TOPOLOGICAL ANALYSIS OF ENERGY HYPERSURFACE

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Topological approximations discussed in the preceeding paper are used for construction of topological energy hypersurfaces of chemical reactions on two levels of a sophistication. A method of a linear change of off diagonal matrix elements reproduces adequately Woodward–Hoffmann rules but it provides only qualitative information about energetical relations. A physically more rigorous hypothesis where the reaction driving force is a function of hybridization changes at reaction sites provides energy hypersurfaces which are correct from a quantitative viewpoint. The method suggested treats the total energy as a function of abstract reaction angles which reflect topological changes accompanying the reaction course. A reaction mechanisms analysis leads then to the analysis of topological energy hypersurfaces which can be treated similarly to that of conventional geometrical hypersurfaces. Formulas for atomic integrals necessary in the construction of Hartree–Fock and CI matrices are derived in the basis of reaction angles mentioned and approximations leading to the semiempirical type of a calculation are discussed.

In the previous paper[1], the approximations were discussed which permit the separation of geometric and topological information within the framework of quantum chemistry. These approximations allow the expression of matrix elements of quantum mechanical operators and the corresponding observables as functions of geometry-independent parameters which are transferable from one molecule to another. The influence of geometry can be treated as a perturbation. On the basis of theoretical and experimental arguments, it was shown that this "perturbation" may be neglected when investigating reactivity of molecules. The next step towards this aim is presented here, namely, structural, topological, geometry-independent variables are introduced, which form a basis for atomic molecular integrals. Expression of the total energy as a function of topological variables permits calculations of topological energy hypersurfaces and analysis of reaction mechanisms by means of optimization procedures along similar lines to those in conventional "geometrical" hypersurfaces. Such an approach has two positive features. First, it may contribute to a deeper understanding of structure-reactivity relationship because it can distinguish between "purely structural" and "purely spatial" effects. Second, it appears that topological calculation of a reaction coordinate is about two orders of magnitude faster than an equivalent geometry-based calculation. Moreover, energy minimization with respect to all structural parameters, calculation of both Hessian matrix and objective reaction coordinates free of chemical hysteresis and discontinuities can be performed with moderate computer-time consumption even for relatively large systems, *i.e.* systems containing 10 to 50 atoms which are of interest to organic chemists.

As mentioned previously[1], within the framework of the topological approximation, reactivity of molecules is studied on energy hypersurfaces which depend on elements

of the Hartree–Fock matrix (or on functions thereof) instead of on geometry coordinates. The crucial problem in this approach is the relationship between the matrix elements of the forming and breaking bonds at an arbitrary point on the energy hypersurface. Two methods will be described in this paper. First, if we do not require quantitative information, the simplest relationship is represented by a simple linear dependence. This possibility was intensively tested in our Laboratory and a few results worth mentioning were obtained. The second method tested turned out to be significantly more useful. It is based on a hypothesis in which the driving force of chemical reactions can be expressed as hybridization changes at reaction sites. A detailed description of both methods follows.

The Method of a Linear Change of Non-Diagonal Matrix Elements

In this procedure[2] the reaction coordinate is a function of a single parameter R ($0 \leqq R \leqq 1$). The matrix elements of the bonds being formed are expressed as

$$H_{\mu\nu} = H_{\mu\nu}^0 R \,, \tag{1}$$

whereas the elements of the bonds being broken have the following valid relationship:

$$H_{\mu\nu} = H_{\mu\nu}^0 (1 - R) \,. \tag{2}$$

If $H_{\mu\nu}^0 > 0$ (Eq. (*1*)), then lobes of the same sign interact; such an interaction is bonding (supra-supra or disrotatory interaction); value $H_{\mu\nu}^0 < 0$ corresponds to interaction between lobes of opposite sign (supra-antara or conrotatory interaction). Introduction of a new parameter, p, permits us to generalize the procedure for non-concerted reactions. Then Eqs (*1*) and (*2*) assume the form:

$$H_{\mu\nu} = H_{\mu\nu}^0 \max \left(0, \, \frac{pR - 1}{p - 1} \right), \tag{3}$$

$$H_{\mu\nu} = H_{\mu\nu}^0 \max \left(0, \, 1 - pR \right). \tag{4}$$

Evidently if $1 < p < 2$, formation of the new bond starts only after an induction period but before complete scission of the respective bond in the reactant. If $p = 2$, then the reaction under study is a pure two-step reaction, *i.e.* first the critical bond of the reactant is completely broken and in a successive step the new bond is formed. A proper choice of p-values for bonds formed permits one to estimate the relative importance of various synchronous and two-step mechanisms.

The described procedure was used to investigate fourty ground state and photo-

chemical reactions. Even though this procedure is poor in comparison with the second method presented *infra*, some useful results have been obtained:

(*i*) The Woodward–Hoffmann rules are completely reproduced. Matching and crossing of bonding and antibonding MO's characterize allowed and forbidden reactions. Crossing or avoided crossing is typical for all forbidden reactions including those in which reactants and products do not possess any element of symmetry. This supports the opinion[3] that the Woodward–Hoffmann rules are not consequences of symmetrical properties of MO's but that they are due rather to topological properties. Moreover, correlation diagrams based on symmetry considerations can be regarded as a tool for correct assignments of MO's of the reactant and product rather than a principle governing these rules.

(*ii*) A misinterpretation of the butadiene-bicyclobutane reaction[4] in terms of the Woodward–Hoffmann rules was discovered. According to our calculation, the reaction $[_\pi 2_s + _\pi 2_a]$ is allowed in both the ground and the first excited states.

(*iii*) Calculations have shown that vanishing activation energy is connected with allowed pericyclic reactions of systems possessing three or four reaction sites. Formation of larger rings is associated with an energy barrier in both ground and excited states. Calculations on electrocyclic reactions suggest that formation of the largest possible ring is preferred (*e.g.* cyclohexa[1,3]diene rather than 3-vinylcyclobutene is formed from 1,3,5-hexatriene). The opposite was found with cyclo-addition reactions, *i.e.* the tendency was to form the smallest possible ring. Specifically, if supra--antara formation of a four-membered ring is considered to be sterically hindered[4] then it is expected that the ground-state reaction between two molecules of butadiene gives 3-vinylcyclohexane rather than cycloocta[1,4]diene which is in agreement with experiment[5]. Moreover, the calculations suggest that energy barriers of concerted electrocyclic reactions are lower than those of cyclo-additions. The same applies to cyclo-additions and sigmatropic rearrangements; the former possess lower barriers.

(*iv*) The calculations do not permit one to distinguish supra- and antara-approaches for reactions proceeding without the formation of a cyclic intermediate. This applies also to the cases where the forming and breaking bonds are exocyclic. Concretely, no decision can be made concerning stereospecificity of the chloride anion release from 3-chlorocyclopropene.

(*v*) Preference of two-step mechanisms to synchronous and concerted ones is a typical feature of excited state reactions. Calculations suggest, for example, that the first step of the butadiene dimerization is the formation of a biradical by the approach of two terminal atoms; with the valence isomerization benzene-benzvalene the initial step is represented by formation of a biradical by joining the atoms in positions 1 and 3. Lack of experimental information prevents a decision as to whether it is a correct prediction or an artifact of the method.

Hybridization Change on Reaction Sites as the Driving Force of a Reaction

The procedure described in the previous paragraph suffers from two shortcomings. First, it is hardly possible to explain theoretically the assumed linear relationship between the matrix elements of the forming and breaking bonds. Second, the energy of a molecule is expressed as a function of a single parameter, R, which prevents the proper description of reactions where bonds are not synchronously formed and broken. A firm basis for the topological study of energy hypersurfaces is obtained by adopting a hypothesis that hybridization change on reaction sites represents a more essential feature of chemical reactions than bonds forming and breaking. For example, not only the Diels–Alder reaction but also the valence isomerization of benzene is characterized by gradual transformation of delocalized π-orbitals in reactants into localized sp^3 orbitals in products. Orbital hybridization, χ_μ, on the reaction site μ, during the reaction course, can be expressed as a linear combination of hybrids in reactant (r), $\chi_{\mu r}$, and product (p), $\chi_{\mu p}$:

$$\chi_\mu = a\chi_{\mu r} + b\chi_{\mu p} . \tag{5}$$

It is assumed that $\int \chi_{\mu r}\chi_{\mu p}\,\mathrm{d}\tau \geqq 0$.

If the orbitals $\chi_{\mu r}$ and $\chi_{\mu p}$ are orthogonal then from the orthogonalization condition the following holds

$$a^2 + b^2 = 1 . \tag{6}$$

It follows that when the individual reaction site is considered, say μ, energy is a function of only one expansion coefficient of Eq. (5), say a. In the Diels–Alder reaction energy will depend on four expansion coefficients of AO's localized on terminal carbon atoms of a diene and a dienophile. Therefore, the topological hypersurface of the ethylene–butadiene supersystem depends only on four variables in contrast to the common geometrical hypersurface where the number of variables amounts to 42. Let us add that standard orthogonalization techniques[6] may be used if the orbitals $\chi_{\mu r}$ and $\chi_{\mu p}$ are not strictly orthogonal. In other words, the normalization condition (6) does not limit the general applicability of the method.

As previously mentioned just one of the coefficients of Eq. (6) is independent. It is not convenient to express energy, for example, by means of vector of coefficients $\boldsymbol{a} \equiv \{a_\mu\}$ because the evaluation of coefficients of the vector $\boldsymbol{b} \equiv \{b_\mu\}$ by means of Eq. (6) is ambiguous. It turns out, however, that a trigonometric transformation can be successfully applied which permits one to express each χ_μ (Eq. (3)) as a function of a single angle variable, φ_μ:

$$\chi_\mu = \cos \varphi_\mu \chi_{\mu r} + \sin \varphi_\mu \chi_{\mu p} . \tag{7}$$

Clearly, if $\varphi_\mu = 0$, $\chi_\mu = \chi_{\mu r}$. For $\varphi_\mu < 0$, the signs of the terms of Eq. (7) are opposite and there is a nodal plane between orbitals $\chi_{\mu r}$ and $\chi_{\mu p}$ of the forming or breaking bond. This is the case with antarafacial or conrotatory interactions and S_N2 rearrangements; an interaction takes place on the lobe bearing an opposite sign than that of the lobe of the releasing group. For $\varphi_\mu > 0$, the interaction takes place on lobes of the same sign and there is no nodal plane separating the forming and breaking bonds. This applies to suprafacial or disrotatory interactions. If $|\varphi_\mu| = \pi/2$, $\chi_\mu = \chi_{\mu p}$ regardless of whether the suprafacial or antarafacial route is applicable. Therefore, the absolute value of φ_μ is a measure of the extent of conversion from reactant to product and the sign of φ_μ expresses the topological stereospecificity of the reaction under study. The vector $\varphi \equiv \{\varphi_\mu\}$ is named the vector of reaction angles.

Expressions for Monocentric and Bicentric Integrals in a Reaction Angle Basis

It follows from Eq. (7) that for the one-electron Hamiltonian, **h**, the following expressions are valid

$$\int \chi_\mu^+ \mathbf{h}\chi_\mu \, d\tau = \cos^2 \varphi_\mu \int \chi_{\mu r}^+ \mathbf{h}\chi_{\mu r} \, d\tau + \sin^2 \varphi_\mu \int \chi_{\mu p}^+ \mathbf{h}\chi_{\mu p} \, d\tau + 2 \sin \varphi_\mu \cos \varphi_\mu \int \chi_{\mu r}^+ \mathbf{h}\chi_{\mu p} \, d\tau \tag{8}$$

$$\int \chi_\mu^+ \mathbf{h}\chi_\nu \, d\tau = \cos \varphi_\mu \cos \varphi_\nu \int \chi_{\mu r}^+ \mathbf{h}\chi_{\nu r} \, d\tau + \sin \varphi_\mu \sin \varphi_\nu \int \chi_{\mu p}^+ \mathbf{h}\chi_{\nu p} \, d\tau +$$
$$+ \cos \varphi_\mu \sin \varphi_\nu \int \chi_{\mu r}^+ \mathbf{h}\chi_{\nu p} \, d\tau + \sin \varphi_\mu \cos \varphi_\nu \int \chi_{\mu p}^+ \mathbf{h}\chi_{\nu r} \, d\tau \, . \tag{9}$$

Eqs (8) and (9) are generally valid for both semiempiric and nonempiric methods
The essential feature of the topological approximation is the omission of matrix elements between non-neighbouring AO's and also

$$\int \chi_{\mu a} \mathbf{h}\chi_{\nu b} \, d\tau = \delta_{ab} \int \chi_{\mu a} \mathbf{h}\chi_{\nu a} \, d\tau \, . \tag{10}$$

With respect to Eq. (10), Eqs (8) and (9) are simplified as follows

$$H_{\mu\mu} = \cos^2 \varphi_\mu H_{\mu\mu,r} + \sin^2 \varphi_\mu H_{\mu\mu,p} \tag{11}$$

$$H_{\mu\nu} = \cos \varphi_\mu \cos \varphi_\nu H_{\mu\nu,r} + \sin \varphi_\mu \sin \varphi_\nu H_{\mu\nu,p} \, , \tag{12}$$

where $H_{\mu\mu}$ and $H_{\mu\nu}$ are the matrix elements of the one-electron operator in an arbitrary

point on the topological hypersurface. $H_{\mu\mu,r}$, $H_{\mu\nu,r}$ and $H_{\mu\mu,p}$, $H_{\mu\nu,p}$ are the elements in the basis of hybrid orbitals of reactants and products, respectively. The first term on the right side of Eq. (12) applies if the bond between atoms μ and ν is broken the latter one if the corresponding bond is formed. In Eqs (11) and (12) an essential positive feature of the topological approach is included, namely the wave function, energy and all values of "observable" for an arbitrary point in a topological hyperspace can be obtained from matrix elements of reactants and products. In other words the necessity to calculate atomic integrals at every point on the hypersurface is avoided. Moreover, calculations of the gradient and Hessian matrix are simple; whereas atomic integrals depend on coordinates in the "geometrical" approximation, they are mere constants within the topological approximation. Accordingly, the evaluation of derivatives of matrix elements with respect to the reaction angles is easy.

If **g** stands for the electron repulsion operator, it follows from Eq. (7):

$$\int \chi_\mu^+(1)\, \chi_\nu^+(2)\, \mathbf{g} \chi_\varrho(1)\, \chi_\sigma(2)\, d\tau_1\, d\tau_2 = \int \left[\cos \varphi_\mu \chi_{\mu r}^+(1) + \sin \varphi_\mu \chi_{\mu p}^+(1)\right]$$

$$\left[\cos \varphi_\nu \chi_{\nu r}^+(2) + \sin \varphi_\nu \chi_{\nu p}^+(2)\right] \mathbf{g} \left[\cos \varphi_\varrho \chi_{\varrho r}(1) + \sin \varphi_\varrho \chi_{\varrho p}(1)\right]$$

$$\left[\cos \varphi_\sigma \chi_{\sigma r}(2) + \sin \varphi_\sigma \chi_{\sigma p}(2)\right] d\tau_1\, d\tau_2 \,. \tag{13}$$

After multiplication on the right-hand side of Eq. (13), the trigonometric terms may be factored. When the topological approximation (Eq. (10)) is introduced, many terms vanish even on the nonempirical level. The ZDO approximation is usually adopted for semiempirical calculations. Eq. (13) has then the form:

$$(\mu\nu|\mathbf{g}|\,\mu\nu) = \int \mathbf{g}\left[\cos^2 \varphi_\mu \chi_{\mu r}^+(1)\, \chi_{\mu r}(1) + \sin^2 \varphi_\mu \chi_{\mu p}^+(1)\, \chi_{\mu p}(1)\right] \,.$$

$$. \left[\cos^2 \varphi_\nu \chi_{\nu r}^+(2)\, \chi_{\nu r}(2) + \sin^2 \varphi_\nu \chi_{\nu p}^+(2)\, \chi_{\nu p}(2)\right] d\tau_1\, d\tau_2 \,. \tag{14}$$

When using an analogous relationship as (10) for the γ-integrals concerning orbitals located on different atoms, namely

$$\int \chi_{\mu a}^+(1)\, \chi_{\mu a}(1)\, \mathbf{g} \chi_{\nu b}^+(2)\, d\chi_{\nu b}(2)\, d\tau_1\, d\tau_2 = \delta_{ab} \int \chi_{\mu a}^+(1)\, \chi_{\mu a}(1)\, \mathbf{g} \chi_{\nu a}^+(2)\, \chi_{\nu a}(2)\, d\tau_1\, d\tau_2 \tag{15}$$

the following expressions are obtained:

$$\gamma_{\mu\mu} = \cos^4 \varphi_\mu \gamma_{\mu\mu,r} + \sin^4 \varphi_\mu \gamma_{\mu\mu,p} + 2 \sin^2 \varphi_\mu \cos^2 \varphi_\mu \gamma_{\mu\mu,rp} \tag{16}$$

$$\gamma_{\mu\nu} = \cos^2 \varphi_\mu \cos^2 \varphi_\nu \gamma_{\mu\nu,r} + \sin^2 \varphi_\mu \sin^2 \varphi_\nu \gamma_{\mu\nu,p} \tag{17}$$

where $\gamma_{\mu\mu}$ and $\gamma_{\mu\nu}$ are the diagonal and nondiagonal elements of the electron repulsion operator in an arbitrary point on the topological hypersurface; integrals on the right-hand side are repulsion integrals of reactants and products. Only one term on right side of Eq. (17) is nonzero similarly as with Eq. (12). The integral $\gamma_{\mu\mu,rp}$ is defined as follows:

$$\gamma_{\mu\mu,rp} = \int \chi_{\mu r}^{+}(1)\, \chi_{\mu r}(1)\, \mathbf{g}\chi_{\mu p}^{+}(2)\, \chi_{\mu p}(2)\, d\tau_1\, d\tau_2 \,. \qquad (18)$$

The formulas (16) and (17) can be used for reactivity calculations on a topological energy hypersurface within the framework of SCF and LCI approximations. The following feature of Eq. (16) requires a comment. If, in Eq. (11), $H_{\mu\mu,r} = H_{\mu\mu,p}$, then the diagonal matrix element $H_{\mu\mu}$ remains constant on the whole topological hypersurface. According to Eq. (16), however, the monocentric γ integral is not constant even if $\gamma_{\mu\mu,r} = \gamma_{\mu\mu,p}$. As $\gamma_{\mu\mu,rp}$ is smaller than any of $\gamma_{\mu\mu,r}$ and $\gamma_{\mu\mu,p}$, the following relationship is generally satisfied:

$$\gamma_{\mu\mu} \leqq \gamma_{\mu\mu,r} = \gamma_{\mu\mu,p} \,.$$

The lowest absolute value of this integral amounts to $\pi/4$.

As already mentioned, the negative value of the reaction angle φ_μ means that the product attacks the reaction site from the opposite side, i.e., the lobe of AO is approached which is opposite to that one which is free by the releasing group. It is apparent from Eqs (11)−(17) that the $H_{\mu\mu}$, $\gamma_{\mu\mu}$ and $\gamma_{\mu\nu}$ values depend only on the absolute value of the angle φ_μ; stereospecific resolution must be based on the sign change with the $H_{\mu\nu}$ element. Specifically, with a pericyclic supra-antara reaction a ring is formed with a single negative nondiagonal element, i.e. a Möbius ring, which fits the idea presented by Zimmermann[7]. Let us note that the stereospecificity of the reaction course may already be interpreted in terms of a one-electron Hamiltonian and that introduction of electron repulsion does not qualitatively influence the interpretation.

In some instances an extension of the theory is desirable. This is mainly true for reactions in which at some reaction site several bonds are formed at differing rates. Such an extension is particularly important in the following situations:

(i) During the reaction course a bridged structure is formed as e.g., with non-classical ions and three-membered rings. This case is rather rare (for some special addition reactions see ref.[8]).

(ii) When making a decision about various reaction mechanisms, it is desirable to consider simultaneously all possible bond formations (in accordance with the mechanisms under consideration) and to select the "correct" mechanism by means of a computer on the basis of optimization of the topological energy hypersurface.

(iii) Finally, the extended theory allows comprehension of secondary interactions (*e.g.*, preference of the *endo* isomer in the Diels–Alder dimerization of butadiene), solvent effects, steric effects *etc.*

Let us denote $\chi_{\mu r}$ the AO of the site μ in the reactant, $\chi_{\mu p}^1, \ldots, \chi_{\mu p}^n$ are AO's of all possible elementary components (*cf.* Part I) of products (one AO for each individual elementary component, *i.e.* σ, π, δ, originating on the site μ. In such a case Eq. (7) may be generalized as follows:

$$\chi_\mu = \cos \varphi_\mu^0 \chi_{\mu r} + \sin \varphi_\mu^0 \sum_{i=1}^n \left(\prod_j \sin \varphi_\mu^j \prod_l \cos \varphi_\mu^l \chi_{\mu p}^i \right). \tag{19}$$

The angle φ_μ^0 is again named the reaction angle because its absolute value is, as before, a measure of the reaction course. The angles φ_μ^1 to φ_μ^n are named discrimination angles because they determine which of the possible new bonds are formed preferentially. The choice of discrimination angles can be made in several ways.

The only requirement is that the functions $\psi_i = \prod_j \sin \varphi_\mu^j \prod_l \cos \varphi_\mu^l$, $i = \langle 1, n \rangle$ have to form an orthonormal set. An algorithm has been developed for computational purposes; its n elementary components are defined as follows:

a) $\sin \varphi_\mu^1$ for $\chi_{\mu p}^1$, $\cos \varphi_\mu^1$ for $\chi_{\mu p}^2$, $\sin \varphi_\mu^2$ for $\chi_{\mu p}^3$ *etc.* up to exhausting of all pairs of orbitals, $\chi_{\mu p}$, except the eventual last (odd) orbital.

b) $\sin \varphi_\mu^1$ for $\chi_{\mu p}^1$ and $\chi_{\mu p}^2$, $\cos \varphi_\mu^1$ for $\chi_{\mu p}^3$ and $\chi_{\mu p}^4$, $\sin \varphi_\mu^{l+1}$ for $\chi_{\mu p}^5$ and $\chi_{\mu p}^6$ *etc.* up to exhausting of all quadruplets of orbitals, $\chi_{\mu p}$, except the remainder of which are not divisible by four.

c) The angles for products of 8, 16, 32, *etc.* of orbitals have been chosen in an analogous manner. The discrimination angles defined in this way are particularly suitable for the purpose of programing. If $n = 2$, it is obtained:

$$\chi_\mu = \cos \varphi_\mu^0 \chi_{\mu r} + \sin \varphi_\mu^0 \sin \varphi_\mu^1 \chi_{\mu p}^1 + \sin \varphi_\mu^0 \cos \varphi_\mu^1 \chi_{\mu p}^2 \tag{20}$$

if $n = 3$, then

$$\chi_\mu = \cos \varphi_\mu^0 \chi_{\mu r} + \sin \varphi_\mu^0 \sin \varphi_\mu^1 \sin \varphi_\mu^2 \chi_{\mu p}^1 + \sin \varphi_\mu^0 \cos \varphi_\mu^1 \cdot$$
$$\cdot \sin \varphi_\mu^2 \chi_{\mu p}^2 + \sin \varphi_\mu^0 \cos \varphi_\mu^2 \chi_{\mu p}^3, \tag{21}$$

when introducing expressions (*19*) or (*20*), (*21*) instead of (*7*) into Eq. (*8*), (*9*) or (*13*) and using the topological approximation (Eqs (*10*) and (*15*)) as well as the ZDO approximation in case of a semiempirical version, the formulas for calculating atomic integrals, for the generalized case, are obtained. Eqs (*11*) and (*16*) remain

unchanged and Eqs (12) and (17) assume now the following form:

$$H_{\mu\nu} = \cos \varphi_\mu^0 \cos \varphi_\nu^0 H_{\mu\nu,r} + \sin \varphi_\mu^0 \sin \varphi_\nu^0 \prod_j \sin \varphi_\mu^j \prod_l \cos \varphi_\mu^l \cdot$$

$$\cdot \prod_k \sin \varphi_\nu^k \prod_m \cos \varphi_\nu^m H_{\mu\nu,p} , \tag{22}$$

$$\gamma_{\mu\nu} = \cos^2 \varphi_\mu^0 \cos^2 \varphi_\nu^0 \gamma_{\mu\nu,r} + \sin^2 \varphi_\mu^0 \sin^2 \varphi_\nu^0 \prod_j \sin^2 \varphi_\mu^j \prod_k \sin^2 \varphi_\nu^k \cdot$$

$$\cdot \prod_l \cos^2 \varphi_\mu^l \prod_m \cos^2 \varphi_\nu^m \gamma_{\mu\nu,p}^i . \tag{23}$$

The angles defined by Eq. (19) are generated automatically by a computer program ZUZANKA written for this purpose. The program provides all atomic integrals and their first and second derivatives.

Topological Study of Energy Hypersurfaces

For the total energy in any approximation on the Hartree–Fock level the following expression is valid

$$E = \tfrac{1}{2} \sum_\mu \sum_\nu \left[P_{\mu\nu}(H_{\mu\nu} + F_{\mu\nu}) + \tfrac{1}{2} Z_\mu Z_\nu R_{\mu\nu}^{-1} \right] , \tag{24}$$

where

$$F_{\mu\nu} = H_{\mu\nu} + \sum_\lambda \sum_\sigma P_{\lambda\sigma} \left[(\mu\lambda|\mathbf{g}|\nu\sigma) - \tfrac{1}{2}(\mu\lambda|\mathbf{g}|\sigma\nu) \right] \tag{25}$$

$$H_{\mu\nu} = \int \phi_\mu^+ \mathbf{h} \phi_\nu \, d\tau \tag{26}$$

$$(\mu\lambda|\mathbf{g}|\nu\sigma) = \iint \phi_\mu^+(1) \phi_\lambda^+(2) \, \mathbf{g}\phi_\nu(1) \, \phi_\sigma(2) \, d\tau_1 \, d\tau_2 \tag{27}$$

$$P_{\lambda\sigma} = 2 \sum_i c_{i\lambda}^+ c_{i\sigma} , \tag{28}$$

where the symbols have their usual meaning[9]. By transforming molecular integrals into the basis of atomic integrals, by assuming the proportionality $R_{\mu\nu}^{-1} \sim \gamma_{\mu\nu}$ (the Dewar's positron approximation[10]) and by expressing atomic integrals by means of formulas (11), (16), (22) and (23), the expression for the total energy, E, can be obtained in terms of reaction and discrimination angles and matrix elements for the reactant and for all considered products. As the matrix elements expressed in the basis of atomic localized orbitals remain unchanged during the reaction course,

it is possible to describe the energy hypersurface simply as a function of the vector of reaction angles and the matrix of discrimination angles. An energy hypersurface defined in such a way permits use of all the well-known procedures, elaborated for analysis of geometry hypersurfaces and for geometrical investigation of reaction mechanisms. As the atomic integrals of the topological approximation are not functions of the reaction and discrimination angles, the first and second derivatives with respect to the topological parameters can be obtained rather easily by differentiation of formulas (11), (16), (22) and (23). It turned out that the Murtagh–Sargent[11] method was especially useful for energy minimization with respect to all parameters. The Levenberg–Marquardt[12] numerical method is suitable for searching for stationary points. In the calculation of the topological reaction coordinate specific problems exist which are however different from those inherent in geometric methods. It is obvious from Eqs (22) and (23) that formation of a bond between reaction sites μ and ν is topologically described as a function of at least two angles, φ_μ^0 and φ_ν^0, whereas in the geometrical approximation by means of a single internal coordinate $r_{\mu\nu}$. This circumstance is inconvenient for graphical maping of topological hypersurfaces as well as for calculating the reaction coordinate by means of the Dewar method[13]. The same applies to the procedure described in ref.[14]. The calculation of the elements of the Hessian matrix has to be done numerically and, moreover, it is sometimes made complicated because of artifacts of a mathematical nature.

Recently the least motion hypothesis[15] was introduced for calculations of reaction coordinates of *ab initio* potential hypersurfaces. Internal energy of a molecule was expressed as a function of generalized interatomic distances and points which fit the reaction coordinate were searched for by the least squares method. As the number of independent variables was redundant it was necessary to use empirical weight factors. The use of the least motion hypothesis within the framework of the topological approximation is significantly easier and the search for points fitting the reaction coordinate the following mathematical procedure may be used:

a) The difference vector defined as the difference between the reaction angles of products and reactants is calculated.

b) All components of the vector are divided by the number of required reaction steps; in this way the vector of the driving force, **f**, is obtained.

c) After performing energy optimization in the i-1 step, the calculated topological coordinates are shifted by a vector **f**.

d) From the gradient obtained for angles in item *c*) the component parallel to the vector **f** is eliminated by projection (*e.g.*, projection operator method may be used); minimization of the total energy of a molecule is carried out by the Murtagh–Sargent method until the gradient component, which is orthogonal to *f* vanishes; in such a way a point on the topological coordinate is obtained.

e) Stationary points on the obtained one-dimensional curve are obtained by a complete optimization of topological parameters from points calculated in item *d*) which are the closest to the extremals. For these points the Hessian matrix is also calculated in order to be able to decide whether the given stationary point is a minimum, maximum or a saddle point on the topological hypersurface.

The described procedure can be used for topological investigation of the following question: What is the ideal, *i.e.* the energetically most convenient transformation of a set of reactants A to a set of products B? The other question is important from the practical chemical viewpoint, namely, which transformation of A is energetically the most favourable one considering all possible products. In such a case it is necessary to suggest, for a given starting set of elementary components of reactants, the reaction and discrimination angles for formation of all potentially possible bonds. The vector of simultaneous change of reaction angles serves as a driving force, the discrimination angles are optimized in each reaction step. This procedure guarantees that, on the basis of energy optimization, such discrimiaation angles will be chosen, which correspond to the optimal reaction coordinate. Therefore, in this way the optimal reaction mechanism is found. Computational details concerning the above mentioned procedures will be described in the next parts of this series.

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