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SCF Perturbation Theory for Unimolecular Reactions*

Vinzenz Bachler, Gottfried Olbrich and Oskar E. Polansky

Institut für Strahlenchemie im Max-Planck-Institut für Kohlenforschung, Stiftstrasse 34–36, D-4330 Mülheim an der Ruhr, Federal Republic of Germany

Yuh-Kang Pan

Department of Chemistry, Boston College, Chestnut Hill, MA 02167, USA

A CNDO/2 SCF perturbation theory is presented for interpreting the form of CNDO/2 potential energy surfaces of unimolecular reactions. The analysis is performed by calculating the energy change ΔE arising from a distortion of the molecular geometry along the reaction coordinate. ΔE is decomposed into different perturbational contributions which are appropriate for an interpretation of the perturbation energy ΔE. Moreover, ΔE is resolved into energy parts arising from a single occupied orbital and contributions due to pairwise orbital interactions. In this way one evaluates numerically how the form of the occupied and unoccupied orbitals determines the magnitude of ΔE. If the distortion occurs along a definite symmetry coordinate, group-theoretical arguments can be applied to discuss the magnitude of characteristic components of the perturbation energy. The SCF perturbation theory is used to analyze the isomerization of ethylene, *cis*-2-butene and *cis*-2-butenenitrile.

Key words: Unimolecular reactions, potential energy surfaces of ~, SCF perturbation theory

1. Introduction

Many qualitative approaches describing chemical reactivity are based on perturbation theory [1, 2]. Bader [3] devised a perturbational method to determine the symmetry (or normal) coordinate along which a unimolecular reaction proceeds preferentially. This procedure has been reformulated and extensively applied by Pearson [4]. Bader and Pearson assume that the symmetry of the transition density between ground state and low-lying excited electronic states determines the

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symmetry of the reaction coordinate [5]. This assumption was also applied by Salem and Wright in an analysis on the pyrolysis of cyclobutane and cyclohexene using a semi-localized molecular orbital method [6]. Gerratt and Mills proposed a perturbational formalism in the Hartree–Fock scheme for the direct calculation of force constants [7]. A semi-empirical SCF perturbation theory has been developed by Vahrenholt for calculating the energy change arising when the molecular geometry is distorted [8]. This procedure has also been applied to analyze reaction paths with respect to characteristic energy contributions [8].

The main advantage of the various perturbational approaches is the possibility of discussing chemical reactivity in terms of properties characteristic for the isolated molecules. Such properties are the nodal form of the frontier orbitals, the net charges on atoms and the magnitude of the LCAO coefficients of interacting molecular orbitals [2]. However, a chemical reaction can be interpreted geometrically as the motion of an image point on the energy hypersurface of the reacting molecules. Generally, when qualitative molecular orbital models are used it is difficult to visualize a relationship between the aforementioned properties of the molecules and the actual form of the energy surface. Therefore, a perturbational approach is desirable for analyzing a potential energy surface quantitatively.

For this purpose a SCF perturbation theory is proposed for the analysis of CNDO/2 potential energy surfaces of unimolecular reactions. In Sect. 2 the formalism of the perturbation method is developed and the magnitude of important energy contributions is estimated by applying group-theoretical arguments. Numerical examples are given in Sect. 3 where the symmetric and asymmetric stretching motions of *cis*-2-butene are analyzed. In addition, the isomerization of *cis*-1,2-dideuteroethylene, *cis*-2-butene and *cis*-2-butenenitrile to their *trans* forms is discussed. The CNDO/2 approximation [9] is used throughout the work.

2. Intramolecular SCF Perturbation Theory

2.1. Solution of the Perturbation Equations

Consider a unimolecular decomposition or rearrangement reaction of a molecule starting from an arbitrary nuclear configuration X^0 belonging to a definite point group. The reaction may proceed along a symmetry coordinate S_i transforming as an irreducible representation of the point group at X^0. For the definite nuclear configuration X^0, the eigenvalue problem, given by

$$F^0C^0=C^0\varepsilon^0 \tag{1}$$

is assumed to be known. Eq. 1 represents the solved unperturbed eigenvalue problem in the CNDO/2 approximation, F^0 is the Hartree–Fock operator, C^0 is a rectangular matrix containing the eigenvectors for the occupied molecular orbitals, and ε^0 is the diagonal matrix of the corresponding one-electron energies. The eigenvalue problem (1) is equivalent to the commutator relation [10, 11]

$$F^0R^0-R^0F^0=0. \tag{2}$$

The unperturbed one-electron density matrix R^0 is a sum of projection operators $C_j^0 C_j^{0\dagger}$ and related to the bond order matrix P^0 by

$$R^0 = \sum_j^{\text{occ}} C_j^0 C_j^{0\dagger} = \tfrac{1}{2} P^0. \tag{3}$$

Now, the nuclear configuration X^0 may be changed along S_i. The geometry of the distorted molecule is designated as $X_i = X^0 + \Delta S_i$. We are interested in the solution of the commutator relation

$$FR - RF = 0 \tag{4}$$

at the nuclear configuration X_i. Proceeding along the usual lines of perturbation theory, Eq. (4) is expanded into a power series of an ordering parameter λ

$$\begin{aligned}(F^0 + \lambda F^1 + \cdots)(R^0 + \lambda R^1 + \cdots)\\ - (R^0 + \lambda R^1 + \cdots)(F^0 + \lambda F^1 + \cdots) = 0.\end{aligned} \tag{5}$$

The first order correction R^1 of the density matrix is determined by the first order perturbation equation

$$F^0 R^1 + F^1 R^0 - R^0 F^1 - R^1 F^0 = 0. \tag{6}$$

The matrix elements of the perturbed F^1 matrix are derived by expanding the CNDO/2 matrix elements [9] into a power series of λ and by collecting all factors of λ^1. The diagonal elements are given by

$$\begin{aligned}F_{\mu\mu}^1 = {} & P_{AA}^1 \gamma_{AA}^0 - \tfrac{1}{2} P_{\mu\mu}^1 \gamma_{AA}^0\\ & + \sum_{B \neq A} (P_{BB}^0 - Z_B) \gamma_{AB}^1 + \sum_{B \neq A} P_{BB}^1 \gamma_{AB}^0.\end{aligned} \tag{7}$$

The off-diagonal elements may be divided into two sets: the atomic orbitals μ and ν are centred on the same atom A

$$F_{\mu\nu}^1 = -\tfrac{1}{2} P_{\mu\nu}^1 \gamma_{AA}^0, \tag{8a}$$

or μ belongs to atom A and ν to atom B

$$F_{\mu\nu}^1 = \beta_{\mu\nu}^1 - \tfrac{1}{2} P_{\mu\nu}^1 \gamma_{AB}^0 - \tfrac{1}{2} P_{\mu\nu}^0 \gamma_{AB}^1. \tag{8b}$$

Generally, several ways of defining the $\beta_{\mu\nu}^1$ and γ_{AB}^1 matrix elements are appropriate. In the method proposed here these matrix elements are calculated numerically

$$\beta_{\mu\nu}^1 = \beta_{\mu\nu}(X^0 + \Delta S_i) - \beta_{\mu\nu}(X^0) \tag{9}$$

and an equivalent formula holds for the γ_{AB}^1-matrix elements. In this way the $\beta_{\mu\nu}^1$ and γ_{AB}^1 are defined as corrections leading to the exact $\beta_{\mu\nu}$ and γ_{AB} matrix elements; higher order corrections do not exist. Second and higher order corrections to the F matrix arise from the higher order corrections to the P matrix. Thus, the perturbational formalism is related to the coupled Hartree–Fock method [13]. The same definition for the first order corrections has been used by O'Shea and Santry for the calculation of molecular geometries using SCF perturbation theory [12]. However, our definition of the perturbation deviates from the first order corrections applied in the SCF perturbation theory of Vahrenholt, where a Taylor series of the matrix elements is used [8].

The first order correction R^1 of the density matrix is determined from Eq. (6) using the projection operator method, as outlined in [10, 11]. Only the final result is given here. The matrix R^1 is completely determined by the off-diagonal projected components

$$R^1 = R^0 R^1 R_u^0 + R_u^0 R^1 R^0. \tag{10}$$

The matrix R_u^0 is the sum of projection operators defined in the subspace of the unoccupied molecular orbitals

$$R_u^0 = \sum_k^{\text{unocc}} C_k^0 C_k^{0\dagger} = 1 - R^0. \tag{11}$$

The off-diagonal projected component is derived by the perturbational expression [10, 11]

$$R^0 R^1 R_u^0 = \sum_j^{\text{occ}} \sum_k^{\text{unocc}} \frac{C_j^0 C_j^{0\dagger} F^1 C_k^0 C_k^{0\dagger}}{\varepsilon_j^0 - \varepsilon_k^0}. \tag{12}$$

Since the F^1 matrix elements contain the R^1 elements via Eqs. (7) and (8), Eq. (12) is solved iteratively.

2.2. *The Perturbation Energies*

The total SCF energy of the molecule at point X^0 on the potential energy surface is calculated from the expression [10, 11]

$$E^0 = \tfrac{1}{2} \operatorname{Tr} P^0 (H^0 + F^0). \tag{13}$$

We are interested in the SCF energy at the point $X^0 + \Delta S_i$

$$E = \tfrac{1}{2} \operatorname{Tr} P(H+F) = E^0 + \Delta E = E^0 + \lambda^1 E^1 + \lambda^2 E^2 + \lambda^3 E^3 + \cdots. \tag{14}$$

Using the same procedure as outlined in [11], the final expression for the first order energy correction E^1 is derived

$$\begin{aligned} E^1 = \sum_{\mathrm{A}<\mathrm{B}}\sum \Bigg[& 2 \sum_\mu^{\mathrm{A}} \sum_\nu^{\mathrm{B}} P_{\mu\nu}^0 \beta_{\mu\nu}^1 \\ & - \frac{1}{2} \sum_\mu^{\mathrm{A}} \sum_\nu^{\mathrm{B}} P_{\mu\nu}^0 P_{\mu\nu}^0 \gamma_{\mathrm{AB}}^1 + (P_{\mathrm{AA}}^0 - Z_{\mathrm{A}})(P_{\mathrm{BB}}^0 - Z_{\mathrm{B}}) \gamma_{\mathrm{AB}}^1 \\ & + Z_{\mathrm{A}} Z_{\mathrm{B}} \left(\frac{1}{R_{\mathrm{AB}}} - \frac{1}{R_{\mathrm{AB}}^0} - \gamma_{\mathrm{AB}}^1 \right) \Bigg]. \end{aligned} \tag{15}$$

The first term of Eq. (15) is designated as E_{res}^1 and can be reformulated as follows

$$\begin{aligned} E_{\text{res}}^1 &= \sum_{\mathrm{A}<\mathrm{B}}\sum 2 \sum_\mu^{\mathrm{A}} \sum_\nu^{\mathrm{B}} P_{\mu\nu}^0 \beta_{\mu\nu}^1 \\ &= \operatorname{Tr} P^0 H^1 = 2 \sum_j^{\text{occ}} C_j^{0\dagger} H^1 C_j^0. \end{aligned} \tag{16}$$

Eq. (16) shows that E^1_{res} is a sum of expectation values of the unperturbed molecular orbitals C^0_j over H^1 containing the first order resonance integrals $\beta^1_{\mu\nu}$. Since the matrix P^0 represents the unrelaxed charge distribution, E^1_{res} can be interpreted as a change in the binding resonance energy measuring the capability of P^0 to retain the molecule in the undistorted geometry X^0. The total first order energy E^1 is a sum of two-centre terms resembling the form of the diatomic E_{AB} contributions. The latter are derived by partitioning the total CNDO/2 energy expression into mono- and diatomic parts [14]. From this analysis the resonance contributions are seen to correlate closely with the total E_{AB} values. Therefore, one may conclude that E^1_{res} represents an important contribution to the total E^1. Considering the form of $H_{\mu\nu}$ in the CNDO/2 approximation a positive E^1_{res} is to be expected if the interatomic distances R_{AB} in the distorted configuration are larger than the R^0_{AB}. This conclusion is confirmed by the numerical applications discussed later.

The second term in (15) arises from a change in the exchange interaction between the centres A and B; in the following examples this term is designated as E^1_{ex} and appears to be smaller than E^1_{res}. The third contribution of (15) arises from the electrostatic interaction between the centres since $(P^0_{\mathrm{AA}}-Z_{\mathrm{A}})$ describes the unperturbed net charge at atom A; these electrostatic terms are denoted as E^1_{el}. For this formulation of E^1_{el} the term $Z_{\mathrm{A}}Z_{\mathrm{B}}\gamma^1_{\mathrm{AB}}$ has been added. The last part of Eq. (15) will be called the nuclear distortion term E^1_{ND}

$$E^1_{\mathrm{ND}} = \sum\sum_{\mathrm{A}<\mathrm{B}} Z^{\mathrm{A}} Z^{\mathrm{B}} \left(\frac{1}{R^{\mathrm{AB}}} - \gamma_{\mathrm{AB}} - \frac{1}{R^0_{\mathrm{AB}}} + \gamma^0_{\mathrm{AB}}\right). \tag{17}$$

In this contribution the change of the nuclear repulsion is contained. In addition $Z_{\mathrm{A}}Z_{\mathrm{B}}\gamma^1_{\mathrm{AB}}$ used in E^1_{el} has been subtracted.

The significance of E^1 may be compared with the first order energies in the perturbation theories of Geratt and Mills [7] and Vahrenholt [8]. These theories are based on Taylor expansions of operators [7, 8]. Consequently, the first order energies represent the first derivative of the energy with respect to a distortion of the molecular geometry. If the latter corresponds to the equilibrium geometry, E^1 should vanish. However, a different result is expected for the model proposed here. Due to the definition of $\beta^1_{\mu\nu}$ and γ^1_{AB} (see Sect. 2.1), E^1 is non-zero, even when the molecule is distorted from the equilibrium geometry. This conclusion is verified by the numerical examples of the following sections.

Using the same general procedure as for E^1, the following formula for the second order energy E^2 is derived

$$\begin{aligned} E^2 = \sum\sum_{\mathrm{A}<\mathrm{B}} \Bigg\{ & \sum_{\mu}^{\mathrm{A}} \sum_{\nu}^{\mathrm{B}} P^1_{\mu\nu}\beta^1_{\mu\nu} - \frac{1}{2}\sum_{\mu} A \sum_{\nu} B P^0_{\mu\nu} P^1_{\mu\nu}\gamma^1_{\mathrm{AB}} \\ & + \frac{1}{2}\left[P^1_{\mathrm{AA}}(P^0_{\mathrm{BB}} - Z_{\mathrm{B}}) + P^1_{\mathrm{BB}}(P^0_{\mathrm{AA}} - Z_{\mathrm{A}})\right]\gamma^1_{\mathrm{AB}} \Bigg\}. \end{aligned} \tag{18}$$

The first term of (18) designated as E^2_{res} is reformulated showing the role of the interacting molecular orbitals

$$E^2_{\text{res}}=\tfrac{1}{2}\operatorname{Tr} P^1H^1=\sum_{j}^{\text{occ}}\sum_{k}^{\text{unocc}}\left[a^1_{jk}C^{0\dagger}_kH^1C^0_j+a^1_{kj}C^{0\dagger}_jH^1C^0_k\right]. \tag{19}$$

The a^1_{jk} are the first order LCMO (linear combination of molecular orbitals) coefficients [11] which provide a measure for the interaction between the occupied and unoccupied molecular orbitals when the molecule is distorted. Eq. (19) indicates that E^2_{res} describes the distortion of the molecule in the relaxed charge distribution represented by P^1; this relaxation occurs via the mixing of the occupied and unoccupied molecular orbitals. Therefore, E^2_{res} is expected to be an energy decreasing contribution to the total ΔE. The interaction coefficients a^1_{jk} of Eq. (19) are determined by the following first order expression

$$a^1_{jk}=\frac{C^{0\dagger}_jF^1C^0_k}{\varepsilon^0_j-\varepsilon^0_k}. \tag{20}$$

Since the range of the indices j and k include the frontier orbitals HOMO and LUMO, the E^2_{res} contribution is related to the frontier orbital concept representing a successful qualitative approach to chemical reactivity [1]. Moreover, E^2_{res} resembles the characteristic second order energy decreasing term employed in the Bader–Pearson procedure [3, 4]. This perturbational approach for chemical reactivity uses many-electron functions for describing ground and excited states [15]. The reformulation of the energy decreasing contribution in terms of molecular orbitals [15] establishes a close relationship to E^2_{res} derived in the perturbational approach proposed here.

By analogy to E^1, the second term of Eq. (18) arises from second order changes in the exchange interaction between the centres A and B; this contribution is denoted as E^2_{ex}. The third term describes the energy due to the polarization of the charge of atom A in the field of the unperturbed net charges $(P^0_{\text{BB}}-Z_{\text{B}})$; this contribution is designated as E^2_{pol}. However, in the numerical applications E^2_{ex} and E^2_{pol} turn out to be rather small.

The third order energy correction E^3 is evaluated by the expression

$$\begin{aligned}E^3=\sum\sum_{\text{A}<\text{B}}&\left[P^1_{\text{AA}}P^1_{\text{BB}}\gamma^1_{\text{AB}}-\frac{1}{2}\sum_{\mu}^{\text{A}}\sum_{\nu}^{\text{B}}P^1_{\mu\nu}P^1_{\mu\nu}\gamma^1_{\text{AB}}\right]\\&-\tfrac{1}{2}\operatorname{Tr} R^0P^1P^1R^0F^1+\tfrac{1}{2}\operatorname{Tr} R^0_uP^1P^1R^0_uF^1.\end{aligned} \tag{21}$$

Notice that P^1 determines the energies up to third order. This result is a special case of a well-known theorem in perturbation theory [16].

2.3. *The Symmetry of Distortion and the Role of Molecular Orbitals*

In this section symmetry arguments are applied to discuss the magnitude of E^1_{res} and E^2_{res} contained in ΣE when the molecule is distorted along a definite symmetry coordinate S_i. The analysis is performed for point groups with only one-dimensional irreducible representations. Furthermore we assume that a distortion of the molecule from configuration X^0 to $X^0 + \Delta S_i$ induces an energy increase.

Referring to the analysis outlined in Sect. 2.2, E^1_{res} is an energy raising contribution, whereas E^2_{res} is an energy decreasing component of ΔE.

In the model applied here only small distortions along S_i are considered. H^1 is defined as the difference between the distorted and undistorted core-Hamilton operator (see Eq. (9)). Consequently, H^1 transforms as the totally symmetric representation of the point group of the distorted molecule. However, the expressions for E^1_{res} and E^2_{res} contain the unperturbed molecular orbitals transforming according to the point group of the undistorted molecule (see Eqs. (16) and (19)). Since the main purpose of the analysis is to discuss the magnitude of ΔE in terms of properties of the undistorted molecule, we investigate the transformation properties of H^1 in the point group of the undistorted molecule.

The symmetry properties of H^1 become apparent when this matrix is expanded into a Taylor series

$$H^1 = \left(\frac{\partial H}{\partial S_i}\right)^0 \Delta S_i + \frac{1}{2}\left(\frac{\partial^2 H}{\partial S_i^2}\right)^0 \Delta S_i^2 + \frac{1}{6}\left(\frac{\partial^3 H}{\partial S_i^3}\right)^0 \Delta S_i^3 + \cdots \tag{22}$$

The matrix representation H at the point X^0 transforms as the totally symmetric representation of the point group at X^0. Consequently, the contributions with odd orders in ΔS_i of (22) transform as the distortion S_i. However, the even order terms in ΔS_i transform as the totally symmetric representation. Since only small distortions along S_i are considered, H^1 may be approximated by the first term, linear in ΔS_i of Eq. (22). Therefore, H^1 transforms predominantly as the symmetry coordinate S_i along which the distortion occurs.

Now we apply group-theoretical arguments to Eq. (16) for E^1_{res}. Substituting the expansion (22) into Eq. (16), the expectation values over the first term and all odd order terms of (22) are zero, unless the direct product $\Gamma_{C_j^0} \times \Gamma_{S_i} \times \Gamma_{C_j^0}$ contains the totally symmetric representation. This direct product has to be considered for all occupied molecular orbitals C_j^0. If the nuclear configuration at point X^0 corresponds to a point group with one-dimensional irreducible representations a large E^1_{res} value is expected for a distortion along a totally symmetric coordinate S_i, since the first order term of (22) contributes. However, a small E^1_{res} is predicted for a distortion transforming not according to the totally symmetric representation, since the expectation values over the first order term in (22) vanish.

A similar symmetry analysis can be performed for the magnitude of E^2_{res}. Using the same procedure as outlined above for H^1, the F^1 matrix transforms approximately as the distortion. Therefore the a^1_{jk}-coefficients contained in E^2_{res} (see Eq. (19)) and evaluated by Eq. (20) will be small, unless the direct product $\Gamma_{C_j^0} \times \Gamma_{S_i} \times \Gamma_{C_k^0}$ contains the totally symmetric representation. Consequently, a large contribution of the two interacting orbitals j and k is expected, when the direct product $\Gamma_{C_j^0} \times \Gamma_{C_k^0}$ contains the irreducible representation of S_i.

If j and k refer to the HOMO and LUMO, respectively, this symmetry condition resembles the Bader–Pearson concept where the symmetry of the preferred distortion is identical with the symmetry of the transition density between the ground and the first excited state [3].

Using the symmetry analysis and the assumption of a positive ΔE we are now in a position to formulate rules concerning the magnitudes of E^1_{res} and E^2_{res}:

a) A small positive E^1_{res} is favoured by a symmetry coordinate S_i not transforming according to the totally symmetric representation; for a totally symmetric distortion a large positive E^1_{res} can be expected. Since E^1_{res} describes a geometry distortion in the unrelaxed charge density P^0 (see Sect. 2.2), a totally symmetric change of the nuclear geometry is not supported by the symmetry of the unrelaxed charge distribution P^0.
b) The negative energy contribution E^2_{res} arising from the relaxation of the charge density is large if unoccupied molecular orbitals with low eigenvalues ε^0_k are available. This condition implies small eigenvalue differences $\varepsilon^0_j - \varepsilon^0_k$ in Eq. (20) determining the a^1_{jk} LCMO coefficients. As an additional requirement the totally symmetric representation has to be contained in the direct product $\Gamma_{C^0_j} \times \Gamma_{S_i} \times \Gamma_{C^0_k}$.

The proposed perturbational approach can be used to relate the form of the unperturbed molecular orbitals and the magnitude of their contribution to E^1_{res} and E^2_{res}. This analysis is performed by calculating ΔE^{res}_j, the contribution of one single occupied molecular orbital C^0_j

$$\Delta E^{\text{res}}_j = \Delta E^1_j + \Delta E^2_j = 2C^0_j H^1 C^0_j + \sum_k^{\text{unocc}} [a^1_{jk} C^{0\dagger}_k H^1 C^0_j + a^1_{kj} C^{0\dagger}_j H^1 C^0_k]. \tag{23}$$

Formula (23) is derived by resolving E^1_{res} and E^2_{res} into energy parts pertaining to the unperturbed molecular orbital C^0_j. The first term arises from the distortion of the nuclear framework in the unperturbed charge distribution due to C^0_j. The second term of Eq. (23) originates from allowing the molecular orbital C^0_j to adjust to the distorted molecular geometry. Inspection of the sign and the magnitude of the ΔE^{res}_j values leads to a classification into energy raising or lowering orbitals. In this way a relationship between the nodal properties of the one-electron orbitals and the form of the potential surface can be established quantitatively in the CNDO/2 formalism.

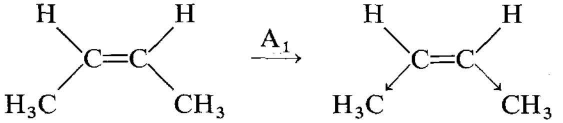
3. Numerical Applications

3.1. Test of the Symmetry Analysis

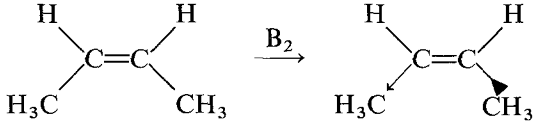
In this section the proposed perturbation theory is applied to the distortion of *cis*-2-butene along different symmetry coordinates. In this way the relationship between the numerical magnitude of the different perturbation terms and the symmetry of distortion is demonstrated.

The equilibrium geometry of *cis*-2-butene was chosen as the undistorted nuclear configuration X^0. This geometry has been determined by minimizing the total CNDO/2 energy with respect to all carbon–carbon bond lengths and the length of the C–H bond adjacent to the double bond ($r_{C_1-C_2} = 1.46$ Å, $r_{C_2-C_3} = 1.33$ Å, $r_{C_2-H} = 1.12$ Å). In addition the C_1–C_2–C_3 and the C_2–C_3–H bond angles were optimized (128.4° and 117.5°, respectively). The geometry of the methyl group was fixed at $r_{C-H} = 1.11$ Å and tetrahedral angles were assumed.

Starting from the nuclear configuration X^0 *cis*-2-butene was distorted along both C–C single bonds in the direction of a symmetry coordinate belonging to A_1 in C_{2v}



and alternatively along another coordinate transforming as B_2 in C_{2v}



The perturbation energy ΔE for the totally symmetric distortion by 0.1 Å and the decomposition into the different perturbational conditions are recorded in Table 1. The numerical value of ΔE (20.9 kcal/mol) calculated to third order agrees almost completely with the ΔE value of 20.8 kcal/mol derived from the CNDO/2 calculations for the distorted and undistorted geometry. This finding shows the good convergence of the perturbation method; a similar convergence has been found in all numerical examples.

The decomposition of ΔE is used to determine the important ΔE raising and ΔE

Table 1. Decomposition of the perturbation energies ΔE (kcal/mol) into different energy contributions when *cis*-2-butene is distorted by 0.1 Å along the A_1 and B_2 symmetry coordinates

	A_1	B_2
1st order: E^1_{res}	128.468	5.121
E^1_{ex}	12.616	−0.402
E^1_{el}	0.000	0.000
E^1_{ND}	−114.934	24.572
E^1	26.150	29.291
2nd order: E^2_{res}	−4.997	−5.498
E^2_{ex}	−0.273	−0.277
E^2_{pol}	0.000	0.000
E^2	−5.270	−5.775
3rd order:		
E^3	−0.026	−0.006
$\Delta E = E^1 + E^2 + E^3$	20.854	23.510

decreasing contributions when *cis*-2-butene is distorted. In accord with the symmetry considerations a large and positive E^1_{res} (128.5 kcal/mol) is calculated for the A_1 distortion. In addition, an energy raising E^1_{ex} (12.6 kcal/mol) is evaluated. These contributions are almost compensated by the energy decreasing nuclear distortion term E^1_{ND} (-114.9 kcal/mol) and to a smaller extent by all other energy components. The absolute value of E^2_{res} is smaller than E^1_{res} by one order of magnitude. Using the interpretation for E^1_{res} and E^2_{res} (see Sect. 2.2) this finding shows that the unfavourable movement of the nuclei in the undistorted charge distribution P^0 is not facilitated by the relaxation of P^0.

A different result is derived for a distortion along the non-totally symmetric B_2 coordinate. The perturbation energy and its decomposition are also recorded in Table 1. In agreement with the symmetry analysis a much smaller E^1_{res} value is calculated compared to the A_1 distortion. The positive E^1_{ND} predominates in E^1 and determines the sign of ΔE. The largest energy lowering contribution is E^2_{res} and compensates the value of E^1_{res}.

Thus, in contrast to the A_1 distortion the energy increase arising from the change of the nuclear framework in the unrelaxed charge density P^0 and the energy decrease due to the relaxation of P^0 are of comparable magnitude.

3.2. *The Role of Molecular Orbitals*

A correlation between the form or the nodal properties of molecular orbitals and a preferred reaction coordinate is inherent in many qualitative theories of chemical reactivity [1, 15, 17]. The proposed perturbational method is related to these qualitative models and has the advantage of providing quantitative information concerning the role of individual molecular orbitals. This information is derived by calculating energy contributions arising from definite molecular orbitals. The procedure is illustrated by comparing the isomerization of 1,2-dideuteroethylene, *cis*-2-butene and *cis*-2-butenenitrile at the beginning of the reaction coordinate.

The activation energies for the isomerization of 1,2-dideuteroethylene and *cis*-2-butene are 65.0 kcal/mol and 62.8 kcal/mol, respectively [18]. A smaller activation energy of 55.7 kcal/mol is observed for *cis*-2-butenenitrile [18].

An important assumption of the applied model is that differences in the activation energies are reflected by differences in the ΔE values calculated in the region of the beginning reaction [19]. The calculated perturbation energies ΔE for rotation about the double bond by 10° are given in Table 2. For all three molecules considered similar ΔE values are calculated. However, the decrease of the activation energies [18] in the series 1,2-di-deuteroethylene, *cis*-2-butene and *cis*-butenenitrile is reproduced by the perturbation energies ΔE.

Inspection of Table 2 indicates that the total ΔE is almost completely determined by the positive E^1_{res} and the negative E^2_{res}. Now the E^1_{res} and E^2_{res} values are resolved into energy contributions ΔE^1_j and ΔE^2_j arising from definite molecular orbitals C^0_j. This decomposition is performed by application of Eq. (23). The purpose of this analysis

Table 2. Decomposition of the perturbation energies ΔE (kcal/mol) into different energy contributions when ethylene, *cis*-2-butene and *cis*-2-butenenitrile are rotated about the double bond by 10°

	$H_2C{=}CH_2$	$H_3CCH{=}CHCH_3$	$NCCH{=}CHCH_3$
1st order: E^1_{res}	2.8059	12.3295	16.8628
E^1_{ex}	0.0000	0.0000	0.0024
E^1_{el}	0.0000	−0.0003	0.0011
E^1_{ND}	−0.0031	−0.0126	−0.0107
E^1	2.8028	12.3166	16.8556
2nd order: E^2_{res}	−1.0121	−10.5860	−15.1038
E^2_{ex}	0.0000	0.0000	−0.0001
E^2_{pol}	0.0000	0.0000	−0.0001
E^2	−1.0121	−10.5860	−15.1040
3rd order:			
E^3	0.0000	−0.0402	−0.0960
$\Delta E = E^1 + E^2 + E^3$	1.7907	1.6904	1.6556

is to correlate the form of orbitals with the magnitude and the sign of their energy contributions to E^1_{res} and E^2_{res}.

The molecular orbitals of ethylene and *cis*-2-butene are classified using the point group C_{2v}, whereas the group C_s is applied for *cis*-2-butenenitrile. All ΔE^i_j values for occupied orbitals of the same irreducible representation Γ_i are added and given in Tables 3 and 4.

The role of the occupied molecular orbitals determining E^1_{res} can be seen in Table 3.

Table 3. Decomposition of E^1_{res} (kcal/mol) into contributions ΔE^1_j arising from molecular orbitals of a definite irreducible representation. All ΔE^1_j values for the occupied orbitals C^0_j of the same irreducible representation are added

	E^1_{res}	a_1	b_2	a_2	b_1
$H_2C{=}CH_2$	2.8059	1.8392	0.9667	0.0000	0.0000
$H_3CCH{=}CHCH_3$	12.3295	5.5490	2.6439	1.2636	2.8730
$H_3CCH{=}CHCN$	16.8628	10.6598 (a′)		6.2030 (a″)	

Table 4. Decomposition of E^2_{res} into contributions ΔE^2_j arising from molecular orbitals of a definite irreducible representation. All ΔE^2_j values for the occupied orbitals C^0_j of the same irreducible representation are added

	E^2_{res}	a_1	b_2	a_2	b_1
$H_2C{=}CH_2$	−1.0121	−0.3791	0.0	0.0	−0.6330
$H_3CCH{=}CHCH_3$	−10.5860	−2.7148	−2.0853	−2.5692	−3.2167
$NCCH{=}CHCH_3$	−15.1038	−6.8791 (a′)		−8.2247 (a″)	

In E^1_{res} of ethylene and *cis*-2-butene the largest contributions arise from the a_1 orbitals, whereas the a' orbitals predominate in the case of *cis*-2-butenenitrile.

In the following discussion the perturbation energy ΔE is analyzed in detail when ethylene is rotated about the C=C bond. In Fig. 1 the molecular orbitals giving rise to the largest ΔE^1_j contributions are depicted; the percentage values compared to the total E^1_{res} are also recorded. E^1_{res} is largely determined by the orbitals $2a_1$ and $2b_2$ being σ-orbitals localized in the C–H bond region. The occupied $1b_1$ π-orbital does not contribute to the ΔE raising E^1_{res} value. Using the interpretation of ΔE^1_j (see Sect. 2.3), the results illustrated in Fig. 1 show that the unperturbed σ-orbitals $2a_1$ and $2b_2$ tend to retain the H atoms in the undistorted geometry. The $1b_1$ π-orbital is not localized in the region of the moving H atoms. Consequently, the contribution to E^1_{res} is zero. The ΔE raising orbitals of Fig. 1 do not possess a nodal surface in the C–H bond region. This property supports the concept that the distortion of the nuclear framework is prevented by molecular orbitals not possessing a nodal surface in the region where the distortion occurs.

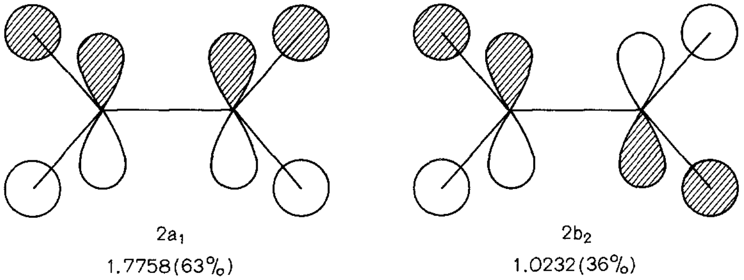


Fig. 1. The form of occupied molecular orbitals giving rise to the largest positive single MO contribution ΔE^1_i to E^1_{res} when ethylene is rotated about the double bond by 10°. The form of these orbitals hinders the isomerization. The ΔE^1_i are given in kcal/mol; the percentage values refer to the total E^1_{res}.

The ΔE lowering contribution E^2_{res} is analyzed in Table 4 and the decomposition into pairwise orbital interactions is shown in Fig. 2. The analysis indicates that the occupied $1b_1$ π-orbital and the $2a_1$ σ-orbital are involved in the negative E^2_{res}. A value of -0.63 kcal/mol is evaluated for the interaction between the $1b_1$ π-orbital with the $4b_2$ σ^*-orbital, whereas the orbital pair $2a_1$ σ and $1a_2$ π^* contributes -0.38 kcal/mol to E^2_{res}. A linear combination of the interacting orbitals gives rise to new orbitals adjusted to the distorted molecular geometry. This relaxation process is manifested by the negative second order contributions. The frontier orbitals HOMO and LUMO are involved in the energy decreasing interaction (see Fig. 2). However, a direct interaction does not occur. Thus, the model classifies the isomerization as unfavourable by the principle of interacting frontier orbitals [1].

According to the analysis performed the σ-orbitals induce the energy increase, whereas the π-orbitals tend to lower the energy via the second order contribution. These results seem to violate the generally accepted concept that a rotation about

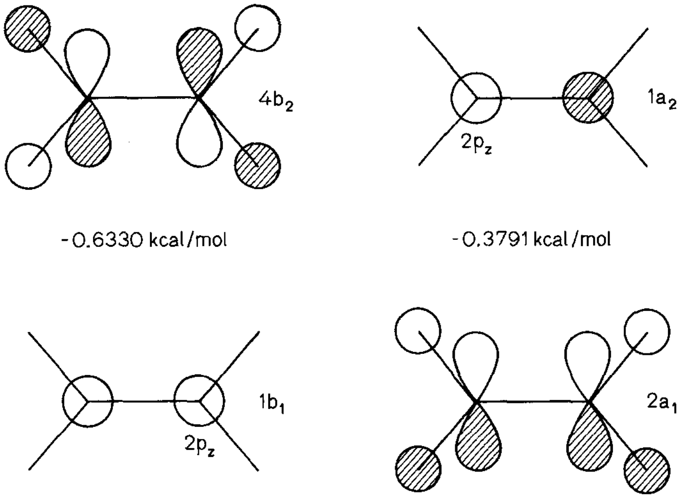


Fig. 2. Pairs of interacting molecular orbitals lowering the perturbation energy ΔE when ethylene is rotated about the double bond. These orbital interactions favour the isomerization

the double bond is hindered by the decoupling of the π-bond. However, the perturbational method is designed to perform an analysis in terms of unperturbed CNDO/2 orbitals calculated in the undistorted molecular configuration. Using this model the rotation about the double bond is visualized as separated into two processes. First, the nuclear configuration is changed but the molecular orbitals remain undistorted; this situation is manifested by the ΔE increasing E^1_{res}. In a second step the molecular orbitals relax towards the new geometry via a linear combination of unperturbed orbitals; this ΔE decreasing process is described by E^2_{res}. A relationship between the perturbation energy ΔE and the energy needed to break the π-bond is established by considering the molecule after the relaxation process. The σ-orbitals are located in the planes of the methylene groups, whereas the π-orbital is partially decoupled; the positive total ΔE indicates a breaking of the π-bond.

A similar pattern is derived from the analysis applied to the distortion of *cis*-2-butene and *cis*-butenenitrile. The largest energy raising part of E^1_{res} due to a single orbital C^0_j arises from the $1b_1$ and $1a''$ orbitals of *cis*-2-butene and *cis*-2-butenenitrile, respectively. The $1b_1$ orbital of *cis*-butene is a π-orbital with a large hyperconjugative contribution from the methyl groups. This orbital does not possess a nodal surface in the C–CH_3 region of the moving CH_3 groups. The same properties characterize also the $1a''$ orbital of *cis*-2-butene-nitrile.

The orbital interaction terms contained in E^2_{res} also decrease the positive E^1_{res} value significantly. In contrast to ethylene all groups of occupied orbitals are involved in E^2_{res} (see Table 4). A detailed analysis indicates that the total E^2_{res} is determined by the interaction of σ- and π-type orbitals, and the same general pattern as for ethylene is retained.

4. Summary and Discussion

In the previous sections an SCF perturbation theory has been proposed for calculating the energy change ΔE arising from a small change of the molecular geometry. If the distortion occurs along a reaction coordinate the magnitude of ΔE is assumed to correlate with the activation energy for the unimolecular reaction. Similar assumptions are used in qualitative perturbational approaches for chemical reactivity [1, 19]. The proposed SCF perturbation theory is characterized by the following properties:

a) The numerical energy values of the CNDO/2 potential energy surface are closely approximated using the perturbational approach. This result is confirmed by the numerical examples of the preceding section and agrees with the convergence behaviour found by O'Shea and Santry [12, 20].
b) The decomposition of the perturbation energy leads to energy contributions arising from the distortion of the nuclear framework in the unrelaxed and relaxed electron distribution. If the distortion occurs along a symmetry coordinate, a group-theoretical analysis can be applied to estimate the magnitude of these energy components.
c) In addition, the proposed SCF perturbation theory can be used to relate the form of the unperturbed molecular orbitals with their contributions to the perturbation energy ΔE. This analysis is performed by calculating energy contributions of the perturbation energy arising from definite molecular orbitals. The signs of these energy contributions classify the unperturbed molecular orbitals as raising or lowering the perturbation energy.

In this way the SCF perturbation theory combines a quantitative analysis of the potential energy surface with the conceptual advantages of the qualitative perturbational approaches to discuss chemical reactivity in terms of nodal properties of the unperturbed molecular orbitals [1].

A different type of qualitative approach towards chemical reactivity is based on correlation diagrams [21]. Recently Halevi proposed a correlation diagram technique where the molecular orbitals are classified according to the largest point group common to reactants and final products [22, 23, 24]. A reaction is allowed when all occupied orbitals of the reactants and the final products are in pairwise correspondence. This condition is defined as containing the totally symmetric representation in the direct products $\Gamma_r \times \Gamma_d \times \Gamma_p$, where Γ_r, Γ_d and Γ_p denote respectively, irreducible representations of a reactant orbital, molecular distortion, and final product orbital. Using this direct product the symmetry Γ_d of the preferred distortion is determined by the symmetry properties of the reactant and product orbitals.

The purpose of the following analysis is to illustrate a relationship between the proposed SCF perturbation method and Halevi's correspondence diagram technique [22]. Consider a definite pair of corresponding initial and final orbitals. The correspondence lines connect an initial orbital and an orbital of the final product passing continuously into each other when MO calculations are performed on different points of the reaction coordinate. Using the CNDO/2 method the difference between eigenvalues of two corresponding orbitals is given by the following formula

$$\Delta\varepsilon_i=\varepsilon_f-\varepsilon_i^0=\frac{C_i^{0\dagger}(F-F^0)C_f}{C_i^{0\dagger}C_f}=\frac{C_i^{0\dagger}F'C_f}{C_i^{0\dagger}C_f}. \tag{24}$$

This expression is deduced from the eigenvalue problems of the reactant and final product and resembles the integral Hellmann–Feynman theorem [25, 26]. If $C_i^{0\dagger}C_f$ is approximated by $C_i^{0\dagger}C_f \simeq 1$, an approximate formula for $\Delta\varepsilon_i$ is derived

$$\Delta\varepsilon_i \approx C_i^{0\dagger}F'C_f. \tag{25}$$

The relation of the $\Delta\varepsilon_i$ and the total SCF perturbation energy ΔE is given by the following expression

$$\Delta E=\sum_i^{\text{occ}}(C_i^\dagger HC_i-C_i^{0\dagger}H^0C_i^0)+\sum_i^{\text{occ}}\Delta\varepsilon_i, \tag{26}$$

deduced from Eqs. (13) and (14).

Assuming that the matrix elements of F' in (25) transform as the irreducible representation Γ_d of the distortion along the reaction coordinate, the correspondence principle of Halevi [22] can be applied to $\Delta\varepsilon_i$. An eigenvalue change $\Delta\varepsilon_i$ is expected when the direct product $\Gamma_{C_i^0}\times\Gamma_d\times\Gamma_{C_f}$ contains the totally symmetric representation. This analysis shows that the correspondence principle applied in a correlation diagram technique [22] also determines the eigenvalue changes $\Delta\varepsilon_i$ contained in the total SCF perturbation energy ΔE.

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