New Theoretical Description of the Carbon-Carbon Triple Bond

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We present new theoretical results on the carbon-carbon triple bond which suggests that such bonds may be better described in terms of "bent bonds" than by the traditional combination of σ and π bonds. By use of correlated wave functions such behavior is explicitly demonstrated for difluoroacetylene. These represent the first quantitative calculations which document a case where a triple "bent-bond" description is energetically favored over a σ-π description.

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In this Letter we report the first theoretical calculations which demonstrate that multiple bent bonds (Ω bonds)[1] are energetically favored over the traditional σ and π bonds for carbon-carbon bonding in C_2F_2. The approach uses wave functions which explicitly include important electronic correlation effects. These correlation effects prove to be crucial to an understanding of the bonding and to the energetic favorability of Ω bonds. Although the resulting physical description obtained is very similar to the qualitative discussion of bonding in acetylene given many years ago[2,3] on the basis of the Heitler-London-Slater-Pauling (HLSP) valence-bond theory,[4] the present results offer the first quantitative justification for this point of view.

According to the HLSP method, one views the tetravalent nature of the carbon atom as due to the formation of four equivalent sp^3 hybrid atomic orbitals which point to the vertices of a tetrahedron. Thus, if we consider two carbon atoms (C_l and C_r) with a set of such atomic hybrid orbitals on each $\{\chi^l_{hi}, \chi^r_{hi}; i=1,\ldots,4\}$, the carbon-carbon triple bond in acetylene would be described by three covalent bonds of the Heitler-London form[5]:

$$\psi_i=(\chi^l_{hi}\chi^r_{hi}+\chi^r_{hi}\chi^l_{hi})\alpha\beta,\quad i=1,2,3. \tag{1}$$

Each ψ_i is a correlated two-electron function with space and spin components. Likewise, the C—H bonds are described by the Heitler-London form

$$\psi_4=(\chi^l_{\mathrm{H}}\chi^l_{h4}+\chi^l_{h4}\chi^l_{\mathrm{H}})\alpha\beta, \tag{2}$$

for the left bond and a similar expression for the right C—H bond, ψ_5. Hence, the many-electron wave function is given by

$$\Psi=A\left[\{\mathrm{core}\}\prod_{i=1}^{5}\psi_i\right], \tag{3}$$

where {core} represents the doubly occupied $1s$ orbitals on each carbon atom and A is the antisymmetrization operator. A schematic representation of this wave function is shown in Fig. 1. The hybrid orbitals on different sites will overlap and each of these orbitals is occupied by one electron (denoted by a dot) and is singlet coupled (denoted by a line) to an orbital on a neighboring atom to form a covalent bond. Equation (3) is the description of the electronic structure and bonding of acetylene first advanced in 1931.[2,3] As was pointed out later,[6] the actual calculation of the energy and properties of acetylene (and practically any molecule other than H_2) based on this valence-bond wave function turned out to be far more difficult than had originally been supposed. The nonorthogonality of the orbitals within a bond and between bonds leads to considerable complexity and the consideration of potentially important alternative spin couplings further compounds the problems. It is also clear that the orbitals appropriate for isolated atoms will not be optimal for chemical bonding between atoms. The orbitals should ideally be obtained by a self-consistent procedure based on the variational principle.

Such complexities, both algebraic and computational, led to many approximations being made in the valence-

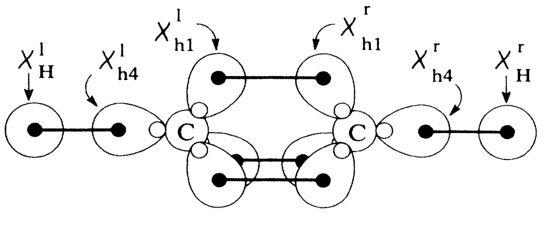


FIG. 1. A schematic representation of the Heitler-London-Slater-Pauling valence-bond description of the acetylene molecule. Each carbon atom has four equivalent sp^3 hybrid atomic orbitals, three of which overlap with hybrids on the other carbon atom to form a triple bond. The remaining hybrid on each carbon overlaps with an atomic hydrogen orbital to form a C—H single bond.

bond approach, so many, in fact, that the method came to be viewed as a qualitative theory with little *a priori* foundation.[7] In 1953, however, Hurley, Lennard-Jones, and Pople[8] proposed an extended valence-band or generalized Heitler-London approach which significantly reduced the complexity of the valence-bond method by allowing the orbitals within a bond to overlap, while restricting the orbitals belonging to different bonds to be orthogonal. That is, if ϕ_{ia} and ϕ_{ib} are the orbitals which describe bond i, $\langle\phi_{ia}|\phi_{ib}\rangle\neq 0$; however, $\langle\phi_{i,\mu}|\phi_{j,\nu}\rangle=0$ for $i\neq j$, with $\mu,\nu=a$ or b. The latter are known as the strong orthogonality constraints. Furthermore, the ϕ_i are not constrained to be pure sp^3 atomic orbitals, but are allowed to rehybridize and delocalize onto other centers. Unlike a completely general valence-bond formulation, however, it is restricted to a single spin-coupling scheme, namely, singlet coupling within the bonds of a unique valence-bond structure.

This method was not implemented as a general computational scheme until many years later when it was rediscovered[9] as a special case of the generalized valence bond (GVB) method[10] and is now frequently referred to as the perfect-pairing (PP) approximation of the GVB method. In one of the first applications of the GVB-PP method, Hay, Hunt, and Goddard[11] discussed the bonding in ethylene (C_2H_4) and acetylene (C_2H_2) and found that a description of the carbon-carbon bonding in terms of σ and π bonds was lower in energy than a description in terms of bonds formed of overlapping, approximately tetrahedral hybrids (such as shown schematically in Fig. 1). Within the context of molecular-orbital theory the question of which description of the bonding is more appropriate cannot be answered because any unitary transformation of the orbitals leaves the total energy invariant. However, within the context of correlated wave functions, such as discussed here, there is a difference in energy between the two descriptions *which allows the more appropriate bonding scheme to be determined by the variational principle.*

The calculations[12] were carried out on C_2F_2 in a linear geometry, with a carbon-carbon bond length of 1.17 Å and a carbon-fluorine bond length of 1.30 Å.[13] A standard valence double-zeta plus polarization basis set was used for all atoms.[14] The GVB-PP calculations allowed for the correlation of all valence-electron pairs, i.e., eleven electron pairs. Within this theoretical framework a series of four sets of calculations were performed which imposed various symmetry constraints on the orbitals.

In the first case, all the orbitals were required to have σ and π symmetries with respect to the internuclear axis. The resulting many-electron wave function is shown schematically in Fig. 2(a). In the second case, the orbitals on the fluorine atoms were constrained to remain σ,π-like, but the orbitals of the two carbon atoms had *no symmetry constraints.* The resulting many-electron wave function is shown schematically in Fig. 2(b), and the actual orbital contour plots of one of the three equivalent Ω bonds that result between the carbon atoms is shown in Fig. 3(a). The wave function of Fig. 2(b) is 0.10 eV lower in energy than that of Fig. 2(a), demonstrating that, variationally, three Ω bonds are preferred over a σ and two π bonds for the carbon-carbon triple bond in C_2F_2. In the third case, Fig. 2(c), the orbitals of the carbon-carbon bonds were constrained to be σ or π, but *no symmetry constraints* on the fluorine orbitals were made. A lowering of 0.39 eV is obtained for the wave function of Fig. 2(c), with respect to the energy of the wave function in Fig. 2(a). It is, therefore, energetically very important to relax the symmetry restrictions on orbitals describing the lone pair of electrons on the fluorine atoms, so that they are no longer required to be at 90° to one another.

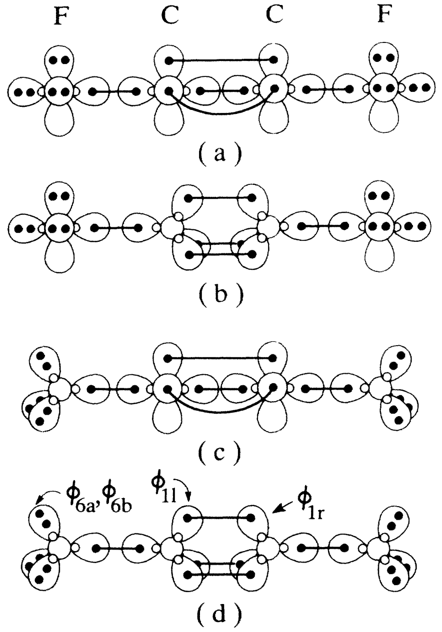
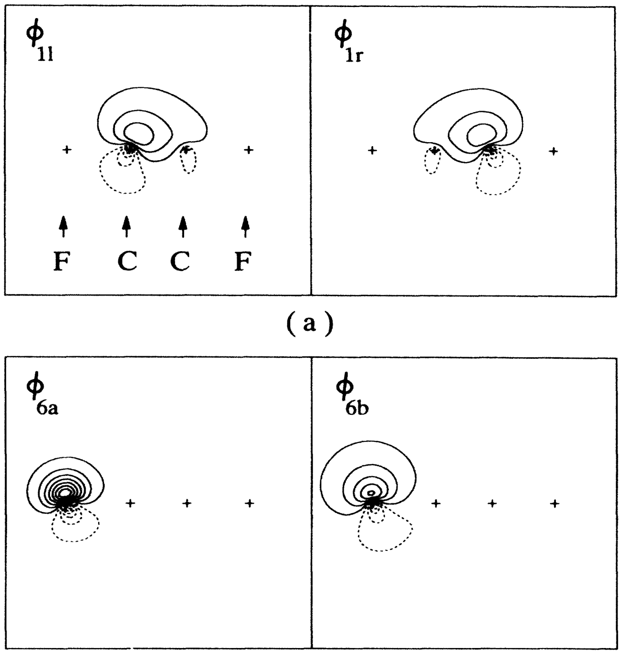


FIG. 2. Schematic representations of four many-electron correlated wave functions. p orbitals perpendicular to the plane of the page appear as circles. (a) From calculations which restrict all orbitals to have either σ or π symmetry. (b) From calculations which relax symmetry restrictions on the carbon atoms. (c) From calculations which relax symmetry restrictions on the fluorine atoms. (d) From calculations with no symmetry restrictions on the orbitals.

Upon removal of *all symmetry constraints,* the many-electron wave function shown schematically in Fig. 2(d) was obtained. A lowering of 0.48 eV is obtained for this wave function with respect to the wave function of Fig. 2(a) with symmetry constraints on all the orbitals. Thus the energy lowerings obtained for the wave functions of Figs. 2(b) and 2(c) are nearly additive, and the removal of all artificial symmetry constraints yields a lowering of almost half an electronvolt. The orbitals calculated for the Ω bonds in the wave functions of Figs. 2(b) and 2(d) are essentially identical; one of them is shown in Fig. 3(a). The orbitals of the equivalent fluorine lone pairs in



(a)

(b)

FIG. 3. Contour plots of orbitals from the many-electron wave function shown schematically in Fig. 2(d). (a) One of the three equivalent Ω bonds of C_2F_2. The hybrids on the left and right carbon atoms overlap to form a bond. (b) One of the six equivalent fluorine lone pairs. The two orbitals are in the same region of space and strongly overlap, but one is closer to the nucleus than the other, allowing the electrons to be "in-out" correlated.

Figs. 2(c) and 2(d) are also nearly identical and one of them is shown in Fig. 3(b).

The orbitals making up the three equivalent carbon-carbon bonds of C_2F_2 resemble a great deal the atomic sp^3 hybrids originally proposed in the description of the acetylene molecule,[2,3] as can be seen in Fig. 3(a). However, we note that in the present case these orbitals have been determined self-consistently, rehybridizing slightly and delocalizing onto the neighboring carbon atom with which they form a chemical bond. The two orbitals of the bond clearly illustrate the "left-right" correlation effect of the electrons achieved within the GVB-PP wave function. The "in-out" correlation of the lone-pair orbitals, e.g., ϕ_{6a} and ϕ_{6b} of Fig. 2(d), is clearly seen in Fig. 3(b), where ϕ_{6a} is observed to be closer to the fluorine nucleus than the more extended ϕ_{6b}. There is a larger degree of overlap between the orbitals of a lone pair than for the case of a bond pair.

In contrast to the mean-field theory (molecular orbital) description of this molecule, which consists of doubly occupied orbitals, the correlated wave function assigns one electron to each orbital. Any wave function, however, can be expressed as a linear combination of Slater determinants with use of orthogonal orbitals. The GVB-PP wave function for C_2F_2, incorporationg important correlation effects among the valence electrons, can be written, in fact, as a configuration-interaction (CI) expansion of 2^{11} determinants. The energy lowering obtained by the GVB-PP wave function of Fig. 2(a) with respect to the Hartree-Fock (molecular orbital) wave function amounts to 3.62 eV.[15] While it is certainly possible to account energetically for these important correlation effects by use of CI wave functions (with perhaps fewer terms), it is a great strength of the valence-band point of view that when these correlation effects are incorporated, the resulting wave function, unlike a general "Hartree-Fock plus CI" wave function, retains a simple physical interpretation because of the single-particle (one electron, one orbital) nature of the GVB-PP wave function as expressed in Eq. (3) by use of overlapping orbitals. Thus, the qualitative nature of the bonding, such as that represented by the schematic diagrams of Figs. 2 and 3, is made apparent, and the relative merits of different bonding descriptions can be judged; e.g., the wave functions corresponding to Figs. 2(a) and 2(d) differ in energy by about 0.5 eV.

An important question to consider is the effect which restrictions in the GVB-PP wave function, particularly the strong orthogonality (SO) constraints between electron pairs, have on the arguments made above with regard to the preference for Ω bonds *vis-à-vis* σ and π bonds. For the wave functions of Fig. 2, there are 55 sets of SO constraints imposed between the eleven pairs of orbitals. For the σ,π case of Fig. 2(a), however, 39 of the 55 sets of constraints are also dictated by symmetry considerations in order to retain a σ,π description of the system so that only 16 constraints are actual restrictions on the wave function. For the Ω-bond case of Fig. 2(d), *all* 55 constraints are effective restrictions on the wave function. Hence, it would appear that the limitations of the GVB-PP approach bias it against the multiple bent-bond (Ω-bond) description with respect to the σ,π description, and relaxing the SO constraints would benefit the Ω-bond description more than the σ,π-bonded one. This bias is not limited to C_2F_2, but extends to all other molecular systems such as C_2H_4 and C_2H_2. Preliminary studies on these and other systems, using CI calculations designed to relax these restrictions, indicate that the above conjecture about the bias is correct. A calculation for C_2H_4 without the SO restrictions actually does find the double bond to be best described by equivalent bent bonds.[16] Therefore, even in cases where the GVB-PP results favor a σ,π description, such as for C_2H_4 and C_2H_2,[11] the best description would likely be Ω bonds were the SO restrictions in the GVB-PP wave function to be removed. In cases where the GVB-PP result favors Ω bonds,[1,17] as is the case here for C_2F_2, the relative stability *vis-à-vis* σ and π bonds will be underestimated.

In summary, we have found, through the use of modern *ab initio* theoretical techniques which include electronic correlation effects, that the usual mean-field

σ,π description of the bonding in C_2F_2 is not adequate. Furthermore, there are good theoretical reasons to expect that the case of C_2F_2 and other molecules for which Ω bonds are favored[1,17] are not isolated examples. In fact, it may well be that multiple bonds in molecules are not σ,π-like, and that the simple valence-band ideas of Slater and Pauling are closer to reality than it has been popular to assume. The important question of how to describe Σ, Π, etc., excited states and ion states of a molecule based on a description of the ground state in terms of Ω bonds will be described elsewhere.[18]

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