

## ANALYSIS OF A THREE-STATE MODEL FOR THE NON-ADIABATIC PROCESSES ACCOMPANYING THE INTERNAL ROTATION OF ETHYLENE

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**ABSTRACT.** — A three-state model for the ground and first two excited singlet states of ethylene has been parameterized from the results of large scale SCFMO-CI calculations on the internal rotation of ethylene with simultaneous pyramidalization of one CH<sub>2</sub> group. Non-adiabatic coupling terms have been calculated from the resulting eigenfunctions and these show that strong coupling occurs over a range  $\sim \pm 10^\circ$  from the perpendicular configuration. This is a much broader range than has been found in some earlier work based on a two-state model.

### Introduction

There has recently been renewed interest in the behaviour of the low energy states of ethylene on internal rotation. The term "sudden polarization"<sup>1</sup> has been coined to describe the establishment of zwitterionic character in the excited states when an unsymmetrical olefine is twisted to a near perpendicular configuration. Weiss, and Warshel<sup>2</sup> claimed that this would be associated with high quantum yields for photochemical cis-trans isomerization and could be an important feature of the primary event in vision processes.

Three singlet spin states can be constructed from configurations which have two electrons in the  $\pi$  orbitals of ethylene (all other electrons being paired in  $\sigma$  orbitals). If **a** and **b** are the  $2p\pi$  atomic orbitals of the two carbon atoms then a suitable basis for the space functions of these singlet states is:

$$\psi_1 = (a(1)b(2) + b(1)a(2))/\sqrt{2}, \quad (1)$$

$$\psi_2 = (a(1)a(2) - b(1)b(2))/\sqrt{2}, \quad (2)$$

$$\psi_3 = (a(1)a(2) + b(1)b(2))/\sqrt{2}. \quad (3)$$

$\psi_1$  is a "covalent" state and is the valence bond ground state of planar ethylene.  $\psi_2$  and  $\psi_3$  are ionic resonance states. In a simple model  $\psi_2$  and  $\psi_3$  become nearly degenerate on twisting the molecule to the perpendicular configuration. If a further perturbation is applied which makes the two ends of the molecule different the eigenstates will be  $\psi_2 \pm \psi_3$  both of which will be zwitterionic. It is the predicted sudden onset of this zwitterionic character near a twist angle of  $\theta = 90^\circ$  that has been called sudden polarization<sup>1,3</sup>.

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There have been several accurate *ab initio* studies of these lower energy states of ethylene when internal rotation is combined with the pyramidalization of one CH<sub>2</sub> group<sup>4-7</sup>. Whilst these are in reasonable accord with the qualitative description given above, there is some disagreement over the "sudden-ness" of the polarizations. The nature of the wave functions produced in these calculations also makes it difficult to calculate the non-adiabatic coupling integrals which are of interest.

In this paper we have an approach which is intermediate between the accurate *ab initio* and the qualitative. We shall establish a 3-state model for twisting and pyramidalizing ethylene with parameters optimized to the *ab initio* energies. The wave functions arising from this model are then used to calculate the non-adiabatic coupling terms.

There have been several discussions of sudden polarization using only the basis functions  $\psi_2$  and  $\psi_3$ <sup>5,8-10</sup>. At  $\theta = 90^\circ$ ,  $\psi_1$  belongs to a different irreducible representation of the point group to  $\psi_2$  and  $\psi_3$ , whether one CH<sub>2</sub> group is pyramidalized or not. However, this is not true at other twist angles and if  $\psi_1$  is omitted from the basis then  $\psi_3$  decreases in energy as the molecule approaches planarity, which is incorrect.

### Parameterization of the model

We parameterize our model to recent calculations on the energies of ethylene as a function of twist angle ( $\theta$ ) and pyramidalization angle ( $\varphi$ ) of one CH<sub>2</sub> group<sup>10</sup>. These angles are defined in figure 1. The calculations were made with a basis of contracted gaussians of double zeta quality and a multireference double excitation CI with a configuration threshold of  $5 \times 10^{-6} E_h$ <sup>11,12</sup>. The surfaces generated from a CI on the triplet SCF wavefunction were fitted as they are the most reliable<sup>10</sup> and do not emphasize one particular state. CH

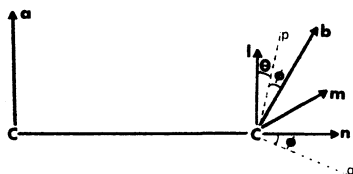


Figure 1. — Basis functions from which the matrix elements of  $\hat{H}$  and  $\hat{S}$  have been calculated.  $\mathbf{p}$  is the projection of  $\mathbf{b}$  on to the plane defined by  $\mathbf{l}$  and  $\mathbf{m}$  and  $\mathbf{q}$  is the bisector of  $\widehat{HCH}$  which is perpendicular to  $\mathbf{b}$ .

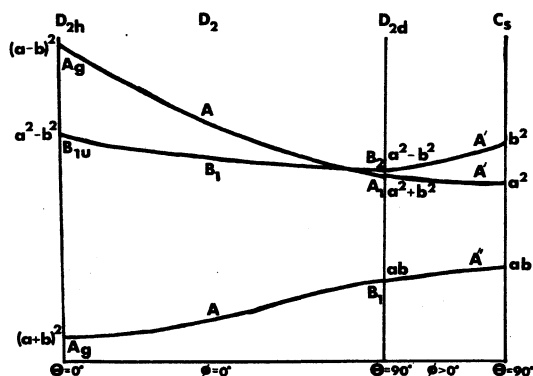


Figure 2. — Correlation diagram for the three singlet states of ethylene with  $\theta$  and  $\phi$  variables. The configurations are defined in the text.

bond lengths and HCH bond angles were fixed at experimental values for planar ethylene and the C-C bond length was taken to be 1.416 Å, the value calculated by Brooks, and Schaeffer for  $\theta = 90^\circ$ <sup>5</sup>.

A key feature of the above calculations is that a crossing of the excited states has been found at  $\theta = 81^\circ$ ,  $\phi = 0^\circ$ . The two states involved have symmetries  $^1A$  and  $^1B_1$  in  $D_2$ . Mulder has shown<sup>13</sup> that this crossing only appears in CI calculations which allow for some  $\sigma$ - $\pi$  mixing.

A correlation diagram for the 3-state model is given in figure 2. States have been identified with MO configurations in  $D_{2h}$  and VB configurations in  $D_{2d}$  and  $C_s$ .

There are six independent elements of the  $3 \times 3$  Hamiltonian matrix for the 3-state model and a direct fitting to the *ab initio* data without any knowledge of the functional form of these elements would be difficult. However, with the chosen basis the elements of the Hamiltonian and overlap matrices can be written in terms of one and two-electron integrals with the functional dependence on  $\theta$  and  $\phi$  being explicit. A semi-empirical fitting can then be achieved with only a few parameters.

We take  $\mathbf{a}$  to be the  $2p\pi$  atomic orbital of the  $\text{CH}_2$  group which remains fixed during the internal rotation and pyramidalization. The angular dependence of the matrix elements is then calculated by transforming  $\mathbf{b}$  to a space fixed basis:

$$\mathbf{b} = \mathbf{l} \cos \theta \cos \phi + \mathbf{m} \sin \theta \cos \phi + \mathbf{n} \sin \phi, \quad (4)$$

where  $\mathbf{l}$ ,  $\mathbf{m}$  and  $\mathbf{n}$  have the orientations shown in figure 1.  $\mathbf{l}$  and  $\mathbf{m}$  are assumed to be pure  $2p$  orbitals and  $\mathbf{n}$  some  $2s$ - $2p$  hybrid of fixed  $s/p$  ratio. Thus  $\mathbf{b}$  is a pure  $2p$  orbital without pyramidalization but  $2s$ -character is introduced for  $\phi \neq 0$ .

Table I gives the scaled elements of  $\hat{H}$  and  $\hat{S}$  in terms of parameters  $X$  and angular functions. To obtain these matrices it has been assumed that the one-electron core Hamiltonian is independent of  $\theta$  and  $\phi$ . A simplification occurs from the identity<sup>18</sup>:

$$J_{lm} + 2K_{lm} = \frac{1}{2}(J_{ll} + J_{mm}), \quad (5)$$

which we extend in the approximation:

$$J_{ln} + 2K_{ln} = \frac{1}{2}(J_{ll} + J_{nn}). \quad (6)$$

A further approximation was the writing of non zero two-centre hybrid integrals using the Mulliken formula<sup>14</sup>, for example:

$$\begin{aligned} (aa|ab) &= \cos \theta \cos \phi (aa|al) \\ &= \cos \theta \cos \phi S_{al} (J_{aa} + J_{al})/2. \end{aligned} \quad (7)$$

Table I. — Parameterisation of matrices used in fitting procedure.  $i$  and  $j$  refer to bases  $\psi_1$ ,  $\psi_2$  and  $\psi_3$  defined in the text.

$i$	$j$	$H_{ij} = \langle \psi_i   \hat{H} - (2H_{aa} + J_{am} + K_{am})   \psi_j \rangle$	$S_{ij} = \langle \psi_i   \psi_j \rangle$
1	1	$X(2) \cos \theta \cos \phi S_{ab} + X(4) \sin^2 \phi$	$1 + S_{ab}^2$
1	2	$-X(4) \sin^2 \phi S_{ab}$	0
1	3	$X(5) \cos \theta \cos \phi + X(4) \sin^2 \phi S_{ab}$	$2S_{ab}$
2	2	$X(7) - (X(2) \cos \theta \cos \phi S_{ab} + X(3) \sin^2 \phi) + X(4) \sin^2 \phi$	$1 - S_{ab}^2$
2	3	$-X(4) \sin^2 \phi$	0
3	3	$X(6) + (X(2) \cos \theta \cos \phi S_{ab} + X(3) \sin^2 \phi) + X(4) \sin^2 \phi$	$1 + S_{ab}^2$
where		$S_{ab} = \cos \theta \cos \phi X(1)$	
and		$X(1) = S_{al}$	
		$X(2) \approx 2(\langle a   H^c   l \rangle - S_{al} \langle a   H^c   a \rangle) + (J_{al} + K_{al})/S_{al} + S_{al}(J_{am} + K_{am})$	
		$X(3) \approx K_{an}$	
		$X(4) \approx \langle n   H^c   n \rangle - \langle a   H^c   a \rangle + \frac{1}{2}(J_{nn} - J_{aa})$	
		$X(5) \approx 2(\langle a   H^c   l \rangle - S_{al} \langle a   H^c   a \rangle) + S_{al}(J_{aa} + J_{al} - 2J_{am} - 2K_{am})$	
		$X(6) = J_{aa} - J_{am}$	
		$X(7) = J_{aa} - J_{am} - 2K_{am}$	

Other components of  $(aa|ab)$ , such as  $(aa|am)$ , are zero by symmetry.  $(ab|bb)$  was evaluated similarly.

In order to fix an energy scale, we took the ground state in the perpendicular configuration ( $\theta=90^\circ$ ,  $\Phi=0^\circ$ ) as the energy zero. This is done by subtracting  $S_{ij}(2H_{aa}+J_{am}+K_{am})$  from the elements of  $\mathbf{H}$ . The parameters  $X(6)$  and  $X(7)$  were then fixed by the energy intervals at  $\theta=90^\circ$ ,  $\Phi=0^\circ$ . Note that  $X(6)-X(7)$  is formally identified with  $2K_{am}$  which one would expect to be positive. However, to achieve a surface crossing at  $\theta=81^\circ$ ,  $\Phi=0^\circ$  it is necessary for  $X(6)-X(7)$  to be negative and we attribute this sign to  $\sigma-\pi$  mixing as already discussed<sup>13</sup>.

Even with these approximations the 2-electron integrals do not rigorously obey the parameterization scheme of Table 1. For example  $X(4)$  for  $H_{ii}$  should depend on  $(J_{an}+K_{an}-J_{am}-K_{am})$  instead of  $1/2(J_{nn}-J_{aa})$ . However, introduction of further parameters to account for these terms gave a negligible improvement in the least squares fit.

The parameters  $X(1)$  to  $X(5)$  were obtained by an equal weighted least squares fit to the energies of the three singlet states at 17 geometries in the range  $\theta > 45^\circ$ ,  $0 \leq \varphi \leq 20^\circ$  and to three points  $(0^\circ, 0^\circ)$ ,  $(20^\circ, 0)$  and  $(30^\circ, 20^\circ)$  for only the first two states. The third singlet in this region is associated with  $\sigma \rightarrow \pi$  excitation which is unconnected with our basis. The crossing point of the two excited states was also fitted.

The optimum parameters are given in Table II and gave a standard deviation of  $1.8 \times 10^{-3} E_h$  ( $4 \text{ kJ} \cdot \text{mol}^{-1}$ ) with the largest error being  $5.1 \times 10^{-3} E_h$  for the first excited state at  $(60^\circ, 20^\circ)$ . The crossing point was reproduced to better than  $1^\circ$  in  $\theta$ .

**Table II.** — Optimum parameters defined in Table I which have been obtained by fitting *ab initio* data.  $X(1)$  is dimensionless,  $X(2)$  to  $X(7)$  are in  $E_h$ .

$I$	1	2	3	4	5	6	7
$X(1)$	0.2843	-0.2059	0.0386	0.0179	-0.1526	0.1414	0.1356

### Evaluation of the non-adiabatic integrals

Diagonalization of the  $3 \times 3$  matrix with parameters chosen by the above procedure gives eigenfunctions of the form:

$$\Psi_i = \sum_{m=1,3} C_{im} \Phi_m, \quad (8)$$

where  $i$  correlates with the  $i$ th state at  $(90^\circ, 0^\circ)$  in our 3 state representation. Thus for  $\Phi > 0$ ,  $\Psi_2$  corresponds to the first excited state for all  $\theta$ . The non-adiabatic coupling for cis-trans isomerization depends on the magnitude of the integrals:

$$G_{ij} = \langle \Psi_i | \partial / \partial \theta | \Psi_j \rangle, \quad (9)$$

$$= \sum_{m=1,3} \sum_{n=1,3} \left\{ C_{im} C_{jn} T_{mn} + C_{im} \frac{\partial C_{jm}}{\partial \theta} \cdot S_{mn} \right\}, \quad (10)$$

where  $\mathbf{S}$  is given in Table I and:

$$T_{mn} = \langle \Psi_m | \partial / \partial \theta | \Psi_n \rangle. \quad (11)$$

The coefficients  $C_{im}$  were found to change smoothly with  $\theta$  over the whole range studied and their derivatives could easily be determined numerically. The matrix  $T_{mn}$  was calculated by taking  $\mathbf{a}$  to be independent of  $\theta$  and, from (4):

**Table III.** — Functional form of the matrix  $T_{mn}$

$$T = \begin{pmatrix} S_{ab} S'_{ab} & -S'_{ab} & S'_{ab} \\ S'_{ab} & -S_{ab} S'_{ab} & S_{ab} S'_{ab} \\ S'_{ab} & -S_{ab} S'_{ab} & S_{ab} S'_{ab} \end{pmatrix}$$

where:

$$S_{ab} = \cos \theta \cos \Phi X(1),$$

$$S'_{ab} = \frac{\partial S_{ab}}{\partial \theta} = -\sin \theta \cos \Phi X(1),$$

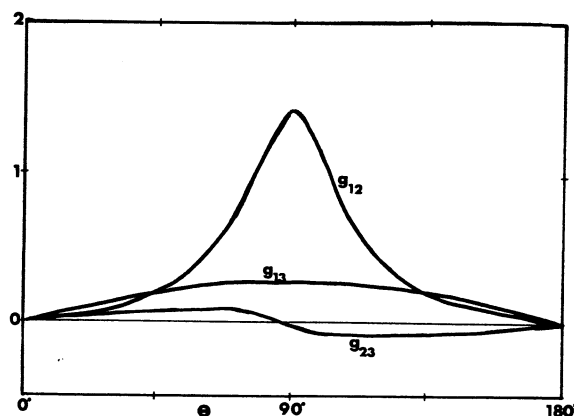
$$X(1) = S_{at}.$$

$$\frac{\partial \mathbf{b}}{\partial \theta} = -1 \sin \theta \cos \varphi. \quad (12)$$

The resulting elements of  $\mathbf{T}$  are given in Table III.

Our calculations show that the first term in (10) is the larger, for configurations close to  $\theta=90^\circ$ ; typically a factor of ten larger. Figure 3 shows the values of  $g_{ij}$  for  $\varphi=0$  as a function of  $\theta$ . There is no erratic behaviour and we note a maximum in  $|g_{12}|$  at  $\theta=90^\circ$ . Figure 4 shows the behaviour of  $g_{ij}$  for  $\varphi=20^\circ$  and the contrast with figure 3 is striking.  $|g_{12}|$  is still a smooth function with a slightly smaller peak than for  $\varphi=0$ .  $g_{13}$  and  $g_{23}$  however have strong oscillations close to  $\theta=90^\circ \pm 10^\circ$ , the region of avoided crossing of the two excited states. These strong oscillations indicate a breakdown of the Born-Oppenheimer approximation for the vibronic states of this system. In figure 3,  $g_{ij}$  represents the non-adiabatic term between states of constant symmetry. This means that  $g_{12}$  only links the ground and first excited states for  $81^\circ < \theta < 99^\circ$ . However, replotting the figure with  $g_{12}$  always between the lowest lying states would only serve to peak  $g_{12}$  slightly more sharply about  $\theta=90^\circ$  but make no qualitative difference to our conclusions.

Our results differ substantially from those of Weiss and Warshel<sup>2</sup> which were based on the unsymmetrical olefine retinal. They found a very rapid change of  $g_{12}$  near the perpendicular configuration which we do not find either for the symmetrical ( $\varphi=0$ ) or unsymmetrical system. Unlike these



**Figure 3.** — Non adiabatic coupling matrix elements  $g_{ij}$  in  $\text{radians}^{-1}$ , as a function of  $\theta$  with  $\varphi=0$ .

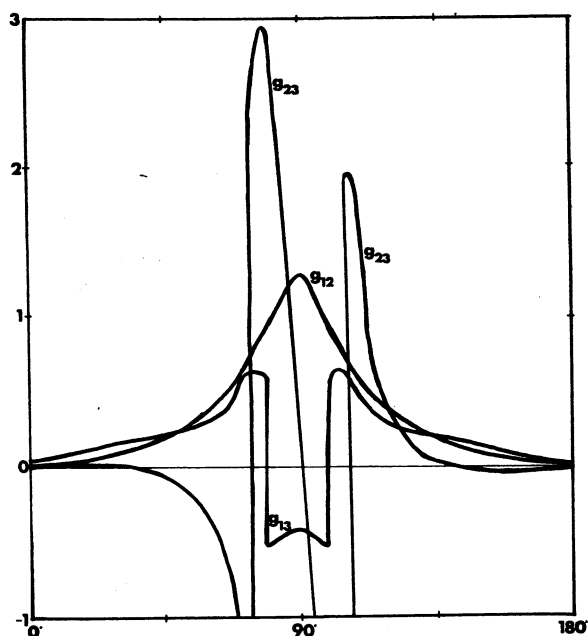


Figure 4. — Non adiabatic coupling matrix elements  $g_{ij}$  in radians<sup>-1</sup>, as a function of  $\theta$  with  $\phi = 20^\circ$ .

workers we see no evidence for a large non adiabatic transition between the first excited state and the ground state near the perpendicular configuration.

Orlandi *et al.*<sup>15</sup> calculated  $g_{23}$  using the two-state model referred to earlier. Their results are parameterized by the splitting ( $\Delta$ ) between the excited states in the perpendicular configuration. For a value  $\Delta = 32 \text{ kJ. mol}^{-1}$ , which accords with our calculations at  $\Phi = 20^\circ$ , they find  $g_{23}$  decays almost to zero within a  $1^\circ$  interval of  $\theta = 90^\circ$ . As can be seen from figure 4 our rate of decay is much slower. As the two-state model produces no crossing of the excited states they fail to obtain the oscillations in  $g_{23}$  and  $g_{13}$  which are associated with this crossing.

Persico<sup>16,17</sup> has calculated  $g_{ij}$  *ab initio* using a minimal basis and a three term configuration interaction. His rate of variation and maximum values of  $g_{ij}$  are similar to those we obtain but again without the crossing point oscillation. We

support his general conclusion that there is no evidence from the ethylene calculations to support the abrupt increase in radiationless transition probability near the perpendicular configuration of an olefine as has been suggested.

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- 17 M. Persico (to be published).
- 18  $J$  and  $K$  are two-electron Coulomb and exchange integrals which we write in the charge-cloud format as  $J_{lm} = (l^2 | m^2)$ , etc.