

Fragment Interaction Analysis in the Framework of *ab initio* UHF MO Computations.

I. Conformational Preference in the Ethyl Radical

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In this paper we describe a procedure which allows to obtain estimates of the energy effects associated with the orbital interactions occurring between the component fragments of a radical species in the framework of *ab initio* Unrestricted Hartree-Fock computations. This procedure is used here to analyze the factors which control the conformational isomerism of the ethyl radical.

Key words: P.M.O. analysis-Quantitative orbital analysis-Conformational analysis-Free radical-Orbital interaction.

1. Introduction

In recent papers [1] we have described a procedure which allows to obtain estimates of the energy effects associated with the orbital interactions occurring between the component fragments of a closed shell molecule in the framework of *ab initio* Restricted Hartree-Fock [2a] (RHF) computations. In this paper we describe a similar procedure which operates in the framework of *ab initio* Unrestricted Hartree-Fock [2b] (UHF) computations and allows to analyze quantitatively structural and reactivity problems involving, in particular, free radicals. This procedure is quite general and can be applied to the analysis of all kinds of orbital interactions. For illustrative purposes we describe here the

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application of such a procedure to the analysis of the factors which control the conformational preferences of the ethyl radical.

2. Computational Procedure

As previously suggested, [1] the whole computational procedure follows as much as possible the line of the qualitative Perturbational MO (PMO) approach [3] and therefore involves a procedure for the computation of the MOs of the component fragments and a procedure for the computation of the energy effects associated with the orbital interactions under examination based on PMO expressions.

Some of the basic features of a perturbative treatment at the UHF have already been discussed in a previous paper [4] where we have investigated the application, in the framework of INDO computations, of a procedure similar to that suggested by Wolfe et al. [5] and limited only to π orbital interactions.

2.1. Computation of the Fragment MOs

The main feature of the computational procedure for obtaining the fragment MOs in the framework of a UHF scheme is that the MOs of α spin and those of β spin are separated into two manifolds and are computed separately. The first step of this procedure involves the computation of the canonical fragment MOs of α and β spin from the solution of the following eigenvalue problems:

$$\mathbf{F}_\alpha^0 \mathbf{C}_\alpha^0 = \mathbf{G}_\alpha^0 \mathbf{C}_\alpha^0 \boldsymbol{\varepsilon}_\alpha^0 \quad (1.1)$$

$$\mathbf{F}_\beta^0 \mathbf{C}_\beta^0 = \mathbf{G}_\beta^0 \mathbf{C}_\beta^0 \boldsymbol{\varepsilon}_\beta^0 \quad (1.2)$$

where \mathbf{F}_α^0 , \mathbf{F}_β^0 and \mathbf{G}_α^0 , \mathbf{G}_β^0 (with $\mathbf{G}_\alpha^0 = \mathbf{G}_\beta^0$) are the Fock matrices and the overlap matrices for the composite system with all non-diagonal matrix elements between atomic orbitals belonging to the different interacting fragments set equal to zero. This procedure is therefore an extension to a UHF scheme of that suggested by Wolfe et al. in the framework of a RHF scheme.

For reactivity problems these canonical MOs can be directly used in the quantitative analysis. On the other hand, in the case of structural problems where the molecule under investigation is dissected into component fragments through the breaking of bonds, these fragment MOs are of limited usefulness in a quantitative analysis [1]: in fact, usually only the canonical fragment MOs of π type are acceptable fragment MO's, while the canonical doubly occupied σ MOs do not have correct orbital occupancies, because of their mixing with the formally singly occupied orbitals arising from the breaking of the bonds.

This problem can be satisfactorily solved in a UHF scheme following the same procedure used in the framework of RHF computations, i.e. through the application of a localization procedure to the set of canonical fragment MOs. The localization procedure is applied separately to the set of α and β MOs and for

each type of spins, to the set of the occupied and to the set of the vacant fragment MOs. In our applications we have used the Boys' method of localization [6].

2.2. PMO Approach

The interaction energy which obtains in the union of the component fragments in the case of a radical species can be estimated on the basis of the following expression:

$$\Delta E = \Sigma \Delta E_{ij}^4 + \Sigma \Delta E_{ij}^2 + \Sigma \Delta E_{ij}^3 + \Sigma \Delta E_{ij}^1 \quad (2)$$

where ΔE_{ij}^4 denotes the destabilization energy arising from the interaction of two doubly occupied MOs ϕ_i and ϕ_j ; ΔE_{ij}^2 the stabilization energy arising from the interaction of a doubly occupied MO ϕ_i with a vacant MO ϕ_j , ΔE_{ij}^3 the energy effect associated with the interaction of a doubly occupied MO ϕ_i and a singly occupied MO ϕ_j , and ΔE_{ij}^1 the stabilization energy arising from the interaction of a singly occupied MO ϕ_i with a vacant MO ϕ_j .

In a UHF treatment, the energy effects associated with the interactions between MOs of α spin and between MOs of β spin have to be computed separately. Since the occupation of an MO of α or β spin can be only 0 or 1, there are only two types of possible orbital interactions between the spin MOs, i.e. a stabilizing interaction occurring between a singly occupied spin MO and a vacant spin MO and a destabilizing interaction occurring between two singly occupied spin MOs. The associated stabilization energy $\Delta E_{ij}^1(\eta)$ and destabilization energy $\Delta E_{ij}^2(\eta)$ are given by the following expressions [4], where η denotes α or β spin:

$$\Delta E_{ij}^1(\eta) = [H_{ij}(\eta) - S_{ij}(\eta)\varepsilon_i(\eta)]^2 / [\varepsilon_i(\eta) - \varepsilon_j(\eta)] \quad (3)$$

$$\Delta E_{ij}^2(\eta) = 2[S_{ij}^2(\eta)\varepsilon_0(\eta) - S_{ij}(\eta)H_{ij}(\eta)] / [1 - S_{ij}^2(\eta)] \quad (4)$$

In these equations ε_i and ε_j denote the orbital energies of the interacting spin MOs ϕ_i and ϕ_j , ε_0 the mean of these energies, H_{ij} the interaction matrix element and S_{ij} the overlap integral.

The various terms appearing in these expressions are then computed using the results of the *ab initio* UHF computations. In particular:

(i) the matrix elements $H_{ij}(\eta)$ and the overlap integrals $S_{ij}(\eta)$ between the interacting fragments MOs are computed according to the following relations:

$$\mathbf{H}_\eta = (\mathbf{C}_\eta^0)^\dagger \mathbf{F}_\eta (\mathbf{C}_\eta^0) \quad (5)$$

$$\mathbf{S}_\eta = (\mathbf{C}_\eta^0)^\dagger \mathbf{G}_\eta (\mathbf{C}_\eta^0) \quad (6)$$

where (\mathbf{C}^0) denotes the coefficient matrix of the α or β canonical or localized fragment MOs depending on the problem, \mathbf{F}_η and \mathbf{G}_η the α or β Fock and overlap matrices for the composite system over the atomic orbital basis;

(ii) the values of the energies of the α or β fragment MOs, $\varepsilon_i(\eta)$, are chosen to be the diagonal elements of the \mathbf{H}_η matrix, either for canonical or localized fragment MOs.

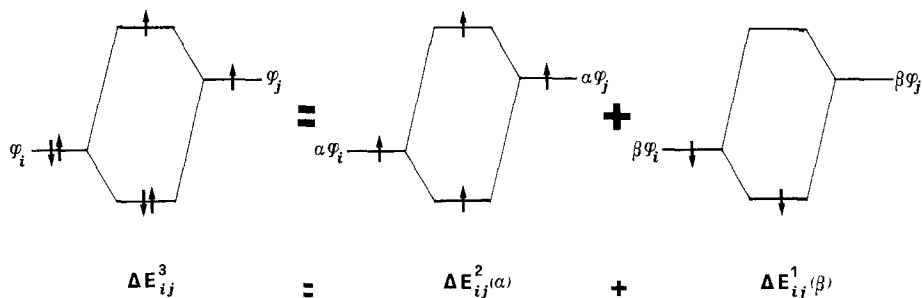


Fig. 1. Schematic decomposition of ΔE_{ij}^3 into the α component $\Delta E_{ij}^2(\alpha)$ which is destabilizing and the β component $\Delta E_{ij}^1(\beta)$ which is stabilizing

The various energy terms appearing in Eq. (2) can be all expressed in terms of the two basic expressions (3) and (4), and therefore computed in the framework of *ab initio* UHF computations, according to the following relationships:

$$\Delta E_{ij}^4 = \Delta E_{ij}^2(\alpha) + \Delta E_{ij}^2(\beta) \quad (7)$$

$$\Delta E_{ij}^3 = \Delta E_{ij}^2(\alpha) + \Delta E_{ij}^1(\beta) \quad (8)$$

$$\Delta E_{ij}^2 = \Delta E_{ij}^1(\alpha) + \Delta E_{ij}^1(\beta) \quad (9)$$

$$\Delta E_{ij}^1 = \Delta E_{ij}^1(\alpha) \quad (10)$$

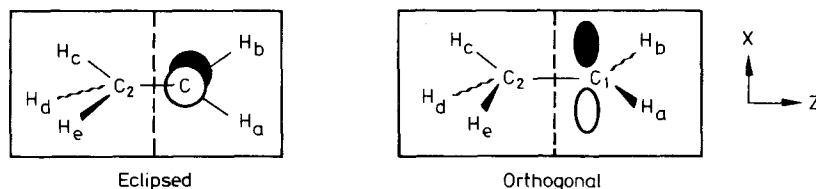
While the component terms of ΔE_{ij}^4 are both destabilizing and those of ΔE_{ij}^2 both stabilizing, the component terms of ΔE_{ij}^3 are one destabilizing, $\Delta E_{ij}^2(\alpha)$, and the other stabilizing, $\Delta E_{ij}^1(\beta)$ (see Fig. 1). Consequently the energy effect ΔE_{ij}^3 can be either destabilizing or stabilizing depending on which of the two component terms dominates.

3. Conformational Preference of the Ethyl Radical

To illustrate the types of information which can be obtained with a quantitative orbital analysis, we apply the procedure previously described to investigate the factors which control the conformational preference and the barrier for internal rotation of the ethyl radical.

Recent experimental results [7] indicate free rotation about the C—C bond. This finding is consistent with the results of an extensive SCF *ab initio* computation [8] which indicate the existence of only one minimum in the ground state energy surface corresponding to the staggered geometry, but with the eclipsed geometry less stable by only 0.2 kcal/mol. This small energy difference vanishes when the radical center in the staggered conformation is planar.

We have therefore analyzed the two conformations shown in the Scheme, denoted as eclipsed (*e*) and orthogonal (*o*), both with a planar radical center.



Scheme

The computations have been performed at the STO-3G [9] UHF level using the GAUSSIAN 76 series of programs [10]. Standard bond lengths and bond angles have been utilized, i.e. $r(\text{C}_1-\text{C}_2) = 1.52 \text{ \AA}$, $r(\text{C}_1-\text{H}) = 1.08 \text{ \AA}$, $r(\text{C}_2-\text{H}) = 1.09 \text{ \AA}$, $\text{HC}_2\text{H} = 109.47^\circ$ and $\text{HC}_1\text{H} = 120^\circ$. At this level the two conformations are found to have the same total energies, in agreement with the more sophisticated calculations [8].

In both conformations the molecule has been dissected as shown in the Scheme into the fragments $\text{H}_3\text{C}-$ and $-\dot{\text{C}}\text{H}_2$. We have first computed the canonical MOs of the two fragments as previously described and we have then performed two different types of localizations, obtaining two different representations for the MOs of the two fragments, denoted as localized and canonical representations.

3.1. Localized Representation

To obtain this representation, we have localized in the $\text{H}_3\text{C}-$ fragment all the canonical MOs and in the $-\dot{\text{C}}\text{H}_2$ fragment all the canonical MOs except the $2p_\pi$ carbon atomic orbital. The orbital energies and orbital occupancies of the resulting fragment localized MOs are listed in Table 1. Therefore the valence localized MOs of the $\text{H}_3\text{C}-$ fragment involve, in order of increasing energy:

- (i) three almost degenerate orbitals, all with occupation ~ 1 for the α and β components, localized along the C—H bonds and bonding between C and H (the bond orbitals σ_{CH});
- (ii) an MO with occupation ~ 0.5 for both the α and β components, localized along the C—C axis and pointing toward C_1 (σ_{C});
- (iii) three vacant almost degenerate orbitals, localized along the C—H bonds and antibonding between C and H (the antibond orbitals σ_{CH}^*).

For the $\text{H}_2\dot{\text{C}}-$ fragment the resulting valence localized MOs, in order of increasing energy, involve:

- (i) two degenerate σ_{CH} bond MOs, with occupation of ~ 1 for both the α and β components;
- (ii) a σ_{C} type MO pointing toward C_2 , with occupation of ~ 0.5 for both the spin components;
- (iii) a carbon $2p$ orbital, with occupation ~ 1 for the α component and ~ 0 for the β component;
- (iv) two degenerate σ_{CH}^* bond MOs.

Table 1. Energies (ϵ_i , a.u.) and gross populations (Q_i) of the α and β orbitals of the CH_2 and CH_3 fragments in $\text{CH}_3\dot{\text{C}}\text{H}_2$, in the localized representation

<i>i</i>	Orthogonal				Eclipsed			
	α -Orbital		β -Orbital		α -Orbital		β -Orbital	
	ϵ_i	Q_i	ϵ_i	Q_i	ϵ_i	Q_i	ϵ_i	Q_i
Fragment $\dot{\text{C}}\text{H}_2$								
$1s_C$	-10.9297	0.9997	-10.9024	0.9994	-10.9297	0.9997	-10.9024	0.9994
σ_{CH_a}	-0.6559	0.9985	-0.6110	0.9996	-0.6558	0.9985	-0.6110	0.9996
σ_{CH_b}	-0.6559	0.9985	-0.6110	0.9996	-0.6560	0.9985	-0.6111	0.9997
σ_C	-0.6116	0.5447	-0.4915	0.4498	-0.6116	0.5447	-0.4915	0.4498
<i>p</i>	-0.3587	0.9903	0.3111	0.0150	-0.3587	0.9903	0.3111	0.0150
$\sigma_{\text{CH}_a}^*$	0.7216	0.0019	0.7593	0.0019	0.7214	0.0020	0.7592	0.0021
$\sigma_{\text{CH}_b}^*$	0.7216	0.0019	0.7593	0.0019	0.7217	0.0017	0.7595	0.0018
Fragment CH_3								
$1s_C$	-10.9540	0.9990	-10.9573	0.9993	-10.9540	0.9990	-10.9573	0.9993
σ_{CH_c}	-0.6289	1.0027	-0.6225	0.9930	-0.6253	1.0005	-0.6287	1.0006
σ_{CH_d}	-0.6262	1.0010	-0.6272	0.9987	-0.6280	1.0021	-0.6241	0.9950
σ_{CH_e}	-0.6262	1.0010	-0.6272	0.9987	-0.6280	1.0021	-0.6241	0.9950
σ_C	-0.5112	0.4487	-0.5392	0.5411	-0.5111	0.4487	-0.5392	0.5411
$\sigma_{\text{CH}_c}^*$	0.7083	0.0067	0.7177	0.0000	0.7157	0.0014	0.7124	0.0013
$\sigma_{\text{CH}_d}^*$	0.7139	0.0027	0.7137	0.0010	0.7102	0.0054	0.7164	0.0003
$\sigma_{\text{CH}_e}^*$	0.7139	0.0027	0.7137	0.0010	0.7102	0.0054	0.7164	0.0003

Table 2. ΔE^4 , ΔE^3 , ΔE^2 , ΔE^1 Energies (kcal/mol) associated with the various orbital interactions between the CH_2 and CH_3 fragments in the orthogonal and eclipsed conformations of CH_3CH_2 in the localized representation (values in brackets give the α and β spin orbital energy components)

Interactions	Orthogonal ^a	Eclipsed ^a
$\Delta E_{\sigma_{\text{CH}_a}\sigma_{\text{CH}_c}}^4$	0.01 (0.00+0.01)	3.24 (1.69+1.55)
$\Delta E_{\sigma_{\text{CH}_a}\sigma_{\text{CH}_d}}^4$	2.37 (1.24+1.13)	1.34 (0.66+0.68)
$\Delta E_{\sigma_{\text{CH}_a}\sigma_{\text{CH}_e}}^4$	3.69 (1.86+1.83)	1.34 (0.66+0.68)
$\Delta E_{\sigma_{\text{CH}_b}\sigma_{\text{CH}_c}}^4$	0.01 (0.00+0.01)	4.86 (2.46+2.40)
$\Delta E_{\sigma_{\text{CH}_b}\sigma_{\text{CH}_d}}^4$	3.69 (1.86+1.83)	0.69 (0.37+0.32)
$\Delta E_{\sigma_{\text{CH}_b}\sigma_{\text{CH}_e}}^4$	2.37 (1.24+1.13)	0.69 (0.37+0.32)
$\Delta E_{\sigma_{\text{CH}_a}\sigma_{\text{CH}_c}}^2$	0.00 (0.00+0.00)	-0.15 (-0.07-0.08)
$\Delta E_{\sigma_{\text{CH}_a}\sigma_{\text{CH}_d}}^2$	-0.11 (-0.05-0.06)	-0.02 (-0.01-0.01)
$\Delta E_{\sigma_{\text{CH}_a}\sigma_{\text{CH}_e}}^2$	-0.06 (-0.03-0.03)	-0.02 (-0.01-0.01)
$\Delta E_{\sigma_{\text{CH}_b}\sigma_{\text{CH}_c}}^2$	0.00 (0.00+0.00)	-0.08 (-0.04-0.04)
$\Delta E_{\sigma_{\text{CH}_b}\sigma_{\text{CH}_d}}^2$	-0.06 (-0.03-0.03)	-0.04 (-0.02-0.02)
$\Delta E_{\sigma_{\text{CH}_b}\sigma_{\text{CH}_e}}^2$	-0.11 (-0.05-0.06)	-0.04 (-0.02-0.02)
$\Delta E_{\sigma_{\text{CH}_a}\sigma_{\text{CH}_c}}^2$	-0.05 (-0.03-0.02)	-0.49 (-0.27-0.22)
$\Delta E_{\sigma_{\text{CH}_a}\sigma_{\text{CH}_d}}^2$	-0.40 (-0.22-0.18)	0.00 (0.00+0.00)
$\Delta E_{\sigma_{\text{CH}_a}\sigma_{\text{CH}_e}}^2$	-0.03 (-0.01-0.02)	0.00 (0.00+0.00)
$\Delta E_{\sigma_{\text{CH}_b}\sigma_{\text{CH}_c}}^2$	-0.05 (-0.03-0.02)	-0.05 (-0.02-0.03)
$\Delta E_{\sigma_{\text{CH}_b}\sigma_{\text{CH}_d}}^2$	-0.03 (-0.01-0.02)	-0.21 (-0.12-0.09)
$\Delta E_{\sigma_{\text{CH}_b}\sigma_{\text{CH}_e}}^2$	-0.40 (-0.22-0.18)	-0.21 (-0.12-0.09)
$\Delta E_{p,\sigma_{\text{CH}_c}}^3$	7.76 (8.68-0.92)	0 (0+0)
$\Delta E_{p,\sigma_{\text{CH}_d}}^3$	1.94 (2.16-0.22)	5.83 (6.51-0.68)
$\Delta E_{p,\sigma_{\text{CH}_e}}^3$	1.94 (2.16-0.22)	5.83 (6.51-0.68)
$\Delta E_{p,\sigma_{\text{CH}_c}}^1$	-1.51 (-1.51+0)	0 (0+0)
$\Delta E_{p,\sigma_{\text{CH}_d}}^1$	-0.36 (-0.36+0)	-1.12 (-1.12+0)
$\Delta E_{p,\sigma_{\text{CH}_e}}^1$	-0.36 (-0.36+0)	-1.12 (-1.12+0)
$\Sigma\Delta E_T$	20.25 (16.29+3.96)	20.27 (16.29+3.98)

^a A net 0 means that the interaction vanishes for symmetry or occupancy reasons

The energy effects associated with the various non-bonded orbital interactions occurring between the MOs of the two fragments are listed in Table 2. The analysis of these data becomes particularly clear when we compare the results in the way illustrated in Fig. 2, where we have indicated the energy effects associated with the various groups of similar orbitals, such as the three σ_{CH} and the three σ_{CH}^* MOs of the H_3C - fragment and the two σ_{CH} and the two σ_{CH}^* MOs of the H_2C - fragment. The $\sigma_{\text{CH}}-\sigma_{\text{CH}}$ repulsions represent steric repulsions while the other interactions can be denoted as conjugative interactions. From these results we obtain the following information:

(i) The total energy effect associated with the non-bonded interactions, $\Sigma\Delta E_T$, has the same value in the two conformations: therefore this result agrees very well with the total energy behaviour. Furthermore $\Sigma\Delta E_T$ is destabilizing, which means that the steric repulsions are more important than the conjugative effects.

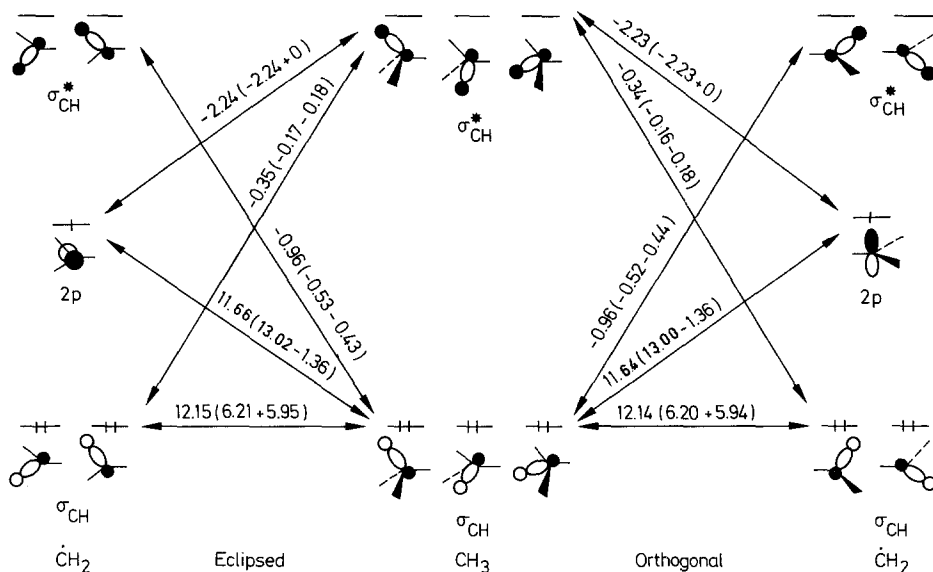


Fig. 2. Interaction diagram between the CH₃ and the CH₂ fragments in the eclipsed and orthogonal conformation of CH₃CH₂ in the localized representation

(ii) The energy effects associated with the groups of similar orbitals (see Fig. 2), e.g. steric ($\Sigma\Delta E^4$) and conjugative ($\Sigma\Delta E^2$) effects, are exactly the same in the two conformations, even though the energy effects associated with each orbital interaction are significantly different (see Table 2).

(iii) The overall energy effects associated with the three-electron two-orbital interactions ($\Sigma\Delta E^3$), as well as each individual energy effect of this type, are destabilizing. Therefore in all cases the destabilizing contribution is larger than the stabilizing one.

(iv) The energy effects associated with the α and β components in the interactions between two formally doubly occupied MOs or between a formally doubly occupied and a vacant MO are of very similar order of magnitude, while those associated with the α and β components in the interactions involving the singly occupied MO (SOMO) are very different.

3.2. Canonical Representation

To obtain this representation, we have localized only the canonical MOs of σ symmetry. The resulting MOs represent fragment orbitals with correct orbital occupancies similar to the fragment canonical MOs and for this reason we have denoted this set of MOs as "canonical representation". Therefore the resulting MOs correspond to the orbitals of the CH₂— and CH₃— groups in the form already described, for instance, by Jorgensen and Salem [11]: here we use also their notation. To complete the description, in Table 3 we have also listed the energies and occupancies of the α and β components of these orbitals.

Table 3. Energies (ϵ_i , a. u.) and gross populations (Q_i) of the α and β orbital of the $\dot{\text{C}}\text{H}_2$ and CH_3 fragments in $\text{CH}_3\dot{\text{C}}\text{H}_2$, in the canonical representation

		Eclipsed						
		Orthogonal			β -Orbital			
		α -Orbital			β -Orbital			
i	ϵ_i	Q_i	ϵ_i	Q_i	ϵ_i	Q_i	ϵ_i	Q_i
Fragment CH_2								
1s	-10.9176	0.9999	-10.8929	0.9997	-10.9176	0.9999	-10.8928	0.9997
σ	-0.7236	0.9753	-0.6606	0.9793	-0.7236	0.9753	-0.6606	0.9793
σC	-0.6723	0.5683	-0.5399	0.4714	-0.6723	0.5683	-0.5399	0.4714
π	-0.5395	0.9978	-0.5226	0.9981	-0.5395	0.9978	-0.5226	0.9981
p	-0.3587	0.9903	0.3111	0.0150	-0.3587	0.9903	0.3111	0.0150
σ	0.6800	0.0002	0.7302	0.0002	0.6800	0.0002	0.7302	0.0002
π^*	0.7631	0.0035	0.7884	0.0036	0.7631	0.0035	0.7884	0.0036
Fragment CH_3								
1s	-10.9406	0.9997	-10.9434	0.9998	-10.9406	0.9997	-10.9434	0.9998
σ	-0.7277	0.9640	-0.7331	0.9736	-0.7277	0.9640	-0.7331	0.9736
σC	-0.6242	0.4925	-0.6518	0.5759	-0.6242	0.4925	-0.6518	0.5759
π_x	-0.5280	0.9997	-0.5255	0.9964	-0.5280	0.9997	-0.5255	0.9964
π_y	-0.5260	0.9966	-0.5195	0.9850	-0.5260	0.9965	-0.5195	0.9851
π_x^*	0.6976	0.0100	0.7061	0.0000	0.6977	0.0100	0.7062	0.0000
π_y^*	0.7039	0.0021	0.7026	0.0019	0.7038	0.0021	0.7025	0.0019
σ^*	0.7347	0.0001	0.7365	0.0001	0.7347	0.0001	0.7365	0.0001

Table 4. ΔE^4 , ΔE^3 , ΔE^2 , ΔE^1 energies (kcal/mol) associated with the various orbital interactions between the $\dot{\text{C}}\text{H}_2$ and CH_3 fragments in the orthogonal and eclipsed conformations of $\text{CH}_3\dot{\text{C}}\text{H}_2$ in the canonical representation (values in brackets give the α and β orbital energy component)

Interactions ^a	Orthogonal ^b	Eclipsed ^b
$\Delta E_{\sigma^*,\sigma}^4$	1.22 (0.68 + 0.54)	1.22 (0.68 + 0.54)
$\Delta E_{\sigma^*,\sigma^*}^2$	0.00 (0.00 + 0.00)	0.00 (0.00 + 0.00)
$\Delta E_{\sigma^*,\sigma}^2$	-0.23 (-0.16 - 0.17)	-0.23 (-0.16 - 0.07)
$\Delta E_{\pi,\pi_z}^4$	0 (0 + 0)	15.50 (8.07 + 7.42)
$\Delta E_{\pi,\pi_y}^2$	15.49 (8.07 + 7.42)	0 (0 + 0)
$\Delta E_{\pi,\pi_x}^2$	0 (0 + 0)	-0.70 (-0.37 - 0.33)
$\Delta E_{\pi^*,\pi_y}^2$	-0.70 (-0.37 - 0.33)	0 (0 + 0)
$\Delta E_{\pi^*,\pi_x}^2$	0 (0 + 0)	-1.23 (-0.62 - 0.61)
$\Delta E_{\pi^*,\pi_y}^2$	-1.23 (-0.62 - 0.61)	0 (0 + 0)
$\Delta E_{\rho,\pi_x}^3$	11.71 (14.44 - 2.73)	0 (0 + 0)
$\Delta E_{\rho,\pi_y}^2$	0 (0 + 0)	11.71 (14.44 - 2.73)
$\Delta E_{\rho,\pi_x}^1$	-2.26 (-2.26 + 0)	0 (0 + 0)
$\Delta E_{\rho,\pi_y}^1$	0 (0 + 0)	-2.26 (-2.26 + 0)
$\Sigma\Delta E_T$	24.00 (19.78 + 4.22)	24.01 (19.78 + 4.23)

^a The first and second index of ΔE refer to orbitals belonging respectively to the CH_2 and CH_3 fragments

^b A net 0 means that the interaction vanishes for symmetry or occupancy reasons

The energy effects associated with the various orbital interactions are listed in Table 4 and summarized in Figs. 3 and 4 where we have evidenced the energy effects associated with the different types of orbital interactions occurring in this representation. In this case the following points are of interest:

(i) The total energy effect $\Sigma\Delta E_T$ has the same value in the two conformations: therefore, also with this representation, the results of the quantitative analysis agree very well with the total energy values. Again $\Sigma\Delta E_T$ is destabilizing, with values very similar in the two representations.

(ii) Also the various component terms, shown in Figs. 3 and 4, i.e. the energy effects associated with the π type interactions occurring between the SOMO and the π MOs of the CH_3 fragment and those associated with the interaction occurring between the π MOs and the σ MOs of the two fragments, assume the same values in the two conformations.

(iii) The largest effects are those associated with the π -type interactions, while those involving the σ -type MOs have a much smaller effect.

4. Conclusions

In this paper we have described a procedure which allows to perform a quantitative orbital analysis in the framework of *ab initio* UHF computations. This procedure has been applied here to analyze the factors which control the

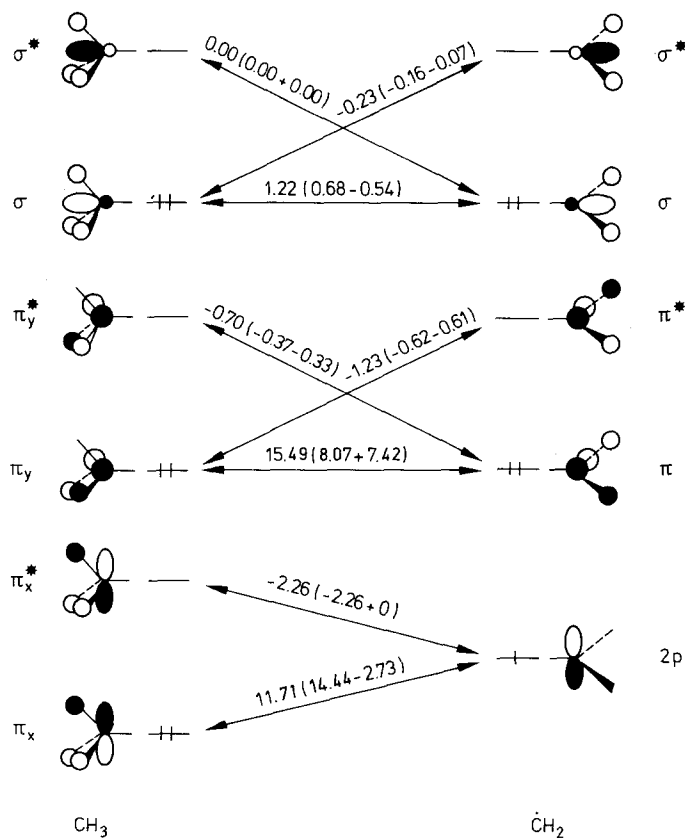


Fig. 3. Interaction between the CH₃ and the CH₂ fragments in the orthogonal conformation of CH₃CH₂ in the canonical representation

conformational problem of the ethyl radical. We have performed this analysis using two different sets of fragment MOs. Both types of quantitative analyses have provided a clear rationalization of the conformational problem of the ethyl radical, even though that based on the canonical representation is more suitable for being described in qualitative terms. In fact, in this representation the problem can be discussed just in terms of the hyperconjugative interactions between the π -type MOs of the two fragments which involve the $2p$, π and π^* MOs of the CH₂ fragment and the π_x , π_x^* , π_y , π_y^* MOs of the CH₃ fragment.

The $2p$ orbital interacts with the π_x and π_x^* MOs in the orthogonal conformation and with the π_y and π_y^* MOs in the eclipsed conformation, while the π and π^* MOs interact with the π_y and π_y^* MOs in the orthogonal conformation and with the π_x and π_x^* MOs in the eclipsed conformation. Since the π MOs of the CH₃ fragment are equivalent and degenerate, it is reasonable to expect that the energy effects associated with the two sets of interactions are the same, as shown by the quantitative analysis [12]. On the other hand, it is not so simple to assess qualitatively, in terms of the localized representation, that the various energy

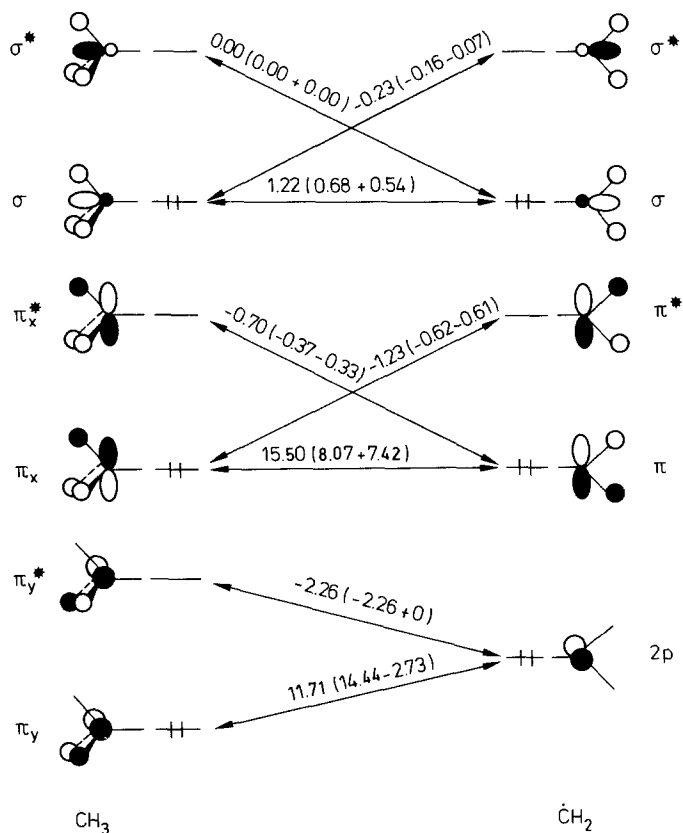


Fig. 4. Interaction diagram between the CH₃ and the CH₂ fragments in the eclipsed conformation of CH₃CH₂ in the canonical representation

effects associated with the interactions of the localized MOs of the two fragments have the same values in the two conformations. In this case we have to resort to the quantitative analysis, whose results show that both the steric and conjugative effects occurring between the MOs associated between the C—H bonds of the two fragments and between the SOMO and the MOs of the CH₃ fragment are the same in the two conformations, as illustrated in Fig. 2.

With both representations the quantitative analysis shows also the important point that the interactions involving the SOMO are important, but equally important are other types of interactions occurring between doubly occupied MOs or between doubly occupied and vacant MOs, such as the $\sigma_{\text{CH}}-\sigma_{\text{CH}}$ bond MOs repulsions in the localized representation and the repulsions between the doubly occupied π MOs in the canonical representation. These results suggest that rationalizations of radical problems based only on the effects associated with the SOMO can often be incomplete.

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Received October 15, 1981