Theor Chim Acta (1995) 92: 49–59

Theoretica
Chimica Acta

The nature of the carbon–carbon bond in the C_2 and C_2H_2 molecules

Alessandra Forni, Maurizio Sironi

Dipartimento di Chimica Fisica ed Elettrochimica, Universita' di Milano, Via Golgi 19,
I-20133 Milano, Italy

Received May 6, 1994/Final revision received October 24, 1994/Accepted December 6, 1994

Summary. The alternative description of the carbon–carbon bond in the C_2 and C_2H_2 molecules in terms of σ/π or bent "banana" orbitals is analyzed here within the framework of the spin-coupled method. In particular, the first all-valence electron calculations on both models are presented. Comparison with previous work on these molecules demonstrates the importance of correlating all the valence electrons, especially for the C_2 molecule which shows a change in relative stability of the two bond models when nonbonding electrons are correlated.

The orbital picture provided by spin-coupled orbitals is presented together with a discussion on similarities and differences between the orbitals of C_2 and C_2H_2.

Key words: Multiple bond – Bent-bond – Spin-coupled wavefunction – Non-orthogonal spin–orbitals

1. Introduction

The description of the nature of multiple bonds is still an open problem, as results from recent work where double and triple bonds in C_2H_4 and C_2H_2 [1, 2] and in some other small molecules [2–4] are extensively studied.

The discussion dates back to the thirties, when two possible qualitative descriptions of carbon–carbon multiple bonds were proposed, that is the classical σ/π scheme [5] with one bond, σ, along the internuclear axis and one (or two) bond(s), π, perpendicular with respect to the same axis and orthogonal to each other, and the scheme with equivalent bent bonds [6], originating from the overlap of tetrahedral lobes on each C atom. Since the shape of the orbitals cannot be established experimentally, the importance of the question lies essentially in which representation is more useful for chemists in rationalizing properties (e.g. ionization potentials) and reactivity of compounds containing multiple bonds. In this sense the valence bond approach in the framework of one-configuration wave functions, where the orbitals on each center are localized hybrid atomic-like orbitals, proved to be a powerful tool.

The first quantitative results about multiple bonds for the C_2H_4, C_2H_2 and C_2 molecules [7] were obtained within the generalized valence bond (GVB) method [8] with the restriction that the orbitals of one pair were orthogonal to the orbitals of all the other pairs (strong orthogonality, SO). In addition only one spin structure was considered (perfect pairing, PP). In this pioneering work the σ/π solution was found to be the most stable one.

The question was raised again several years later, and the effect of the SO and PP constraints was systematically analyzed [1–4, 9–13]. For most of the small molecules considered the GVB-PP(SO) wave function involves greater stability for the σ/π-bonds with respect to the bent bonds, only a few cases (CO_2 [13], C_2F_4 [2], Si_2H_4 [2]) showing the opposite trend.

When no strong orthogonality is assumed, as first remarked by Palke [9] for the case of the C_2H_4 and C_2H_2 molecules, the bent bond model becomes the more stable one and a significant overlap between hybrids on the same carbons is obtained. From these results, the SO approximation, which constrains this overlap to be zero, was interpreted as a serious bias, leading to an increase of energy for the bent bonds solution. In contrast, the σ/π model is not subject to any extra constraint, the orbitals being in any case orthogonal by symmetry. This consideration provides a plausible explanation for the energetic reordering observed when the strong orthogonality constraint is removed.

For the same reason, for the cases where this approximation favors the bent bonds, the relative stability with respect to the σ/π model should be underestimated [10].

The complete removal of the SO and PP constraints produces the "full GVB" wave function, which is identical to the spin coupled (SC) wave function. The results obtained within these approaches for C_2H_4 and C_2H_2 [1, 2] and several other molecules [2–4, 12, 13] show a common trend, equivalent bent orbitals yielding a lower-energy description of multiple bonds for most of the molecules considered. In this respect, the PP constraint does not appear such a serious limitation as the SO approximation. Nevertheless, in all of these last calculations only the electrons associated with the multiple bonds were correlated and it was our purpose to investigate the energetic trend when all the valence electrons are explicitly correlated. In fact, the anomalous behavior of N_2 [2], with the σ/π bond model favored with respect to the bent bond, was ascribed with high probability to the neglect of the correlation of lone-pair electrons.

Further calculations which support the bent-bond models have been recently carried out by Murphy et al. in the framework of a new generalized valence bond representation of CASSCF wave function [14].

Our calculations support the result cited above that for C_2H_2 the bent bond description is the most stable one, while for C_2 we found that correlation of all the valence electrons stabilizes the σ/π bond model with respect to the bent one. For this molecule the inclusion of all spin couplings is seen to be particularly important.

2. The spin coupled wave function

In this section we briefly review the main concepts of spin-coupled theory, since they are essential to understand the reported results. For a complete account of spin-coupled theory the reader is referred to other papers [15].

The spin-coupled wave function for a system of N electrons can be written as

$$\Psi_{S,M} = \sum_{k=1}^{f_S^N} c_{S,k} \hat{\mathscr{A}}(\phi_1 \phi_2 \cdots \phi_N \Theta_{S,M,k}^N) \qquad (1)$$

where $\hat{\mathscr{A}}$ stands for the antisymmetrizing operator, $\phi_1, \phi_2, \ldots, \phi_N$ are the N spin coupled orbitals describing the N electrons. $\Theta^N_{S,M,k}$ is the kth spin eigenfunction whose contribution to the spin coupled wave function is determined by the kth spin coupling coefficient, $c_{S,k}$. For a system of N electrons and total spin S (and projection M), there are f^N_S linearly independent spin eigenfunctions:

$$f^N_S = \frac{(2S+1)N!}{(\frac{1}{2}N+S+1)!(\frac{1}{2}N-S)!}.$$

The present calculations were carried out in the Rumer basis [16, 17], the transformation to other spin basis being straightforward [18].

It is worthwhile to observe that if in Eq. (1) we limit the summation to just the first Rumer basis function, i.e. the perfect pairing one, then the spin-coupled wave function coincides with the GVB–PP wave function [8]. If, in addition, we impose the strong orthogonality constraint between the spin-coupled orbitals, we obtain the GVB–PP(SO) wave function.

In order to determine the spin-coupled orbitals, ϕ_i, they are expanded in a set of basis functions ξ_j:

$$\phi_i = \sum_j^m c_{ij}\xi_j, \tag{2}$$

where m is the size of the basis set.

The coefficients c_{ij} are determined variationally together with the spin-coupling coefficients $c_{S,k}$, by means of a modified Newton–Raphson technique [19] which requires the computation of the first and second derivatives of the energy with respect to the variational coefficients [20].

In order to converge to a σ/π or a bent description of the electronic structure of the molecules under investigation, we have modified our code to include the possibility of establishing some constraints on the c_{ij} coefficients in Eq. (2).

The σ/π description is easily obtained constraining the c_{ij} coefficients to be zero when i belongs to the σ set and j to the π set or vice versa.

The bent description is obtained by taking just one spin-coupled orbital, say ϕ_1, which can assume both σ and π components, as independent; two other orbitals are obtained from it by 120-degree rotations:

$$\begin{aligned} \phi_2 &= C_3\phi_1, \\ \phi_3 &= C_3\phi_2 = C_3^2\phi_1. \end{aligned} \tag{3}$$

Finally the three other orbitals are obtained by reflection through a plane perpendicular to the molecular axis and located in the middle of the carbon–carbon bond:

$$\begin{aligned} \phi_4 &= \sigma_h\phi_1, \\ \phi_5 &= \sigma_h\phi_2 = \sigma_h C_3\phi_1, \\ \phi_6 &= \sigma_h\phi_3 = \sigma_h C_3^2\phi_1. \end{aligned} \tag{4}$$

Eqs. (3) and (4) give rise to constraints on the c_{ij} coefficients of Eq. (2).

It should be noted that these constraints ensure that the SC wave functions exhibit, in both bonding models, the correct spatial symmetry.

3. The spin-coupled wave function for C_2 and C_2H_2

We first performed a restricted closed shell Hartree-Fock calculation on each molecule, obtaining a set of m molecular orbitals: $\{MO_j\}_{j=1}^{m}$, m being the number of atomic basis functions. The first two MOs describe essentially the $1s^2$ core of the carbon atoms and hence are kept fixed in the successive spin-coupled calculations, while all the valence electrons are explicitly correlated. The spin-coupled wave function can be written as

$$\Psi_{S,M} = \sum_{k=1}^{f_S^N} c_{S,k} \hat{\mathscr{A}}(\mathrm{MO}_1\,\mathrm{MO}_1\,\mathrm{MO}_2\,\mathrm{MO}_2\,\Theta_{\mathrm{PP}}^4\,\phi_1\,\phi_2 \cdots \phi_N\,\Theta_{S,M,k}^N)$$

where Θ_{PP}^4 is the spin eigenfunction describing the perfect pairing between the first two pairs of molecular orbitals. Hence we are left with 8 spin-coupled orbitals for C_2 with 14 spin couplings ($f_0^8 = 14$) and 10 spin-coupled orbitals for C_2H_2 with 42 spin couplings ($f_0^{10} = 42$). In order to keep the valence orbitals orthogonal to the core orbitals, each of them is expanded in a basis consisting of the $m - 2$ remaining MOs:

$$\phi_i = \sum_{j=3}^{m} c_{ij} \mathrm{MO}_j$$

4. Computational details

We performed all the calculations at the experimental equilibrium nuclear geometries for C_2 [r(C–C) = 1.242 Å] [21] and C_2H_2 [r(C–C) = 1.208 Å, r(C–H) = 1.058 Å, linear] [22].

We used four different basis sets: a standard double-ζ basis set [23, 24] of ($9s5p/4s$) Gaussian functions contracted to [$4s2p/2s$], which we will denote DZ basis. This basis set was extended by adding a d polarization function on the C atoms with exponent 0.72 and a p polarization function on the H atoms with exponent 1.0, giving rise to a DZP basis. A larger basis set, which we will denote TZP basis, was obtained using a triple-ζ basis set of ($10s6p/5s$) Gaussian functions contracted to [$5s3p/3s$] and with the inclusion of the same polarization functions used in the DZP basis described above. Finally, the largest basis set that we used in these calculations, denoted as TZPE, was obtained leaving the basis functions of the TZP basis set uncontracted. Unit scaling factors have been used in all basis sets, with the exception of the hydrogen s functions in the DZ and DZP basis sets (scaling factor of 1.20 [23]).

The sizes of the basis sets employed for C_2 (C_2H_2) were: 20 (24), 30 (40), 38 (50), 66 (82) respectively for the DZ, DZP, TZP and TZPE basis sets.

The spin-coupled calculations were performed on the 8 valence electrons for the C_2 molecule, and on the 10 valence electrons for the C_2H_2 molecule, with the core electrons occupying the first two RHF molecular orbitals (essentially the $1s^2$ cores of the carbon atoms), which are kept frozen during the SC calculations.

All spin pairings were included in the calculations. For comparison, we separately carried out calculations with the perfect pairing only. All the calculations were carried out for both the σ/π and bent models. In addition we also report CASSCF results obtained with 8 electrons in 8 active orbitals for C_2 and 10 electrons in 10 active orbitals for C_2H_2.

5. Results and discussion

The values of the total energies obtained in the different calculations are reported in Table 1 for C_2 and in Table 2 for C_2H_2, together with the percentages of the correlation energy recovered with respect to the CASSCF wave function.

In Table 3 we show the differences between the energy values corresponding to the σ/π and bent descriptions of the triple bond, for the different basis sets. In all

Table 1. Total energies (in hartrees) for the two models of the triple bond for C_2 with different basis sets

Calculation		DZ basis set	DZP basis set	TZP basis set	TZPE basis set
RHF		– 75.356 44 (0.0)	– 75.389 46 (0.0)	– 75.398 48 (0.0)	– 75.398 92 (0.0)
SC-PP	σ/π	– 75.510 65 (61.5)	– 75.536 14 (61.8)	– 75.546 39 (61.9)	– 75.547 01 (62.0)
SC	σ/π	– 75.559 39 (80.9)	– 75.578 18 (79.5)	– 75.588 84 (79.7)	– 75.589 59 (79.8)
SC–PP	bent	– 75.518 58 (64.6)	– 75.544 90 (65.4)	– 75.554 91 (65.5)	– 75.555 53 (65.5)
SC	bent	– 75.557 40 (80.1)	– 75.576 85 (78.9)	– 75.587 21 (79.0)	– 75.587 85 (79.0)
CASSCF		– 75.607 28 (100.0)	– 75.626 97 (100.0)	– 75.637 24 (100.0)	– 75.637 96 (100.0)

The basis sets employed are described in text. RHF stands for restricted Hartree–Fock calculation. SC–PP stands for spin-coupled calculation with one structure, and SC for spin-coupled calculation with all the 14 allowed structures. The values in parentheses refer to the percentages of the correlation energy recovered. (All the calculations, with the exception of CASSCF, were performed with five *d* components)

Table 2. Total energies (in hartrees) for the two models of the triple bond for C_2H_2 with different basis sets

Calculation		DZ basis set	DZP basis set	TZP basis set	TZPE basis set
RHF		– 76.799 10 (0.0)	– 76.831 14 (0.0)	– 76.846 21 (0.0)	– 76.847 08 (0.0)
SC–PP	σ/π	– 76.886 84 (56.7)	– 76.913 91 (56.3)	– 76.930 16 (56.5)	– 76.931 49 (56.6)
SC	σ/π	– 76.903 87 (67.7)	– 76.928 94 (66.5)	– 76.944 70 (66.3)	– 76.946 18 (66.5)
SC–PP	bent	– 76.894 32 (61.5)	– 76.922 28 (62.0)	– 76.938 01 (61.8)	– 76.939 32 (61.9)
SC	bent	– 76.904 98 (68.4)	– 76.931 08 (67.9)	– 76.946 80 (67.7)	– 76.948 26 (67.9)
CASSCF		– 76.953 83 (100.0)	– 76.978 25 (100.0)	– 76.994 84 (100.0)	– 76.996 16 (100.0)

The basis sets employed are described in text. RHF stands for restricted Hartree–Fock calculation. SC–PP stands for spin-coupled calculation with one structure, and SC for spin-coupled calculation with all the 42 allowed structures. The values in parentheses refer to the percentages of the correlation energy recovered. (All the calculations, with the exception of CASSCF, were performed with five *d* components)

Table 3. Differences between the energies of the σ/π and bent models for C_2H_2 and C_2 using different basis sets (values are reported in millihartrees, a positive value indicates that the bent model is the favored one). The basis sets employed are described in text. SC–PP stands for spin-coupled calculation with one structure, and SC for spin-coupled calculation with all the allowed structures

		DZ basis set	DZP basis set	TZP basis set	TZPE basis set
SC–PP	C_2H_2	+ 7.48	+ 8.37	+ 7.85	+ 7.83
SC–PP	C_2	+ 7.93	+ 8.76	+ 8.52	+ 8.52
SC	C_2H_2	+ 1.11	+ 2.14	+ 2.10	+ 2.08
SC	C_2	– 1.99	– 1.33	– 1.63	– 1.74

cases the differences obtained are very small, of the order of a millihartree. An interesting aspect is the greater stability of the bent triple bond for C_2H_2 in contrast to the greater stability of the σ/π bond for C_2, in spite of the obvious similarity of the molecules. The same ordering is found with all the basis sets used, when all the spin couplings are included, and the energy gap is nearly independent of the basis set.

With the inclusion of just one structure, the opposite ordering in energy is observed in the case of the C_2 molecule, thus demonstrating the importance of including all spin couplings in order to obtain a proper description of the electronic structure of the molecule. The fundamental role played by spin couplings other than the perfect-pairing one in stabilizing the σ/π solution for the C_2 molecule is highlighted when the energy is computed with all spin couplings using the optimized orbitals obtained with just one structure. In this case the energy difference between the σ/π and the bent-bond model using the TZP basis set is -3.06 millihartrees, confirming that the inclusion of all spin couplings, even without a complete optimization of the orbitals, is by itself sufficient to stabilize the σ/π solution.

From the values reported in Tables 1 and 2 we note that the SC wave function recovers 65% to 80% of the correlation energy with respect to the CASSCF, which, due to invariance under linear transformation of the active orbitals among themselves, cannot discriminate between the σ/π and bent-bond models. However the differences in energy between the two models at the SC level are always less than 1% of the correlation energy, thus indicating that we cannot really choose between the two models just on the basis of the energies values.

The greater stability of the bent-bond description for C_2H_2 is in accord with previous SC calculations of Karadakov et al. [1] where just the electrons of the triple bond were correlated, while the core electrons were optimized simultaneously with the SC valence orbitals.

Our results are also in agreement with previous work of Schultz et al. [2] who, again considering just the six triple-bond electrons, found that only the inclusion of the strong-orthogonality and perfect-pairing approximations leads to greater stability of the σ/π solution.

On the other hand, the C_2 results are not supported by the work of Schultz et al. [2] who in this case found that the bent-bond model is still favored by 2.06 millihartrees at the full GVB level.

The disagreement is probably due to the fact that for the C_2 molecule as well those authors correlated at the GVB level only six valence electrons. In this case, as opposed to the C_2H_2 molecule, this can be a severe approximation, as the two nonbonding electrons are expected to be more important in the overall description of the electronic structure of the molecule, as Schultz et al. themselves pointed out [2].

Support for the idea that correlating all the valence electrons is more important for C_2 than for C_2H_2 will be given by the following discussion about the nature of the SC orbitals. Despite the interchange in the stability order of the σ/π vs. the bent description of the carbon–carbon bond in C_2 and C_2H_2, there are no great differences in the shape of the orbitals between the two molecules. We begin with analyzing the orbitals of the σ/π case for C_2 and C_2H_2 which are illustrated in Figs. 1 and 3 respectively.

Orbital φ_1 (Figs. 1a and 3a) is essentially an sp^x orbital localized on a carbon atom and pointing towards the other carbon atom. φ_2 is obtained by reflection of φ_1 through a plane perpendicular to the molecular axis and located in the middle

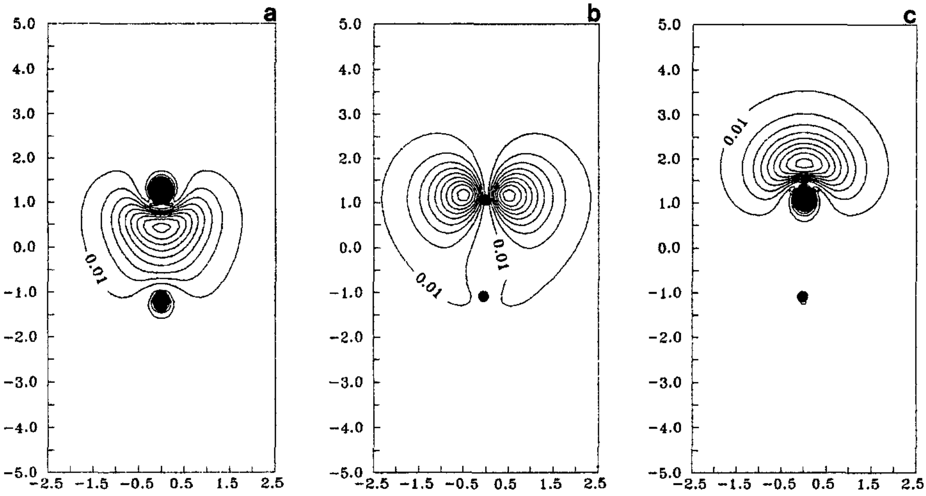

Fig. 1. The SC orbitals for the σ/π bond description for the C_2 molecule at the experimental equilibrium geometry, localized on a C atom involved a) in the CC σ bond (φ_1), b) in the CC π bond (φ_3); c) the SC orbital describing the unpaired electron (φ_7). The other five orbitals are related by symmetry

of the CC bond, and it has large overlap with φ_1 (0.88 for C_2 and 0.84 for C_2H_2), thus describing the σ CC bond.

Orbital φ_3 (Figs. 1b and 3b) is essentially a *p* orbital localized on one of the two carbon atoms and slightly distorted towards the other carbon atom. Due to the σ/π constraints it is orthogonal to φ_1 and φ_2 and it has a significant overlap (0.64 for C_2 and 0.68 for C_2H_2) with orbital φ_4 (which is symmetry related to φ_3), thus describing the first π CC bond. The other π CC bond is described by the overlap between orbitals φ_5 and φ_6 which are obtained from φ_3 and φ_4 respectively by a rotation of 90° along the CC bond.

For the C_2 molecule there are two additional orbitals, φ_7 (Fig. 1c) and φ_8, each of them localized on one of the two carbon atoms, and pointing along the molecular axis, away from the other carbon atom. They describe the nonbonding electrons and have nonnegligible overlaps with the orbitals responsible for the σ CC bond, the overlap between $\varphi_7(\varphi_8)$ and $\varphi_3(\varphi_4)$ being 0.39.

On the other hand, for the C_2H_2 molecule we have two additional *pairs* of orbitals describing the two CH bonds. Each pair consists of one orbital $\varphi_7(\varphi_9)$ (Fig. 3c) localized on a carbon atom and pointing towards the hydrogen atom, and another orbital $\varphi_8(\varphi_{10})$ (Fig. 3d) localized on the hydrogen and slightly distorted toward the carbon atom. The two paired orbitals overlap strongly (0.82).

Figures 2 and 4 show the SC orbitals of the bent-bond description of C_2 and C_2H_2, respectively. We will denote the six equivalent orbitals by $\varphi_1^b, \varphi_2^b, \ldots, \varphi_6^b$ (Figs. 2a and 4a), each of them having the same sp^x hybridization. They are interchanged by the symmetry operations described above. The other valence orbitals, say φ_7^b and φ_8^b (Fig. 2b) for C_2 and $\varphi_7^b, \varphi_8^b, \varphi_9^b, \varphi_{10}^b$ (Figs. 4b and 4c) for C_2H_2, are substantially the same orbitals described in the case of the σ/π triple bond.

The orbital picture emerging from the orbitals of the C_2 molecule seems to indicate the existence of a triple bond between the two C atoms, both in σ/π and bent bond descriptions. This picture contrasts with the traditional MO model of

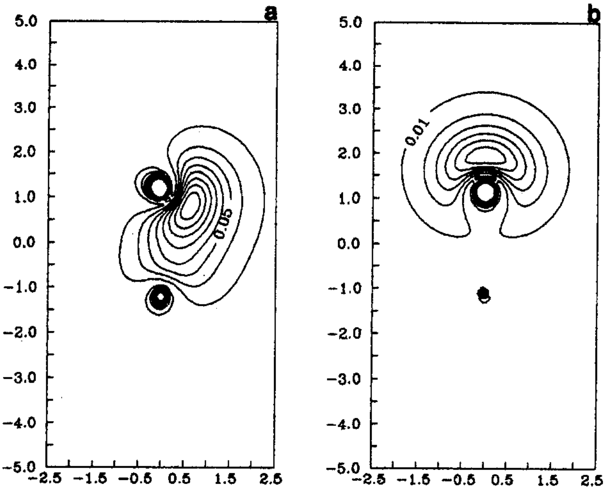

Fig. 2. The SC orbitals for the bent bond description for the C_2 molecule at the experimental equilibrium geometry. a) The SC orbital localized on a C atom involved in the CC bent bond (φ_1^b); b) the SC orbital describing the unpaired electron (φ_7^b). The other six orbitals are related by symmetry

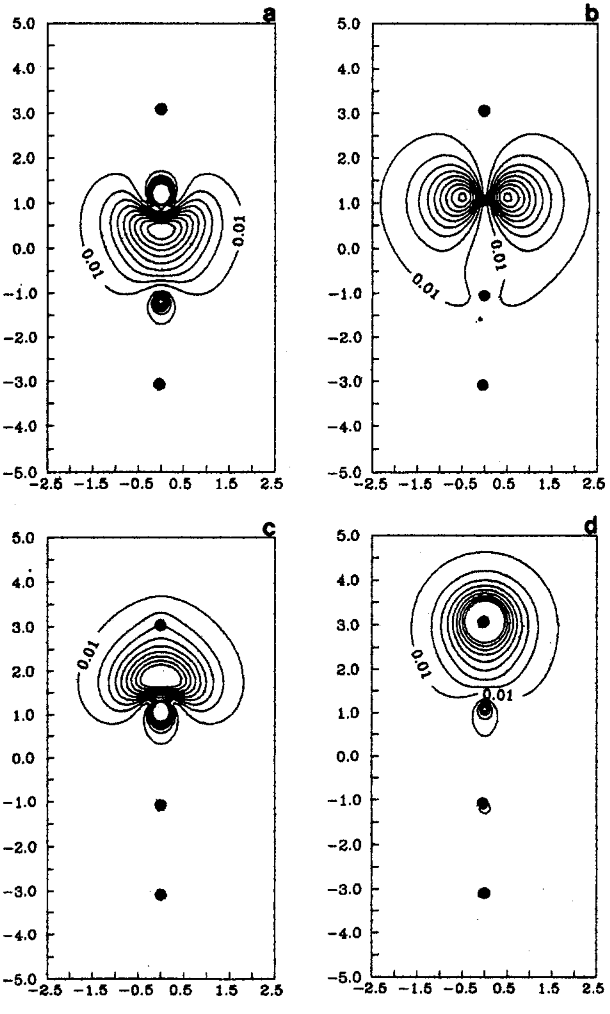

Fig. 3. The SC orbitals for the σ/π bond description for the C_2H_2 molecule at the experimental equilibrium geometry, localized on a C atom involved a) in the CC σ bond (φ_1), b) in the CC π bond (φ_3); c) in the CH bond (φ_7); d) the SC orbital localized on H atom involved in the CH bond (φ_8). The other six orbitals are related by symmetry

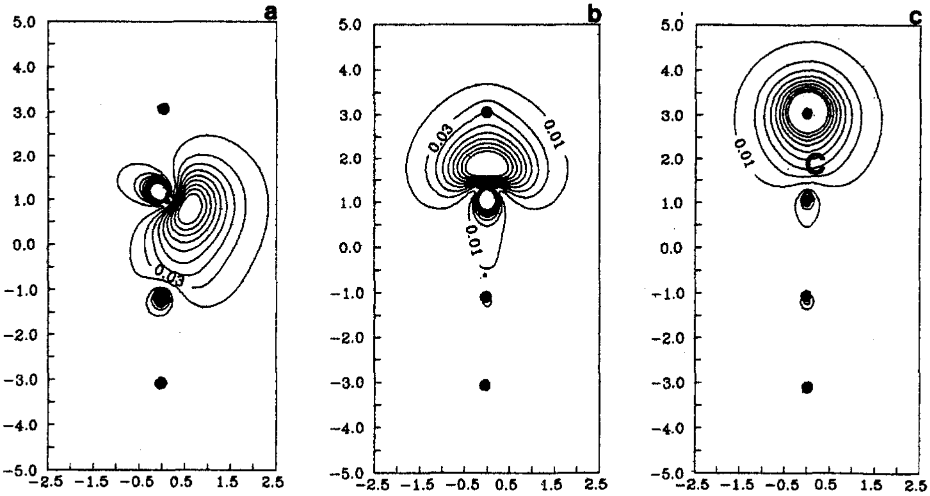

Fig. 4. The SC orbitals for the bent bond description for the C_2H_2 molecule at the experimental equilibrium geometry. The SC orbital localized on a C atom involved a) in the CC bent bond (φ_1^b), b) in the CH bond (φ_7^b); c) the SC orbital localized on H atom involved in the CH bond (φ_8^b). The other seven orbitals are related by symmetry

this molecule where the CC bond is described as a double bond with no σ contributions, as indicated by its ground state configuration $1\sigma_g^2 1\sigma_u^2 2\sigma_g^2 2\sigma_u^2 1\pi_u^4$. However it must be noted that C_2 is stabilized [25,26] by the near degenerate configuration $1\sigma_g^2 1\sigma_u^2 2\sigma_g^2 3\sigma_g^2 1\pi_u^4$. Its inclusion increases the bond order beyond the SCF value of 2, introducing some kind of σ bond. The occupation numbers of our CASSCF calculations are also indicative of this aspect: the occupation numbers of the orbitals $2\sigma_u$ and $3\sigma_g$ are 1.59 and 0.42, respectively (these values refer to the TZP basis set, but they are substantially unchanged for the other basis sets). Anyway it is clear that in the framework of the MO theory the bond order of the C_2 molecule is less than 3, in agreement with the observed increase in the bond length going from C_2H_2 to C_2 and C_2H_4. The discrepancy between the MO results and the model emerging from the SC wave function can be partially resolved using the following argument. In the SC wave function describing the C_2 molecule, although the structure corresponding to perfect pairing is still dominant, there are significant contributions from *all* spin couplings; some of them introduce a degree of pairing between the orbitals responsible for the CC bond and the orbitals describing the two nonbonding electrons. We can ascribe to the introduction of these alternative pairings a decrease in bond order of the C_2 molecule from the value of 3 expected in the perfect pairing only case. An empirical bond-order formula recently proposed in the framework of spin-coupled theory by Raos et al. [18] gives a value of 2.5 when applied to the σ/π SC model of the C_2 molecule.

As for the nonbonding electrons of C_2, we note that their orbitals significantly overlap the bent orbitals, the value of the overlap reaching the value of 0.63 between orbitals localized on the same carbon atom, i.e. between φ_7^b and φ_1^b. The corresponding overlap in the case of C_2H_2, where φ_7^b is the carbon-centered orbital involved in the description of the CH bond, is only 0.03.

This observation illustrates the importance of explicitly correlating all valence electrons, especially in the case of C_2, and explains why previous work, where the nonbonding electrons were not correlated, failed to obtain for this molecule the correct energy ordering for the σ/π and bent models. It is also interesting to observe that the sum and difference of orbitals φ_7 and φ_8 (or φ_7^b and φ_8^b) give essentially the $2\sigma_u$ and $3\sigma_g$ orbitals of MO theory which are both necessary for a correct description of the electronic structure of C_2, as discussed above.

The main difference between the bent orbitals of C_2H_2 and C_2 is the greater percentage of *p* character in the C_2H_2 orbitals. This can be confirmed, in a comparison between orbitals taken from the two alternative models, by looking at the overlap between a bent orbital and the orbitals localized on the same carbon atom involved in the σ and π bonds, i.e. between the pairs φ_1^b, φ_1 and φ_1^b, φ_3; the overlap φ_1^b, φ_1 decreases from 0.84 for C_2 to 0.74 for C_2H_2, and the overlap φ_1^b, φ_3 increases from 0.52 for C_2, to 0.66 for C_2H_2, thus indicating that the bent orbitals of C_2H_2 have greater π character. Intuitively this fact can be understood in the following way: in the C_2 molecule the absence of the hydrogen nuclei permits the unpaired electrons to be more diffuse (compare Fig. 2b with Fig. 4b) and this constrains the "structure" of the orbitals of the bent bond to be less "open", reducing their *p* character. This aspect was further confirmed by analyzing the orbitals according to the method proposed by Kirtman et al. [27]: an $sp^{0.62}$ and $sp^{1.40}$ hybridization was obtained for the bent orbitals of C_2 and C_2H_2, respectively. The orbitals possess a greater degree of *s* character than one might have expected, but this is due to their nonorthogonal nature, as already pointed out by Palke [9] and Kirtman et al. [27].

Lastly it should be noted that the possibility of symmetry broken solutions, lower in energy than both the σ/π and bent bond models, whose importance has been emphasized by Bauschlicher et al. [28], has not been analyzed in the present paper due to the symmetry constraints imposed on the orbitals (see Eqs. (3) and (4)).

6. Conclusions

The nature of the CC bond in C_2 and C_2H_2 molecules has been investigated within the framework of the spin-coupled method, performing the first calculations that include all valence electrons for both bent and σ/π models.

In spite of the strong chemical similarity between C_2 and C_2H_2, the relative stability of the bent and σ/π models in the two molecules is different.

In the C_2H_2 case the bent model is more stable, this result being independent from the inclusion of all spin couplings. Previous work on this molecule has shown that this result remains true when only the six triple bond electrons are explicitly correlated.

In the C_2 case the σ/π model is more stable and we have shown that the inclusion of all spin couplings is essential to its greater stability. The qualitative picture of the orbitals and the values of the overlaps are compatible with the existence of a CC triple bond. A correspondingly naive application of MO theory would predict a bond order of two. A more sophisticated MO treatment, however, leads to a bond order intermediate between 2 and 3. An argument which taking into account the role of all spin-couplings decreases the bond order with respect to the value of 3, so reconciliating the SC and MO results, is presented. Comparison with previous work demonstrates that explicit correlation of the nonbonding electrons is essential to proper description of the electronic structure of this molecule.

Acknowledgments. We thank the authors of Ref. [1] for having provided us with their results prior to publication. We are also greatful to Prof. Mario Raimondi and Dr. Fabio Penotti for useful discussions on the present work. We finally wish to fully acknowledge the computational resources made available by the Centro CNR per lo Studio delle Relazioni tra Struttura e Reattivita' Chimica, Milano (Italy).

References

1. Karadakov PB, Gerratt J, Cooper DL, Raimondi M (1993) J Am Chem Soc 115:6863
2. Schultz PA, Messmer RP (1993) J Am Chem Soc 115:10925
3. Schultz PA, Messmer RP (1993) J Am Chem Soc 115:10938
4. Schultz PA, Messmer RP (1993) J Am Chem Soc 115:10943
5. Hückel EZ (1930) Phys 60:423
6. Pauling L (1931) J Am Chem Soc 53:1367
7. Hay PJ, Hunt WJ, Goddard III WA (1972) J Am Chem Soc 94:8293
8. a) Goddard III WA (1967) Phys Rev 157:73; b) Goddard III WA (1967) Phys Rev 157:81; c) Goddard III WA, Ladner RC (1971) J Am Chem Soc 93:6750; d) Hay PJ, Hunt WJ, Goddard III WA (1971) Chem Phys Lett 13:30; e) Hunt WJ, Hay PJ, Goddard III WA(1972) J Chem Phys 56:738
9. Palke WE (1986) J Am Chem Soc 108:6543
10. Messmer RP, Schultz PA (1986) Phys Rev Lett 57:2653
11. Schultz PA, Messmer RP (1987) Phys Rev Lett 58:2416
12. Schultz PA, Messmer RP (1988) J Am Chem Soc 110:8258
13. Messmer RP, Schultz PA, Tatar RC, Freund HJ (1986) Chem Phys Lett 126:176
14. Murphy RB, Messmer RP (1993) J Chem Phys 98:7958
15. a) Gerratt J (1971) Adv Atom Mol Phys 7:141; b) Pyper NC, Gerratt J (1977) Proc R Soc London, Ser A 355:407; c) Cooper DL, Gerratt J, Raimondi M, Sironi M, Thorsteinsson T (1993) Theor Chim Acta 85:261; d) Karadakov PB, Gerratt J, Cooper DL, Raimondi M (1992) J Chem Phys 97:7637. For recent reviews see also; e) Cooper DL, Gerratt J, Raimondi M (1988) Int Rev Phys Chem 7:59; f) Cooper DL, Gerratt J, Raimondi M (1990) Top Curr Chem 153:41; g) Gerratt J, Cooper DL, Raimondi M (1990) In: Klein DJ, Trinajstic N (eds) Valence bond theory and chemical structure. Elsevier, Amsterdam; h) Raimondi M, Sironi M (1990) In: Klein DJ, Trinajstic N (eds) Valence bond theory and chemical structure. Elsevier, Amsterdam; i) Cooper DL, Gerratt J, Raimondi M (1991) Chem Rev 91:929
16. Pauncz R (1979) Spin Eigenfunctions. Plenum, New York
17. Simonetta M, Gianinetti E, Vandoni I (1968) J Chem Phys 48:1579
18. Raos G, Gerratt J, Cooper DL, Raimondi M (1993) Mol Phys 79:197
19. Goldfield S, Quandt R, Trotter F (1966) Econometrica 84:541
20. Gerratt J, Raimondi M (1980) Proc R Soc London, Ser A 371:525
21. Rosen B (1970) Spectroscopic data relative to diatomic molecules. Pergamon, New York
22. Herzberg G (1966) Molecular spectra and molecular structure. III. Electronic spectra and electronic structure of polyatomic molecules. Van Nostrand Reinhold, New York
23. Dunning TH (1970) J Chem Phys 53:2823
24. Dunning TH (1971) J Chem Phys 55:716
25. Zeitz M, Peyerimhoff SD, Buenker RJ (1978) Chem Phys Lett 58:487
26. Dupuis M, Liu B (1980) J Chem Phys 73:337
27. Kirtman B, Chipman DM, Palke WE (1977) J Am Chem Soc 99:1305
28. Bauschlicher CW, Taylor PR (1988) Phys Rev Lett 60:859