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Double Bonds Are Bent Equivalent Hybrid (Banana) Bonds

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Abstract: Valence-bond calculations without the imposition of any orthogonality constraints show the equivalent hybrid (banana) description of the double bond in ethylene to be more stable than a σ plus π bond description.

For many years, chemists have described the carbon–carbon double bond in two different ways. Pauling[1] considered the double bond to consist of two equivalent bonds sometimes referred to as banana bonds, each of which is formed from the pairing of an electron in a hybrid orbital on one atom with a symmetrically equivalent orbital on the other atom. The alternate description suggested by Hückel[2] utilizes one σ bond plus one π bond. The point of this work is to consider which of these descriptions is better.

Because we are interested in a description of the double bond in terms of orbitals, we must use wave functions that provide an independent particle interpretation of the behavior of the electrons in a molecule.[3,4]. Each orbital of such a wave function is the best orbital for an electron in the field of the nuclei and the averaged electron repulsion of the other electrons in the molecule. We then conclude that the optimum independent particle orbitals provide the best description of the molecule because they constitute the lowest energy independent particle wave function for that molecule. To this end, we will consider explicitly both Hartree–Fock (HF) and valence-bond (VB) models of electronic structure.

Hartree–Fock

If a doubly occupied orbital wave function (HF) is adopted, the two descriptions of the double bond become equivalent. Solution of the "canonical" Hartree–Fock equations for ethylene yields a set of σ orbitals plus a π orbital,[5,6] but as is well known, the σ orbitals are delocalized throughout the molecule. In order to obtain a bond orbital description of ethylene, the canonical HF orbitals must be localized; this is possible because a doubly occupied orbital wave function is invariant with respect to a unitary transformation. So the σ canonical orbitals can be localized, and one of those localized orbitals will be the carbon–carbon σ bond.[6] This σ plus the canonical π orbital then provide a description of the double bond.

A more general HF localization allows the σ and π orbitals to mix in the unitary transformation. The result is an even more localized set of orbitals with the double bond consisting of two equivalent bent banana orbitals.[6] Notice that the σ–π and banana bond descriptions of ethylene are each unitary transformations of the canonical HF orbitals. The total wave function expressed in terms of σ–π or banana orbitals is identical with the canonical Hartree–Fock wave function. Because all three are merely unitary transformations of one another, they have the same energy and the same total charge distribution. The only distinction between them is that one satisfies the localization criterion better than the other. But that localization criterion is arbitrary and does not arise from the HF orbital optimization equations. The HF method itself provides no criterion for preferring banana bonds to σ plus π bonds.

Table I. Calculated Energies in Hartrees

molecule	method	energy
C_2H_4	HF	−78.0406
C_2H_4	GVB	−78.1608
C_2H_4	OTTO	−78.1712
CH_2 triplet	OTTO	−38.9650

Valence Bond

In a perfect-pairing valence-bond wave function, each electron pair consists of two different orbitals paired into a singlet. In order to determine the fully optimized VB wave functions for our studies, every electron pair (including the carbon inner shells) is allowed to split. That is, no orbitals are restricted to be doubly occupied. The resulting wave function is not invariant with respect to a unitary transformation. Hence, the orbitals satisfying the optimization equations will, in general, all be nonorthogonal.[4]

In this work, each orbital of a perfect-pairing VB wave function is fully optimized as an LCAO function with use of the OTTO method described previously[7] to obtain a self-consistent-field result. The converged wave function consists of an inner shell pair on each carbon, four equivalent CH bond pairs plus two symmetrically equivalent CC bond pairs. Each of the CC bonds is formed from the singlet pairing of a hybrid on one carbon with an equivalent hybrid on the other carbon. One CC bond lies primarily above the plane of the nuclei, and the other is symmetrically situated below that plane. Figure 1 shows a contour plot of one of these hybrid orbitals. It is paired with an orbital which is a left/right reflection of the one shown. It is clear from the figure that the bond is bent with each hybrid of the pair curving toward the bond midpoint to overlap with the other. It should be stressed that the localization of the VB orbitals results completely from the optimization of the energy of the total wave function.

The VB equations have also been solved with the simplyifying constraint that the orbitals be strongly orthogonal.[8] This procedure has been termed the "generalized" valence-bond (GVB) method. Strong orthogonality requires each VB orbital to be orthogonal to every other orbital in the molecule except the one it is paired with. GVB wave functions for ethylene (which predict a σ plus π double bond) have been reported previously,[9] but in order to obtain the closest comparison to the present work, they have been redetermined by using our basis set.[10]

Calculational Details

For all the calculations, an optimized double-ζ plus d orbital basis set of Slater-type orbitals was used. First, the exponents of a double-ζ basis were optimized with the Hartree–Fock energy as the optimization criterion. Then a set of 3d orbitals was added to each carbon, and the d orbital exponent was optimized with use of the same criterion. Stevens' programs were used to carry out the integral and HF computations.[11]

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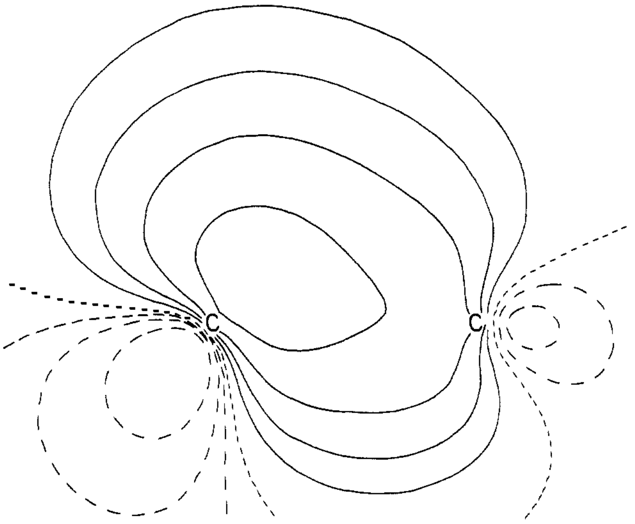

Figure 1. One hybrid orbital from the CC bond of ethylene.

This basis set was used for all subsequent calculations.[12] All calculations used the experimental ethylene geometry.[13]

Discussion

The total energies of the three different independent particle wave functions are given in Table I. The energy of a nonorthogonal orbital VB wave function for the ground state (triplet) of CH_2 is also included for comparison.[14] The CC bond strength which the OTTO energies predict is 151 kcal/mol and is fairly close to the experimental value of 171 kcal/mol.[15]

According to the best nonorthogonal orbital (OTTO) wave function, the double bond consists of two equivalent bonds—one mostly above and one mostly below the plane of the molecule. This is just the qualitative picture suggested by Pauling[1] in which each bond is formed by the overlapping of one hybrid orbital from each carbon. The overlap integral of the two bonded hybrids is 0.828. This is a large overlap, and it indicates significant bond strength even though a rigorous relationship between overlap and bond strength has not been established. By comparison, the GVB function, which has an energy 6.5 kcal/mol higher, consists of one σ bond with an orbital overlap of 0.890 and a π bond whose overlap is 0.642. Thus, the banana bond configuration provides two moderately large overlaps whereas σ and π bonds have one very large and one much smaller overlap.

How closely does the banana bond wave function correspond to Pauling's picture? Pauling's hybrids are sp^3 orbitals with 50% p character. Each of the orbitals in the OTTO wave function is $sp^{1.37}d^{0.07}$ and has 24% π character. This excess s occupancy is typical of the nonorthogonal VB orbitals.[16] The complete wave function contains a very large number of terms arising from the antisymmetrization of the orbital product, so there must be considerable cancellation of parts of the wave function in a complicated way. One way to account for, and eliminate, this "overuse" and cancellation of s orbitals is to orthogonalize (symmetrically) the orbitals of one CC bond to the orbitals of the other CC bond. This has been done, and the resulting orbital has hybridization of $sp^{2.14}d^{0.07}$ and is 50.0% π—much closer to Pauling's assumptions.

How different are the banana bond and the σ plus π bond wave functions? The four-electron overlap of the banana bond portion of the OTTO wave function with the σ plus π portion of the GVB wave function provides a measure of their similarity. That overlap is 0.939. The four hybrid orbitals of the banana bonds do, of course, generate electron density in the same region of space as the σ plus π bond orbitals; they just arrange themselves differently in the many-electron wave function. It would be of interest to compare the banana bonds to the σ plus π picture with both wave functions having the same overall form and with the same orthogonality constraints. However, optimization of a wave function of orbitals which do not provide the absolute lowest energy is a delicate procedure, and neither the OTTO nor GVB methods converged to proper wave functions when we attempted to determine self-consistent-field orbitals for their less stable bonding form allowing all pairs to split.

The overlap of the two hybrids on the same carbons which are involved in different CC bonds is 0.516. This value is constrained to be zero by the adoption of strong orthogonality. If one considers just the two pairs of electrons that form the double bond, strong orthogonality is not a constraint on the σ plus π wave function. The σ orbitals are orthogonal to the π orbitals by symmetry. Strong orthogonality is a constraint on the equivalent hybrid wave function, however. Indeed, it is a serious one judging from the optimum overlap reported above. Constraining this overlap to be zero forces the orbital to distort and leads to an increase in energy. The actual situation is more complicated because of interactions with the carbon–hydrogen bonds and the inner shells. The overlaps of the hybrid orbitals of the double bond with the other orbitals in the molecule are all smaller than 0.2, so these terms are less important, and the major effect of strong orthogonality is its effect on the orbitals of the double bond. Nevertheless, the strong orthogonality approximation itself favors a σ plus π description of the double bond, so in that light it is understandable that the GVB method predicts a σ plus a π bond in ethylene.

Despite its built in bias against banana, bonds, the GVB method does predict them to occur[17] in Si_2H_4 and in C_2F_4. Our preliminary results using the OTTO method for the acetylene molecule indicate that a wave function consisting of equivalent hybrid bonds (three pairs in that case) is lower in energy than a σ plus two π bond wave function. 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.

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Registry No. $CH_2{=}CH_2$, 74-85-1.

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[12] Optimum exponents are the following: for H 1s (1.486, 1.872); for C 1s (5.099, 7.563), 2s (1.252, 1.780), 2p (1.125, 2.220), 3d (2.157).

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