for C_2H_2 in the DZ (TZVP) basis. This contrasts with the results of Messmer and Schultz, who obtain differences of 0.005 56 and 0.006 98 hartree between the energies of the σ–π and bent-bond "full" GVB solutions for C_2F_4[15] and C_2F_2,[14] respectively, using a basis of double-ζ quality augmented with polarization functions on the carbons only [the results for C_2F_4[15] are as follows: HF energy, –473.488 80 hartrees); "full" GVB energy (σ–π), –473.533 84 hartrees; "full" GVB energy (bent-bond), –473.539 40 hartrees; the choice of the core orbitals is not specified]. Our preliminary calculations for C_2F_4[29] (DZ basis as defined in this Section, D_{2h} geometry optimized at the HF level in the DZ basis), using a completely variational SC wave function with four valence electrons and 22 doubly-occupied core orbitals indicate a difference of 0.003 57 hartree betwen the σ–π and bent-bond models [HF energy, –473.370 250 hartrees; SC energy (σ–π), –473.419 17 hartrees; SC energy (bent-bond), –473.422 74 hartrees]. A comparison with our results for ethene demonstrates that the larger stabilization energies of the bent-bond solutions for fluorinated ethene and ethyne do not necessarily have to be observed in other systems containing multiple carbon–carbon bonds. At this point, it is appropriate to repeat Palke's concluding sentence:[12] "It is tempting to presume that banana bonds are the best description in general for multiple bonds, but conjugated systems may prove to be interestingly different." The results of our calculations suggest that the repeated demonstrations of the supremacy of the bent-bond model for a variety of systems containing multiple bonds, based predominantly on calculations at the GVB-PP-SO level performed by Messmer *et al.*,[30] require additional verification in the framework of the fully-variational SC (or an analogous "full" GVB) wave function, combined with comparisons to the corresponding "N in N" CASSCF results, before a final assessment can be made of their chemical relevance.

The discussion of the possible existence of broken-symmetry SC solutions lower in energy than both the σ–π and bent-bond models for C_2H_4 and C_2H_2 is beyond the scope of the present paper. However, it should be mentioned that the GVB-PP-SO study of C_2F_4 performed by Carter and Goddard[11] has indicated that the lowest solution does not possess the full symmetry of the system and is characterized by "skewed" σ and π orbitals. We are currently performing investigations aimed at locating the possible broken-symmetry SC solutions for several systems, including C_2H_4 and C_2H_2. The results of these investigations, the implications of the related SC "symmetry dilemma", and the ways to resolve it, which generally might involve abandoning the one-configuration approximation, will be published separately.

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(27) The identity of the bent-bond and σ–π models for the CH fragments follows from the fact that the spins of the three electrons occupying the active orbitals on each fragment are coupled to the maximum spin ($^3/_2$). It can be shown[28] that in such cases the energy of the SC wave function is invariant with respect to any nonlinear transformation of the active orbitals involved in each of the high-spin subsystems.

(28) Gerratt, J. *Adv. Atom. Molec. Phys.* **1971**, *7*, 141.

(29) Karadakov, P. B.; Gerratt, J.; Cooper, D. L.; Raimondi, M., manuscript in preparation.

(30) See, e.g.: Schultz, P. A.; Messmer, R. P. In *Molecules in Natural Science and Medicine*; Maksić, Z. B., Eckart-Maksić, M., Eds.; Ellis-Horwood: New York, 1991; p 309 and references therein.