

INTRAAOMIC EXCHANGE AND THE VIOLATION OF HUND'S RULE IN TWISTED ETHYLENE

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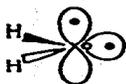
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It is demonstrated that the reason the singlet state lies below the triplet state in twisted ethylene (in violation of Hund's rule) is because there remains a significant component of the antiferromagnetic coupling of two triplet methylenes optimal for the methylene-methylene separated limit. We find that this effect can be completely described using a simple generalized valence bond wavefunction.

1. Introduction

Normally atoms and molecules with two electrons in orthogonal orbitals (φ_a and φ_b) have a triplet ground state with a corresponding singlet state higher by $2K_{ab}$, the two-electron exchange integral between φ_a and φ_b . Atomic examples include C and Si where the $(np)^2$ configuration leads to a 3P ground state. Molecular examples include (a) O_2 , where the ground configuration has two electrons in π_g orbitals leading to a $^3\Sigma_g^-$ ground state with the $^1\Delta_g$ state 1 eV higher [1] and (b) CH_2 , where the $(\sigma)(\pi)$ configuration

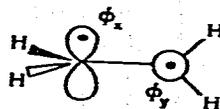


(1)

leads to a 3B_1 state with the corresponding 1B_1 state 1.6 eV higher [2].

Exceptions to this molecular Hund's rule are known. One example is the 90° -twisted form of ethylene. Since the two unpaired electrons are in

orthogonal orbitals (φ_x and φ_y),



(2)

we would expect a ground state triplet with the singlet state at ≈ 1.4 kcal ($K_{xy} = 0.7$ kcal at $R_{CC} = 1.48 \text{ \AA}$). However, while Hartree-Fock calculations lead to just such results ($E_s - E_t = 1.4$ kcal for $R_{CC} = 1.48 \text{ \AA}$), various calculations including electron correlation show that the singlet state actually lies 1-2 kcal *below* the triplet [3,4]. Another example is square cyclobutadiene, for which molecular orbital theory predicts a triplet coupling between the two singly occupied, degenerate π orbitals. As with twisted ethylene, Hartree-Fock yields a triplet ground state, but correlated wavefunctions indicate the singlet is ≈ 10 kcal lower than the triplet.

Kollmar and Staemmler [3] analyzed these and two other systems, square planar H_4 and planar methane, in terms of a configuration interaction wavefunction involving single excitations from the Hartree-Fock wavefunction. From this analysis, they provided an explanation involving *dynamic*

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spin polarization (DSP), an effect first proposed by Borden [5]. Since their work, the DSP concept has been discussed and invoked by others [6], and has thus gained some acceptance as an explanation for Hund's rule violations. We wish to offer an alternative view of the origins of these exceptions.

In each of the above systems, the correct prediction of a ground state singlet arises naturally when a valence bond (VB) analysis is employed in place of the molecular orbital description. In cyclobutadiene, for example, the four π electrons are readily coupled into two π bonds (singlet state).



Similarly, square H_4 forms two sigma bonds (singlet state),



In each of these cases there is a resonance between two equivalent structures, leading to additional stabilization of the singlet state. In this paper we treat the twisted-ethylene case, which requires a somewhat more sophisticated analysis. We show that the VB approach not only predicts the singlet-triplet inversion for twisted ethylene but also more directly exhibits the physical origin of this effect – *intraatomic spin coupling*. Thus we find that violation of Hund's rule arises naturally from the *static electron correlation* effects intrinsic to the VB description, and it is *not* necessary to invoke dynamic correlation effects.

2. Analysis for two electrons

Consider a system with one electron in orbital φ_a and one electron in orbital φ_b . We can form two different two-electron states: a singlet state

$$\Psi_s = (\varphi_a\varphi_b + \varphi_b\varphi_a)(\alpha\beta - \beta\alpha) \quad (3a)$$

and a triplet state

$$\Psi_t = (\varphi_a\varphi_b - \varphi_b\varphi_a)(\alpha\beta + \beta\alpha). \quad (3b)$$

The energies of these wavefunctions can be written

as

$$E_s = \frac{E_{ab} + E_{ab}^x}{1 + S_{ab}^2} = E_{ab} + \frac{\tau}{1 + S_{ab}^2}, \quad (4a)$$

$$E_t = \frac{E_{ab} - E_{ab}^x}{1 - S_{ab}^2} = E_{ab} - \frac{\tau}{1 - S_{ab}^2}, \quad (4b)$$

in which E_{ab} is the energy of the product wavefunction $\varphi_a\varphi_b$,

$$E_{ab} = \langle \varphi_a\varphi_b | H | \varphi_a\varphi_b \rangle = h_{aa} + h_{bb} + J_{ab}, \quad (5)$$

S_{ab} is the overlap $\langle \varphi_a | \varphi_b \rangle$, and E_{ab}^x is the "exchange energy" [7] *,

$$E_{ab}^x = \langle \varphi_a\varphi_b | H | \varphi_b\varphi_a \rangle = 2S_{ab}h_{ab} + K_{ab}, \quad (6)$$

where H is the full electronic hamiltonian, h_{ab} is the one-electron integral $\langle a | h | b \rangle$ **, J_{ab} is the two-electron Coulomb integral, and K_{ab} is the two-electron exchange integral. Here

$$\tau = E_{ab}^x - S_{ab}^2 E_{ab} \quad (7)$$

is the quantity determining whether the singlet state or triplet state is lower; negative τ leads to singlet, while positive τ leads to triplet. For cases where φ_a and φ_b overlap, the one-electron terms (including h_{ab}) generally dominate the positive two-electron terms ($K_{ab} - S_{ab}^2 J_{ab}$) so that τ is negative, leading to a singlet ground state. An example of this is H_2 in which the singlet lies below the triplet, even at large R when S_{ab} is quite small. It is this negative τ term that gives rise to the bonding between overlapping orbitals, and we can say that the singlet state is bonding, while the triplet state is antibonding.

If φ_a and φ_b are orthogonal, as in twisted ethylene (2), then $\tau = K_{ab}$ is positive, so that the triplet state lies below the singlet state by $2K_{ab}$. This is the basis of Hund's rule. For configurations having singly occupied orthogonal orbitals, the high-spin state should be lowest since it maximizes the number of exchange integrals that con-

* The "exchange energy" E^x arises due to the Pauli principle.

** This two-electron analysis also applies to systems with more than two electrons, if the additional electrons are all in doubly occupied orbitals common to both states. For such a case, the field terms arising from the extra electrons are contained in the one-electron operator h .

tribute to the energy with a negative sign. Applying these principles to twisted ethylene (2), we calculate

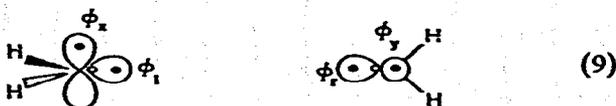
$$\tau = K_{xy} = 0.7 \text{ kcal}, \quad (8)$$

suggesting that the triplet state should lie lower by $2K_{xy} = 1.4$ kcal. In fact, however, quality calculations find the singlet state below the triplet by 2.3 kcal. To understand this effect we must consider more than just the two π electrons.

3. Analysis for four electrons

3.1. Long R case

Consider two methylene molecules, oriented as in twisted ethylene, but separated by a large distance R ,



Each methylene is a ground state triplet, so that the total spin function should maintain this intrafragment coupling. This leads to the well-known Heisenberg spectrum of states for two weakly coupled, interacting high-spin systems, in which the energy can be expressed as [8,9]

$$E(S) = a - JS(S + 1), \quad (10)$$

where S is the total spin of the system, a is a base energy independent of S , and J is the Heisenberg coupling constant that depends on internuclear distance and can be positive or negative. We find that a more useful expression is

$$E(S) = b + f(S)\tau_{\text{inter}}, \quad (11)$$

where b is a base energy independent of S (analogous to E_{ab} in the two-electron case), and $f(S)$ is given by

$$f(S) = [-S(S + 1) + n]/n^2 \quad (12)$$

for the case with n electrons in each fragment (the general expression is given in appendix A). τ_{inter} is the sum of all interfragment exchange energies, defined exactly as in the two-electron case (6). For the methylene-methylene case (9), this exchange energy becomes

$$\tau_{\text{inter}} = \tau_{I_r} + \tau_{I_y} + \tau_{x_r} + \tau_{x_y} = \tau_{I_r} + K_{I_y} + K_{x_r} + K_{x_y} \quad (13)$$

Since φ_l and φ_r are the only interfragment orbitals that overlap, τ_{inter} represents simply a bond between φ_l and φ_r (this negative bonding term τ_{I_r} is much larger than the positive exchange integrals $K_{I_y} + K_{x_r} + K_{x_y}$), and we can see from (11) that this bonding is all that distinguishes the different spin states energetically. Evaluating $f(S)$ for the three possible states ($S = 0$, $S = 1$, $S = 2$) yields

$$E_s^{\text{TT}} = b + \frac{1}{2}\tau_{\text{inter}}, \quad (14a)$$

$$E_t^{\text{TT}} = b, \quad (14b)$$

$$E_q^{\text{TT}} = b - \tau_{\text{inter}}. \quad (14c)$$

Thus, of these three states that maintain the character of two triplet methylenes (TT states), the singlet state has half a sigma bond, the triplet is non-bonding, and the quintet is antibonding. Hence, at long R we expect the singlet to be lowest, with the splitting pattern

$$(E_q^{\text{TT}} - E_t^{\text{TT}})/(E_t^{\text{TT}} - E_s^{\text{TT}}) = 2, \quad (15)$$

just as predicted by (10).

3.2. Short R case

At short R the sigma bonding becomes quite important, and to maximize this effect, the wavefunction tends toward a VB coupling of φ_l and φ_r

$$(\varphi_l\varphi_r + \varphi_r\varphi_l)(\alpha\beta - \beta\alpha). \quad (16)$$

The orthogonal orbitals, φ_x and φ_y , which are not involved in this bonding, may be coupled into a singlet or a triplet as discussed in section 2. For

each of these states there is a full sigma bond, so the triplet lies below the singlet by $2K_{xy}$. In the VB wavefunction, the σ and π orbitals on each carbon are no longer coupled into the triplet state appropriate for the methylene fragment. Hence, the VB wavefunctions allow a full sigma bond (worth ≈ 90 kcal at R_c) at the expense of half the intrafragment exchange, while the TT states maximize the intrafragment exchange ($K_{xt} + K_{yr} \approx 40$ kcal) but with reduced sigma bonding. As might be anticipated, the optimum wavefunction is a compromise between these two limits. If the states were purely VB at R_c , the triplet would be lower (in accord with Hund's rule), but because of residual long R (TT) character in both states, the singlet still lies below the triplet.

4. Description of the bonding from GVB calculations

We present here the results of spin-optimized generalized valence bond [10] (GVB) calculations on twisted ethylene that confirm the qualitative explanation presented above.

The details of the calculation are in appendix B. All calculations were performed using orthogonal orbitals, but the wavefunctions may be rigorously rewritten as [11]

$$\Psi_s = A [\varphi_l \varphi_r \varphi_x \varphi_y (C_s^{VB} \chi_s^{VB} + C_s^{TT} \chi_s^{TT})] \quad (17)$$

and

$$\Psi_t = A [\varphi_l \varphi_r \varphi_x \varphi_y (C_t^{VB} \chi_t^{VB} + C_t^{TT} \chi_t^{TT})], \quad (18)$$

in which φ_l and φ_r may overlap. The spin functions χ_s^{VB} and χ_t^{VB} are the VB spin couplings appropriate for short R , and χ_s^{TT} and χ_t^{TT} are the long- R (TT) spin couplings. It is important to note that these spin functions are not orthogonal, but were chosen because the spin coefficients in this representation give a direct accounting of the amount of long- R versus short- R character in the wavefunction. In fig. 1 we show the variation of the spin character as a function of R . As expected, both the singlet and triplet states are completely TT-coupled at long R , and examination of fig. 2 shows a nearly quantitative Heisenberg splitting

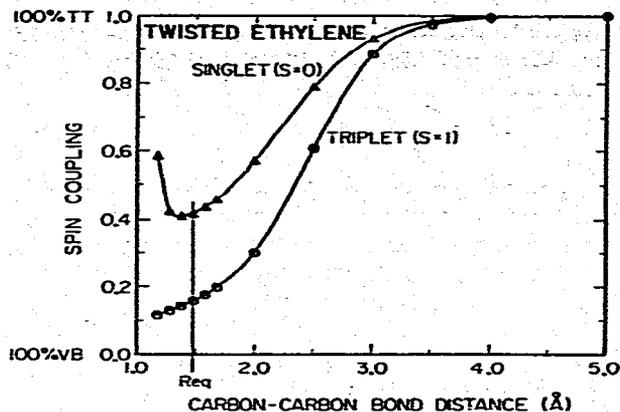


Fig. 1. The variation of the spin character as a function of R . The quantity plotted is the angle between the VB spin vector and the optimum spin vector divided by the angle between the VB and TT spin vectors (30° for singlet, and 45° for triplet). This yields a quantity that ranges from 0 for a pure VB spin function to 1.0 for pure TT.

pattern [as given by (15)] for R greater than 3 \AA . We notice also in this region that the amount of VB character in the triplet is roughly twice that of the singlet, which is reasonable since the triplet gains a full bonding interaction by mixing in VB, while the singlet gains only a half bonding interaction. As R is further decreased, both states be-

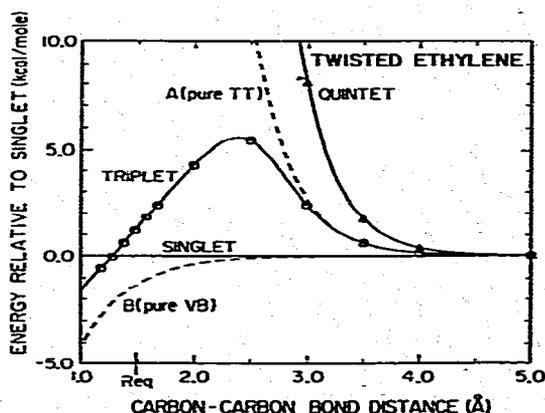


Fig. 2. The energies of the triplet and quintet states referenced to the energy of the singlet state. The dashed lines represent the idealized behavior of the triplet state for the two limiting cases; A: (pure TT case - Heisenberg splitting) $E_t - E_s = (E_q - E_s)/3$, and B: (pure VB case) $E_t - E_s = -2K_{xy}$.

come dominated by VB coupling for which the triplet is better than the singlet. However, since this bias is only $2K_{xy}$, the residual TT character keeps the triplet above the singlet at R_c . As the triplet energy approaches the $E_s - 2K_{xy}$ asymptote at short R (dashed line in fig. 2), the triplet does cross over and becomes the lowest state (for $R < 1.28 \text{ \AA}$).

Even at the equilibrium bond length, there is roughly 14% TT character in the triplet state, indicating the importance of the intra-methylene triplet coupling. The singlet state, which loses only half as much bonding as TT character is mixed in, is over 40% TT at the energy minimum. At very short R , the TT character in the singlet state actually begins to increase again. This may be due to a decrease in bonding strength as the carbons are forced too close together, enabling the TT character to be built in with less penalty.

5. Conclusions

We find that GVB wavefunctions for twisted ethylene quantitatively reproduce the singlet-triplet inversion obtained by other workers using higher levels of correlation. In addition, our simple wavefunctions properly dissociate to ground state methylenes, enabling us to examine the singlet-triplet splitting as a function of R . From this study emerges a conceptual model in which the importance of maintaining the triplet character in the methylene fragments is seen to play a key role. The model predicts an antiferromagnetic Heisenberg spectrum at long R , with a singlet ground state that persists until very short R , where the splitting approaches $2K_{xy}$. Hund's rule does not apply until R is 0.2 \AA shorter than R_c , where $2K_{xy}$ is large enough to compensate for the residual TT singlet stabilization.

We have been aware of the importance of maintaining optimal intraatomic exchange coupling in transition-metal systems, leading, for example, to the antiferromagnetic bonding in Cr_2 and Mo_2 [12], but were surprised to find a main-group system for which the ground state is determined by an analogous intrafragment coupling. The importance of such effects may have been under-

estimated for non-metal systems, and it is hoped that the concepts presented here will be useful in predicting and interpreting future occurrences.

Finally, we want to emphasize that the deviation from Hund's rule involves only the static electron correlation effects implicit to a VB description; thus one need not think of this effect as arising from dynamic spin correlations.

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Appendix A: Heisenberg coupling

Consider a system of N electrons divided into two weakly interacting high-spin subsystems containing m electrons and n electrons. The total spin S may have values from $|m - n|/2$ to $(m + n)/2$ in unit increments. We seek to evaluate $f(S)$, the coefficient of exchanging two one-electron spatial orbitals, one from the m set and the other from the n set. By the Pauli principle, this is equivalent to evaluating the negative of the exchange of the spin coordinates of the two electrons, which is equivalent to the spin operator $-\tau_{ij} = -\frac{1}{2} - 2s_i \cdot s_j$. The sum of all exchanges among the $N = m + n$ electrons is

$$\begin{aligned} \langle \chi(S) | \sum_{i>j} -\tau_{ij} | \chi(S) \rangle \\ &= \langle \chi(S) | \sum_{i>j} \left(-\frac{1}{2} - 2s_i \cdot s_j\right) | \chi(S) \rangle \\ &= \langle \chi(S) | \sum_{i>j} \left(-\frac{1}{2}\right) + \sum_i (s_i^2) - S^2 | \chi(S) \rangle \\ &= -\frac{1}{2}N(N-1)/2 + \frac{3}{4}N - S(S+1) \\ &= -N(N-4)/4 - S(S+1). \end{aligned} \quad (\text{A.1})$$

Each of the exchange coefficients between orbitals in the same set is -1 , while each of the exchange

Table 1
Summary of results from various levels of wavefunction. Total energies are in hartree, relative energies are in kcal relative to singlet, angles are in degree, and distances are in angstrom

	Hartree-Fock			GVB(PP) ^{a)}			Spin-optimized GVB ^{b)}			SD CI ^{c)}		
	singlet	triplet	triplet	singlet	triplet	triplet	singlet	triplet	quintet	singlet	triplet	
	2	1	2	4	2	4	10	4	1	51,292	36,702	
determinants												
opt. FICH angle	117.57	117.54	117.62	117.65	117.62							
opt. CC distance	1.477	1.473	1.494	1.498	1.494	1.497						
CC distance	Total E	Rel. E ^{d)}	Rel. E ^{d)}	Total E	Rel. E ^{d)}	Rel. E ^{d)}	Total E	Rel. E ^{d)}	Rel. E ^{d)}	Total E	Rel. E ^{d)}	
1.18	-77.867134	-2.78	-2.78	-77.874031	-2.78	-0.58	-77.878535	-0.58	335.88			
1.28	-77.929632	-2.20	-2.20	-77.938473	-2.20	-0.05	-77.943161	-0.05	328.44			
1.38	-77.958178	-1.74	-1.74	-77.969212	-1.74	0.60	-77.974486	0.60	315.83			
1.48	-77.965417	-1.37	-1.37	-77.978900	-1.37	1.21	-77.984923	1.21	296.12		1.24	
1.58	-77.959472	-1.08	-1.08	-77.975674	-1.08	1.80	-77.982601	1.80	266.03			
1.68	-77.945617	-0.85	-0.85	-77.964826	-0.85	2.38	-77.972828	2.38	227.78			
2.00	-77.881022	-0.39	-0.39	-77.912136	-0.39	4.22	-77.925021	4.22	118.13		2.00	
2.50	-77.783505	-0.10	-0.10	-77.842692	-0.10	5.35	-77.867846	5.35	33.74			
3.00	-77.712548	-0.02	-0.02	-77.810665	-0.02	2.38	-77.847191	2.38	8.01			
3.50	-77.664095	-0.01	-0.01	-77.800971	-0.01	0.594	-77.842223	0.594	1.735			
4.00	-77.631273	0.00	0.00	-77.798724	0.00	0.131	-77.841200	0.131	0.358			
5.00	-77.593116	0.00	0.00	-77.798219	0.00	0.006	-77.841001	0.006	0.015			

^{a)} GVB perfect pairing.

^{b)} The GVB wavefunctions for singlet and triplet are given by eqs. (17) and (18). For the quintet state, the consistent level of wavefunction is Hartree-Fock.

^{c)} Singlet and double CI from two GVB(PP) dominant configurations.

^{d)} In the text these relative energies are equated to $2K_{xy}$. This is approximate since different orbitals are used for the singlet and triplet states. This is, however, a good approximation; thus, for the GVB(PP) wavefunction at $R = 1.48 \text{ \AA}$, the K_{xy} for the singlet state leads to $2K_{xy} = 1.34 \text{ kcal}$, whereas the singlet-triplet energy difference is 1.37 kcal .

coefficients between orbitals in different sets is $f(S)$. The sum of all exchanges is

$$(-1)[m(m-1)/2 + n(n-1)/2] + f(S)[mn]. \quad (\text{A.2})$$

Equating the two expressions for the sum of all exchanges leads to

$$f(S) = \left[-S(S+1) + \frac{1}{2}(m+n) + \frac{1}{4}(m-n)^2 \right] / mn. \quad (\text{A.3})$$

The total energy (to first order) is

$$E(S) = E_{\text{intra}} + E_{\text{inter}}^{\text{C}} + f(S)\tau_{\text{inter}}, \quad (\text{A.4})$$

where E_{intra} is the sum of all intra-set energies, $E_{\text{inter}}^{\text{C}}$ is the sum of all inter-set Coulomb energies, and τ_{inter} is the sum of all inter-set exchange energies,

$$\tau_{\text{inter}} = \sum_i^m \sum_j^n \tau_{ij}, \quad (\text{A.5})$$

with τ_{ij} defined by (6). Comparing this result with eq. (10), we see that the Heisenberg coupling constant J is simply the average of all inter-set exchange energies:

$$J = \tau_{\text{inter}} / mn. \quad (\text{A.6})$$

Appendix B: Computational details

All calculations used the Dunning valence double-zeta contraction [13] of the Huzinaga 9s5p gaussian basis [14] plus a d polarization function ($\alpha = 0.75$) on carbon, and a four-gaussian double-zeta basis* on hydrogen. The experimental geometry was used [15] ($R_{\text{CC}} = 1.339 \text{ \AA}$, $R_{\text{CH}} = 1.085 \text{ \AA}$, $\theta_{\text{HCH}} = 117.8^\circ$), except that the methylenes were twisted 90° with respect to each other, and the C-C bond length was varied from 1.18 to 5.0 \AA . This geometry is completely compatible with previous studies [3,4], and it is interesting to note that our optimal HCH angle for the twisted geometry

* The four-gaussian hydrogen basis from ref. [13] was scaled by 1.2 and contracted 3.1.

is within 0.3° of the experimental angle for the planar form (see table 1). The Caltech GVB3 program [16] was used to optimize an MC SCF wavefunction with a four-orbital active space with all other orbitals doubly occupied and optimized self-consistently. The four-orbital active space consisted of two natural orbitals (σ and σ^*) for the sigma bond pair and two open shells (π_x and π_y). A single particle description (spin-optimized GVB) requires only three occupations of σ , σ^* , π_x , π_y . Two occupations (2011 and 0211) yield the VB coupling of σ_i and σ_r , while a third occupation (1111) is necessary for the other spin couplings. For singlet, the occupation (1111) has two spin couplings: (1) $(\sigma\sigma^*)_s(\pi_x\pi_y)_s$ and (2) $(\sigma\sigma^*)_t(\pi_x\pi_y)_t$. Only the second coupling can interact with the VB singlet, since the first coupling has different D_{2d} symmetry. For triplet, the occupation (1111) has three spin couplings: (1) $(\sigma\sigma^*)_s(\pi_x\pi_y)_t$, (2) $(\sigma\sigma^*)_t(\pi_x\pi_y)_s$, and (3) $(\sigma\sigma^*)_t(\pi_x\pi_y)_t$. Only the second coupling can interact with the VB triplet, since the first and third wave have different D_{2d} symmetry from VB. For both singlet and triplet, the first coupling of the occupation (1111) is ionic in σ_i and σ_r and must be omitted from a single-particle description – even in the absence of symmetry. With D_{2d} symmetry, the third triplet coupling is omitted, so that both singlet and triplet have only one degree of freedom in spin coupling.

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