

Origin of the conical intersection between the singlet ionic excited surfaces of twisted ethylene

Padeleimon Karafiloglou and Jean-Paul Malrieu

Laboratoire de Physique Quantique (ERA 821 au CNRS), Université Paul Sabatier, 118, Route de Narbonne, F-31062 Toulouse Cedex, France

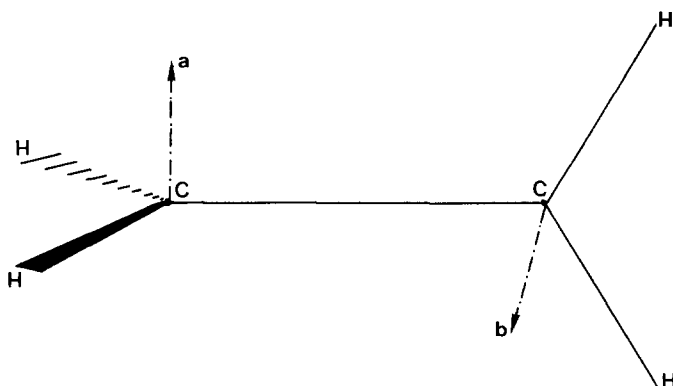
The potential surfaces of the two valence ionic singlet excited states of twisted ethylene are known to exhibit a conical intersection for a twist angle of the double bond near $\theta \cong 82^\circ$, and no pyramidalization of the CH_2 groups. The factors responsible for the stabilization of the symmetric excited state near $\theta \cong 90^\circ$ are shown to be $(\sigma \rightarrow \pi)^2$ and $(\pi \rightarrow \sigma^*)^2$ double excitations. The analysis is performed in the Quasi Degenerate Perturbation Theory formalism. The analogy with the ${}^1A_g \leq {}^3B_u$ ordering problem of the diradical ground and lower triplet states through a double spin polarization of the σ system is established.

Key words: Ethylene excited states—conical intersection—quasi degenerate perturbation theory

1. Introduction

The twisting of a double bond breaks the double bond description, induces near degeneracies and gives rise to surprising events. As an example one may quote the unusual ordering of the nearly degenerate neutral states of ethylene at 90° twist; the lowest singlet remains the ground state, the nearly degenerate triplet state lies a few kcal/mole above, while they both are represented by a typical

diradicalar openshell situation. Reducing the wavefunction to



its π part, one would write

$${}^1\psi = \frac{1}{\sqrt{2}}[|a\bar{b}\rangle + |b\bar{a}\rangle]$$

$${}^3\psi = \frac{1}{\sqrt{2}}[|a\bar{b}\rangle - |b\bar{a}\rangle]$$

which would lead to the prediction of a typical $E({}^3\psi) \leq E({}^1\psi)$ energy ordering, due to the non vanishing $2K_{ab}$ exchange integral splitting. The correct ordering $E({}^1\psi) \leq E({}^3\psi)$ has been explained by Kollmar and Staemmler [1] in terms of double spin polarization of the σ system (and especially the central C-C bond).

The ionic excited states of ethylene, and especially the 1B_u singlet excited state, have been the subject of a large number of studies since they are the simplest members of the family of $\pi\pi^*$ excited states of conjugated molecules. The attention has concentrated first on the vertical excitation, the amount of Rydberg/valence mixing and the ability to reproduce the vertical transition energy. The dominantly valence character of the state (with strong valence/Rydberg mixing) and the 8 eV vertical transition energy are now well established [2]. A second series of questions concerned the twisting of the double bond which is known to lower the energy of the excited 3B_u and 1B_u $\pi\pi^*$ excited states. The question became especially attractive when Salem et al. [3, 4] evidenced the so-called "sudden polarization" phenomenon, i.e. an instability of the charge repartition on the double bond under a slight external field (chemical substitution by a CH_3 group) or a slight geometrical symmetry breaking (pyramidalization of one CH_2 group). This high sensitivity has been recognized as due to the near degeneracy between the ${}^1B_u(\pi \rightarrow \pi^*)$ excited state and the ${}^1A_g(\pi \rightarrow \pi^*)^2$ doubly excited state in the $\theta = 90^\circ$ twisted conformation. The shapes of the potential surfaces of these two (essentially or purely ionic in the sense of Valence Bond Theory) states have been explored near the minimum by Brooks and Schaefer [5] and Trinquier and Malrieu [6], and in a systematic way by Buenker et al. [7]. (For a qualitative drawing of these surfaces see Ref. [8]). An intriguing feature

of these accurate calculations is that an intersection occurs between the two 1B_1 (V) and 1A_1 (Z) ionic surfaces for $\theta \cong 82^\circ$; this means that for $82^\circ \leq \theta < 98^\circ$ the doubly excited state 1A_1 becomes lower in energy than the singly excited one 1B_1 . When the central symmetry is broken by the pyramidalization of one of the $-\text{CH}_2$ groups, the two surfaces can no longer cross and the intersection at $\theta \cong 82^\circ$ may be viewed as a conical intersection. The purpose of the present work is to give interpretation of this conical intersection, and essentially of the $E({}^1A_1) \leq E({}^1B_1)$ energy ordering near $\theta = 90^\circ$. This work is in some sense parallel to the interpretation of the antiferromagnetic coupling between the two neutral states by Kollmar and Staemmler [1]. It will be shown that in both cases the coupling with the σ electrons is responsible for the unexpected behavior of the ionic states.

2. Method and modelization

As is well known, the two electron π problem of ethylene may be treated first in the valence (minimal) basis set, although diffuse orbitals are necessary for a quantitative treatment of the ionic excited states, and d orbitals for the correct account of angular electronic correlation in the ionic situations.

Let us suppose that one starts from an openshell HF calculation for the 3B_u state, or from a two (π^2, π^{*2}) MCSCF calculation for the ground state. These calculations deliver two π and π^* MO's essentially built from the a and b " $2p_\pi$ " AO's of the carbon atoms. The π and π^* MO's will become nearly degenerate (non bonding) when θ tends to 90° . A simple unitary transformation

$$a = (\pi + \pi^*)/\sqrt{2}$$

$$b = (-\pi + \pi^*)/\sqrt{2}$$

defines two local MO's which are essentially defined on a and b respectively, with hyperconjugation tails. In view of this local character one may use the Valence Bond picture for these two electrons and consider two neutral determinants $|a\bar{b}|$ and $|b\bar{a}|$, and two ionic determinants $|a\bar{a}|$ and $|b\bar{b}|$. The σ part of the wavefunction is for the moment kept frozen in an MO form and does not appear explicitly at this stage. In other words $|a\bar{b}|$ stands for $|\sigma_1\bar{\sigma}_1 \cdots \sigma_n\bar{\sigma}_n a\bar{b}|$ where σ_i is a σ SCF-MO, etc. . . . Then the VB-CI matrix reduced to the four π determinants keeps the form

neutral		ionic	
$ a\bar{b} $	$ b\bar{a} $	$ a\bar{a} $	$ b\bar{b} $
E_0	K_{ab}	F_{ab}	F_{ab}
	E_0	F_{ab}	F_{ab}
		E_1	K_{ab}
			E_1

E_0 and E_1 are the expectation values of the neutral and ionic determinants respectively; K_{ab} is the exchange integral, always positive, which decreases to a small non zero value when θ goes to 90° . F_{ab} is the hopping integral between neutral and ionic determinants, it behaves as the overlap between the local “ $2p_\pi$ ” AO’s, i.e. vanishes for $\theta = 90^\circ$. Of course this is only a reduced part of the VB-CI matrix which would involve σ excitations, promotion to diffuse AO’s and so on.

For small values of θ , F_{ab} is large, and is responsible for the large interaction between the symmetrical combinations of neutral and ionic determinants

$$\frac{1}{2}(|a\bar{b}| + |b\bar{a}| |H| |a\bar{a}| + |b\bar{b}|) = 2F_{ab}.$$

Resulting in a two by two matrix for 1A_1 states

$$\begin{array}{cc} \frac{1}{\sqrt{2}}(|a\bar{b}| + |b\bar{a}|) & \frac{1}{\sqrt{2}}(|a\bar{a}| + |b\bar{b}|) \\ E_0 + K_{ab} & 2F_{ab} \\ & E_1 + K_{ab} \end{array}$$

The ground state is a combination of (predominantly) neutral and ionic determinants, while the singlet ${}^1A_1^*$ excited state is a positive combination of neutral and predominantly ionic determinants. The 1B_1 state is purely ionic

$$\psi({}^1B_1) = \frac{1}{\sqrt{2}}(|a\bar{a}| - |b\bar{b}|)$$

and therefore is much lower in energy than $\psi({}^1A_1^*)$ if F_{ab} is large enough. Since

$$E({}^1B_1) = E_1 - K_{ab},$$

it should remain lower in energy than the excited (${}^1A_1^*$) state, even for $\theta = 90^\circ$ since,

$$E({}^1A_1^*) = E_1 + K_{ab}$$

K_{ab} remains positive and one should expect a $E({}^1B_1) < E({}^1A_1^*)$ ordering.

However, K_{ab} is very small for $\theta = 90^\circ$, and the situation may be considered as nearly degenerate, other couplings involving σ levels or σ electrons may reverse the ordering, as occurred for the neutral states.

The best instrument to treat nearly degenerate situations is of course the Quasi Degenerate Perturbation Theory (QDPT) in one of its numerous versions [9, 10]. We shall use the Rayleigh Schrödinger version using the intermediate normalization, and an Epstein-Nesbet [11] definition of H_0 . The reader who is not familiar with this field may convince himself that at the second order level, for a two state degeneracy, the treatment reduces to the diagonalization of an effective Hamiltonian built on the (nearly degenerate) determinants I and J , the matrix elements of which are

$$\langle I | H^{\text{eff}} | J \rangle = \langle I | H | J \rangle + \sum_{K \neq I, J} \frac{\langle I | H | K \rangle \langle K | H | J \rangle}{E_J^0 - E_K^0}. \quad (1)$$

The two degenerate determinants of our problem are $|a\bar{a}|$ and $|b\bar{b}|$ respectively and the zeroth order effective hamiltonian reduces to the right lower sub-matrix of page 4. Now one must analyze the second order corrections. The diagonal corrections to $\langle a\bar{a}||H^{\text{eff}}||a\bar{a}\rangle$ or to $\langle b\bar{b}||H^{\text{eff}}||b\bar{b}\rangle$ are not interesting for us when the two carbon atoms remain equivalent (no pyramidalization of a single $-\text{CH}_2$ group). The only factor that determines the ${}^1A_1^*/{}^1B_1$ energy ordering is the sign of the $\langle a\bar{a}||H^{\text{eff}}||b\bar{b}\rangle$ off-diagonal matrix element of the effective Hamiltonian

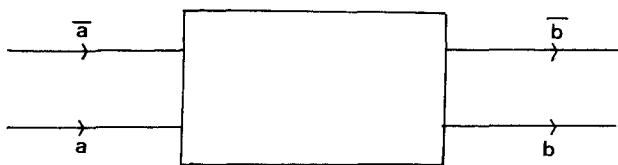
$$\langle a\bar{a}||H^{\text{eff}}||b\bar{b}\rangle = K_{ab} + \sum_{K \neq |a\bar{a}|, |b\bar{b}|} \frac{\langle a\bar{a}||H|K\rangle\langle K|H||b\bar{b}\rangle}{E_1 - E_K}. \quad (2)$$

Since $E({}^1A_1^*) - E({}^1B_1) = 2\langle a\bar{a}||H^{\text{eff}}||b\bar{b}\rangle$, when $\langle a\bar{a}||H^{\text{eff}}||b\bar{b}\rangle > 0$, ${}^1A_1^*$ is higher in energy than 1B_1 while the reverse is true when $\langle a\bar{a}||H^{\text{eff}}||b\bar{b}\rangle$ is negative. The existence of a conical intersection for $\theta \cong 82^\circ$ implies that $\langle a\bar{a}||H^{\text{eff}}||b\bar{b}\rangle$ vanishes for this angle.

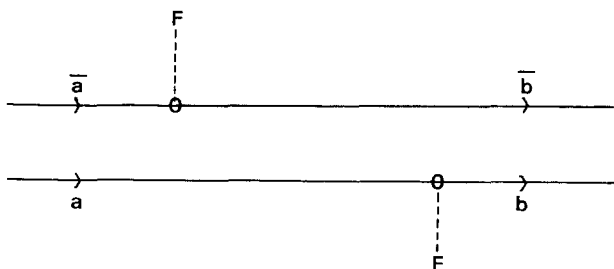
The determinants $|K\rangle$ appearing in the perturbation sum will be the already mentioned neutral determinants $|a\bar{b}|$ and $|b\bar{a}|$ and others. The second order contribution from the neutral determinants to the effective interaction is

$$\mathcal{A} = 2 \frac{\langle a\bar{a}||H||a\bar{b}\rangle\langle a\bar{b}||H||b\bar{b}\rangle}{E_1 - E_0} = \frac{2F_{ab}^2}{E_1 - E_0}. \quad (3)$$

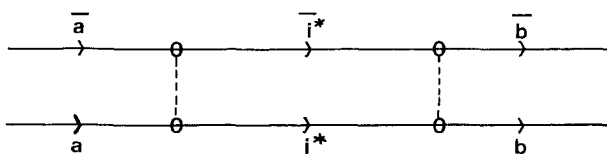
Since E_1 is larger than E_0 , this contribution is positive and, as already mentioned, acts in favor of the ${}^1A_1^* > {}^1B_1$ ordering. The other contributions to the effective coupling in the minimal basis set imply the σ electrons or the σ^* levels. The determinants which allow to go from $|a\bar{a}|$ to $|b\bar{b}|$ may be searched in a systematic manner through a diagrammatic expansion, taking the SCF σ electron sea as the vacuum state. All the two step procedures may be visualized from the scheme



The already studied effect of the neutral configurations is given by

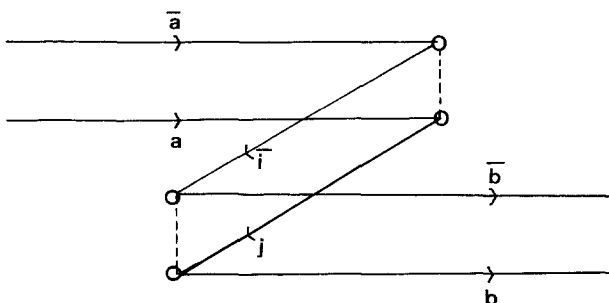


Besides this effect the most important contributions are



$$\mathcal{B} = (ai^*, aj^*)(bi^*, bj^*) / (E_i - E(\Sigma i^* j^*)) \quad (4)$$

through the doubly excited state $\Sigma_{ij^*} = (1/\sqrt{2})[|\sigma_1 \cdots \bar{\sigma}_n \sigma_{i^*} \bar{\sigma}_{j^*}| + |\sigma_1 \cdots \bar{\sigma}_n \sigma_{j^*} \bar{\sigma}_{i^*}|]$ which sends the two “ $2p_\pi$ ” electrons on virtual MO's i^* and j^* , and



$$\mathcal{C} = (b\sigma_b, b\sigma_j)(a\sigma_b, a\sigma_j) / (E_1 - E(\phi_i \phi_j a\bar{a}b\bar{b})) \quad (5)$$

through the doubly excited state $\phi_i \phi_j a\bar{a}b\bar{b} = (1/\sqrt{2})[|\sigma_1 \cdots \sigma_i \cdots \bar{\sigma}_j \cdots \bar{\sigma}_n a\bar{a}b\bar{b}| + |\sigma_1 \cdots \sigma_j \cdots \bar{\sigma}_i \cdots \bar{\sigma}_n a\bar{a}b\bar{b}|]$. Let us concentrate first on the \mathcal{C} term, which may be written using K_a and K_b exchange operators

$$\mathcal{C} = \langle \sigma_i | K_a | \sigma_j \rangle \langle \sigma_j | K_b | \sigma_i \rangle / (E_1 - E(\phi_i \phi_j a\bar{a}b\bar{b})). \quad (6)$$

Due to the local character of the K_a and K_b operators, σ_i and σ_j should have large components on both carbon atoms, and one may expect a large contribution from the case $\sigma_i = \sigma_j = \sigma_{CC}$ where the two electrons jump from the σ_{CC} bond MO. In this case both integrals are of the same sign, while the denominator is necessarily negative and if this contribution is dominant,

$$\mathcal{C} < 0. \quad (7)$$

Notice that hyperconjugation, which delocalizes the a and b MO's on the H atoms linked to the other carbon, also insures a non negligible contribution from the case $\sigma_i = \sigma_j = \sigma_{CH}$.

The \mathcal{B} term may be written as well

$$\mathcal{B} = \langle i^* | K_a | j^* \rangle \langle j^* | K_b | i^* \rangle / (E_1 - E(\Sigma i^* j^*)), \quad (8)$$

where the $i^* j^*$ distribution must be important on both carbon atoms. In the minimal basis set, one contribution appears to be dominant, namely the one resulting from $i^* = j^* = \sigma_{CC}^*$ (i.e. the excitation of the two “ $2p_\pi$ ” MO's into the

σ_{CC}^* antibonding level of the CC bond). The sign of the contribution (reinforced by closed shell excitations to σ_{CH}^* levels relative to CH antibonding MO's) is of course negative

$$\mathcal{B} < 0. \quad (9)$$

If one leaves the minimal basis set, adding diffuse virtual MO's or *d* type MO's, it becomes less easy to predict dominant contributions. Cancellations should occur between various terms and one may expect that the main phenomenon rests in the valence shell.

One should notice that the \mathcal{B} contribution is due to the promotion of the two π electrons into σ^* levels, it concerns $\Pi^{(-2e^-)\Sigma^{(+2e^-)}}$ contributions while the \mathcal{C} contribution involves excitations of the σ electrons into the π MO's, i.e. situations of the type $\Pi^{(+2e^-)\Sigma^{(-2e^-)}}$.

One should also compare these processes with the double spin polarization phenomenon of the σ core, responsible for the unexpected $E(^1A_1) < E(^3B_1)$ ordering at the 90° twisted conformation which was given by

$$E(^1A_1) - E(^3B_1) = 2K_{ab} - \sum_{\sigma_i \sigma_j^*} \frac{\langle \sigma_i | K_a | \sigma_j^* \rangle \langle \sigma_j^* | K_b | \sigma_i \rangle}{E_{\sigma_j^*} - E_{\sigma_i}} \quad (10)$$

the second term was dominated by the $\sigma_i = \sigma_{\text{CC}}, \sigma_j^* = \sigma_{\text{CC}}^*$ contribution and which involved the same K_a and K_b local exchange operators, and CC σ bond.

Then in the energy splitting between the two ionic states

$$2 \langle |a\bar{a}\rangle | H^{\text{eff}} | |b\bar{b}\rangle \rangle = 2(K_{ab} + \mathcal{A} + \mathcal{B} + \mathcal{C}) \quad (11)$$

the two first terms of the right-hand side are positive, while the two last ones are negative. K_{ab} is very small around $\theta \cong 90^\circ$, while \mathcal{A} is vanishing since it varies as F_{ab}^2 i.e. as $\cos^2 \theta$. On the other hand the \mathcal{B} and \mathcal{C} terms are not very sensitive to the torsional angle θ ; the contribution from the CC bond is almost independent of θ , while the contributions from the CH bonds should increase with hyperconjugation. Thus for $\theta = 90^\circ$, $2 \langle |a\bar{a}\rangle | H^{\text{eff}} | |b\bar{b}\rangle \rangle$ should be negative while for $\theta = 0^\circ$, this term is by far dominated by \mathcal{A} , i.e. by the coupling with neutral configurations; somewhere near 90° , $\langle |a\bar{a}\rangle | H^{\text{eff}} | |b\bar{b}\rangle \rangle$ should vanish, and the $^1A_1^*$ and 1B_1 singlet states must become degenerate.

3. Numerical results

Numerical calculations have been performed using a minimal Valence Basis set for a 1.40 Å C—C bond length, without pyramidalization of the CH groups. The use of a minimal basis set does not modify the qualitative behaviour of the problem since a crossing actually occurs near $\theta = 79^\circ$ (see Fig. 1, full lines) (instead of 82° in the work of Buenker et al. [7]) and the separation between the *Z* and *V* states for $\theta = 90^\circ$ are calculated to be 6 kcal/mole in our work instead of 4 kcal/mole in Ref. [7]. These results are obtained through a large scale CI from a multireference zeroth order wavefunction according to the CIPSI algorithm

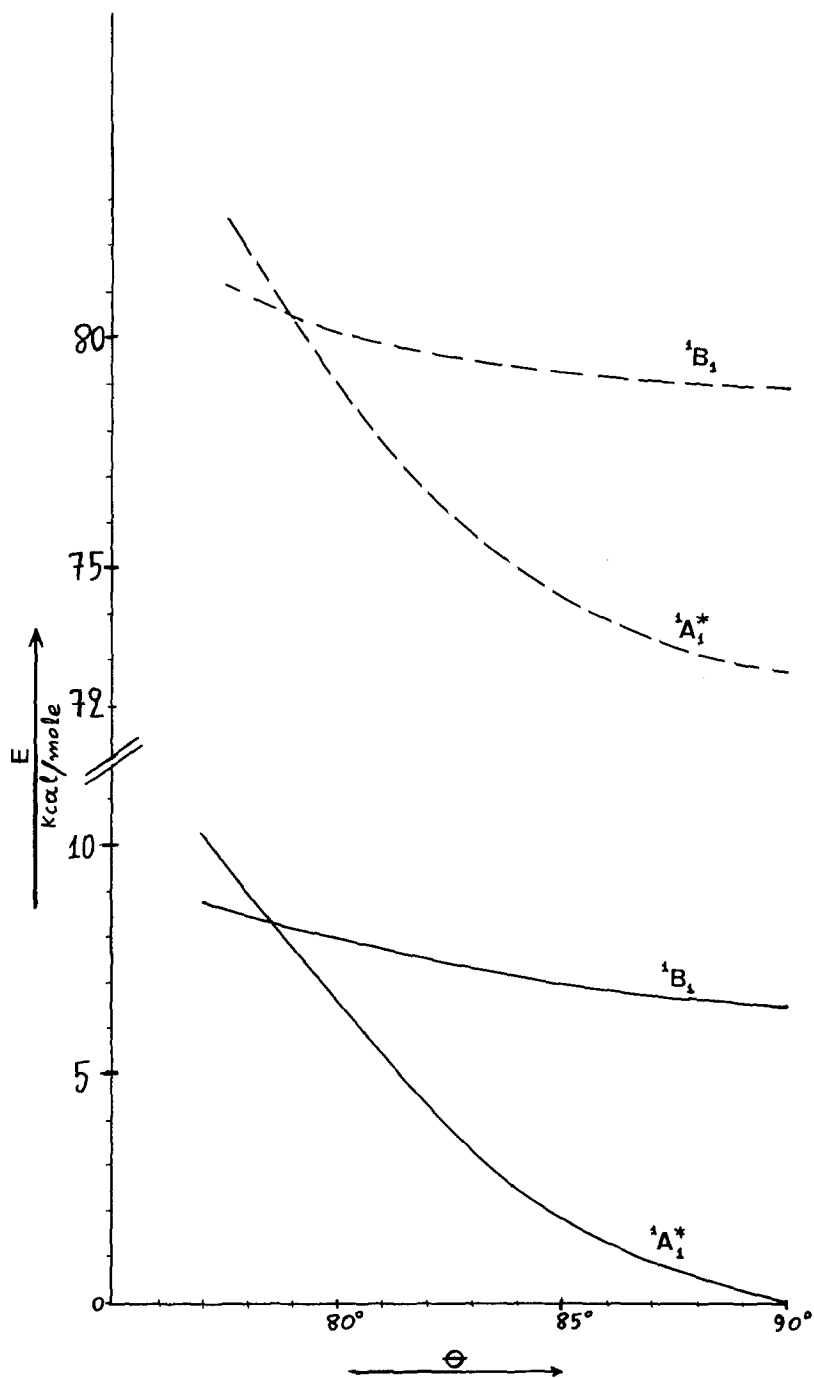


Fig. 1. Position of the ${}^1A_1^*$ and 1B_1 potential curves of the ionic singlet state of ethylene, as function of the twist angle θ ($r_{CC} = 1.40 \text{ \AA}$) in a minimal basis set. Full curves = extended CI, dotted curves = diagonalization of a CI restricted to $(\sigma \rightarrow \pi^*)^2$ and $(\pi \rightarrow \sigma^*)^2$ double excitations

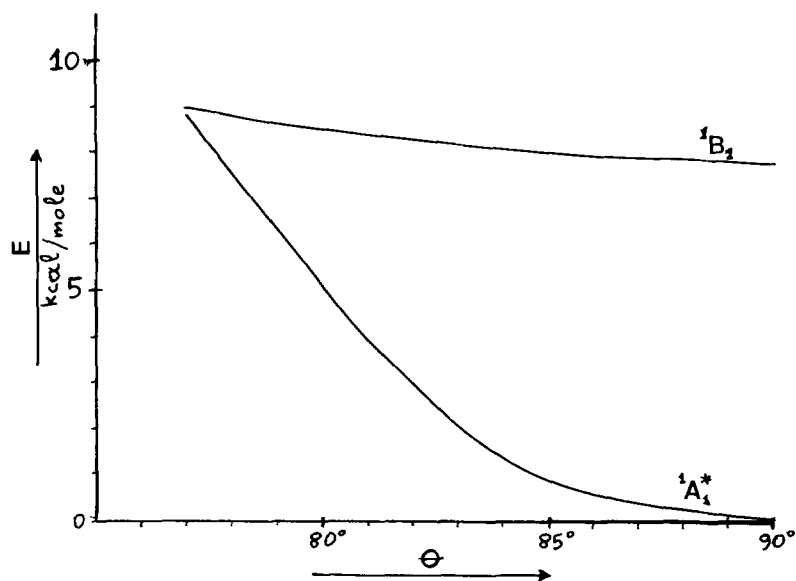


Fig. 2. ${}^1A_1^*$ and 1B_1 potential curves resulting from the diagonalization of a second order 4×4 effective Hamiltonian defined on the $|ab\rangle$, $|b\bar{a}\rangle$, $|a\bar{a}\rangle$ and $|b\bar{b}\rangle$ determinants

[13]. To check the above developed model a CI diagonalization restricted to the determinants suspected to play the key role in the problem have been performed, which gives an almost perfect parallelism with our large CI result (see Fig. 1, dotted lines). This limited CI proves that the curve crossing results from the balance between the ionic-neutral coupling and the effect of the double excitations involving $(\pi \rightarrow \sigma^*)^2$ and $(\sigma \rightarrow \pi^*)^2$ double excitations (contributions \mathcal{B} and \mathcal{C}).

A direct calculation has been performed in terms of a 4×4 effective Hamiltonian built on the four basic valence determinants $|ab\rangle$, $|b\bar{a}\rangle$, $|a\bar{a}\rangle$ and $|b\bar{b}\rangle$ using a second order only perturbation theory in the above mentioned limited CI basis. The results appear in Fig. 2 showing that the main effects are qualitatively reproduced: the $Z < V$ energy ordering is obtained for $\theta = 90^\circ$, but the energy difference is somewhat overestimated due to the 2nd order limitation, and this overestimation of the perturbations stabilizing the Z state results in a slight shift of the curve-crossing toward smaller values of θ ($\approx 77^\circ$).

4. Conclusion

A conical intersection had been shown to occur from the extensive *ab initio* calculation [7] of the potential surfaces of the two ionic excited singlet states of ethylene, in the twisted conformation. The present work has interpreted the change in the energy ordering of the ${}^1B_1/{}^1A_1^*$ states occurring near $\theta \approx 80^\circ$. This has been done using the Quasi Degenerate Perturbation Theory and Effective Hamiltonian formalism [14], since the local ionic configurations $|a\bar{a}\rangle(A^-B^+)$ and $|b\bar{b}\rangle(A^+B^-)$ are degenerate and *weakly* interacting near $\theta = 90^\circ$. For small values

of θ , the coupling with the neutral configurations is dominant and insures $({}^1B_1) < ({}^1A_1^*)$. When θ approaches 90° , this coupling tends to vanish while some double excitations of σ electrons to the π levels or of the π electrons to the σ^* levels induce some negative effective couplings insuring

$$({}^1A_1^*) < ({}^1B_1).$$

The numerical calculations which agree well with the accurate calculations of Buenker et al. [7] confirm the analytically derived mechanism. One should notice that in a recent work using non orthonormal CI, Petsalakis et al. [15] were compelled to include $(\sigma \rightarrow \pi^*)^2$ and $(\pi \rightarrow \sigma^*)^2$ double excitations to obtain the relevant ${}^1A_1^*/{}^1B_1$ energy ordering. The present work shows that this result is independent on the use of state adapted non orthogonal MO's.

It is amazing to see from Eqs. (6), (8) and (10) that the local exchange operators K_a and K_b which explained the unexpected (Hund's violating, or antiferromagnetic) ordering of the neutral diradical states near 90°

$$({}^1A_1) < ({}^3B_1)$$

are also responsible for the conical intersection in the ionic surfaces, and that they act through a coupling with the σ levels (essentially of the σ_{CC} bond). The double spin polarisation of the σ system, responsible for the antiferromagnetic coupling, was due to the passage into a ${}^3\Pi(S_z = \pm 1) \times {}^3\Sigma(S_z = \mp 1)$ situation, while the $({}^1A_1^*) < ({}^1B_1)$ ordering is due to a two-electron jump between σ and π systems. Schematically, the double spin polarization of the σ system

$${}^1\Sigma \times a\bar{b} \rightarrow \left\{ \begin{array}{c} {}^3\Sigma(S_z = 1) \times {}^3\Pi(S_z = -1) \\ \text{or} \\ {}^3\Sigma(S_z = -1) \times {}^3\Pi(S_z = 1) \end{array} \right\} \rightarrow {}^1\Sigma \times a\bar{b}$$

explains the $({}^1A_1) < ({}^3B_1)$ ordering while $\sigma - \Pi$ two electron jumps

$${}^1\Sigma \times a\bar{a} \rightarrow \left\{ \begin{array}{c} {}^1\Sigma^{(+2e^-)} \times \Pi^{(-2e^-)} \\ \text{or} \\ {}^1\Sigma^{(-2e^-)} \times \Pi^{(+2e^-)} \end{array} \right\} \rightarrow {}^1\Sigma \times b\bar{b}$$

explain the $({}^1A_1^*) < ({}^1B_1)$ ordering.

In the \mathcal{B} term (Eqs. (4) and (8)), the two electrons located on \mathcal{A} jump in the σ^* MO, and get out on the B atom, using the monocentric $K_{p_x p_x}$ or $K_{p_x s}$ exchange integrals; in the \mathcal{C} term (Eqs. (5) and (6)) starting again from $|a\bar{a}|$ two electrons jump from a σ MO to the empty p orbital on B ; then the two electrons on A move back into the σ sea to fill up the temporarily emptied σ level, again through monocentric exchange integral. The σ bonding and antibonding levels act as channels for left-right two-electron jumps between the two " $2p_\pi$ " AO's, while one-electron jumps (mechanism \mathcal{A}) become prohibited for $\theta = 90^\circ$. The three mechanisms are schematically pictured in Fig. 3.

From a fundamental point of view one must remember that the ${}^3B_1/{}^1A_1$ degeneracy is a problem of weak spin coupling, in a fluctuating spin problem,

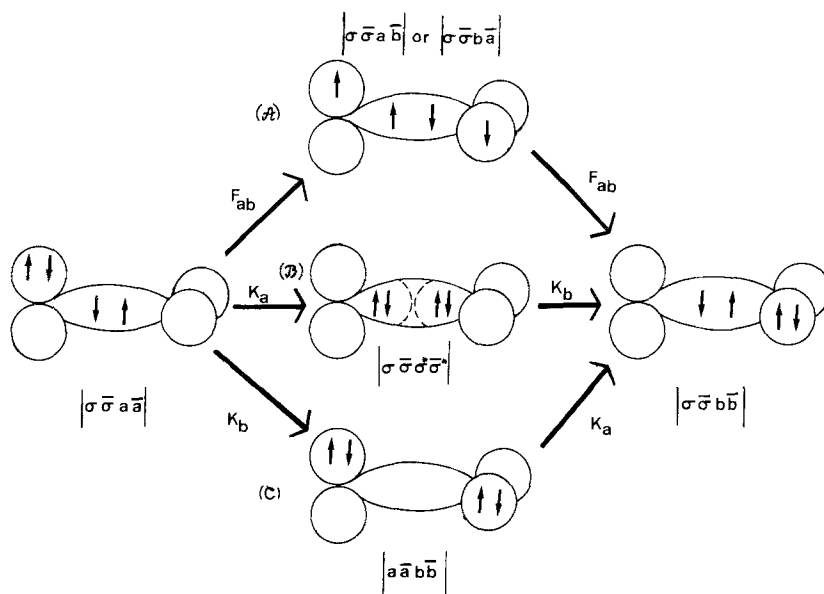


Fig. 3. Illustration of the three mechanisms responsible for the ${}^1A_1^*/{}^1B_1$ energy difference

and the answer is given by a fluctuation of the σ/π spin distributions (passing through a product of Σ and Π triplets), while the ${}^1A_1^*/{}^1B_1$ problem is a charge fluctuation problem, which finds its answer in a fluctuation of the σ/π electronic populations. This isomorphism is structural.

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References

- Kollmar, H., Staemmler, V.: *Theoret. Chim. Acta (Berl.)*, **48**, 223 (1978)
- a, Brooks, B. R., Schaefer III, H. F.: *J. Chem. Phys.* **68**, 4839 (1978); b. Buenker, R. J., Shih, S. K., Peyerimhoff, S. D.: *Chem. Phys.* **36**, 97 (1979)
- Bonacic-Koutecky, V., Bruckmann, P., Hiberty, P., Koutecky, J., Leforestier, C., Salem, L.: *Angew. Chem. Int. Ed. Engl.* **14**, 575 (1975)
- Salem, L., Bruckmann, P.: *Nature (London)* **258**, 526 (1975); Salem, L.: *Science* **191**, 822 (1976)
- Brooks, R., Schaefer III, H. F.: *J. Amer. Chem. Soc.* **101**, 307 (1979)
- Trinquier, G., Malrieu, J. P.: *Chem. Phys. Letters* **72**, 328 (1980)
- Buenker, R. J., Bonacic-Koutecky, V., Pogliani, L.: *J. Chem. Phys.* **73**, 1836 (1980)
- Malrieu, J. P.: *Theoret. Chim. Acta (Berl.)* **59**, 251 (1981)
- a. Van Vleck, J. H.: *Phys. Rev.* **33**, 467 (1929); b. des Cloiseaux, J.: *Nucl. Phys.* **20**, 321 (1960); c. Brandow, B. H.: *Rev. Mod. Phys.* **39**, 771 (1967)
- Shavitt, I., Redmon, T.: *J. Chem. Phys.* **73**, 5711 (1980)
- a. Epstein, P. S.: *Phys. Rev.* **28**, 695 (1926); b. Nesbet, R. K.: *Proc. R. Soc. (London) Ser. A* **230**, 312, 322 (1955)
- Claverie, P., Diner, S., Malrieu, J. P.: *Int. J. Quantum Chem.* **1**, 751 (1967)

13. Huron, B., Malrieu, J. P., Rancurel, P.: *J. Chem. Phys.* **58**, 5745 (1972)
14. Such an approach has been presented formally in Daudey, J. P. and Malrieu, J. P.: *Current Aspects of Quantum Chemistry*, Carbo, R. ed. Amsterdam: Elsevier, 1982; for the treatment of diradical near degeneracy problem see a. de Loth, P., Cassoux, P., Daudey, J. P., Malrieu, J. P.: *J. Am. Chem. Soc.* **103**, 4007 (1981); b. Karafiloglou, P.: *Int. J. Quantum Chem.* **24**, 283 (1984); and Thèse d'Etat, Université de Paris XI (Orsay) 1983
15. Petsalakis, I. D., Theodorakopoulos, G., Nicolaidis, C. A., Buenker, R. J., Peyerimhoff, S. D.: private communication

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