GEODESIC FORMULATION OF THE LEAST MOTION PRINCIPLE IN CHEMICAL REACTIVITY

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In this study an attempt is presented at the quantitative formulation of the old intuitive criterion for the characterization of chemical reactivity known as the principle of the least motion. The proposed formulation originates from the abstract mathematical model, within the framework of which the criterion of minimal structural changes is realized by the requirement of minimal changes of the state vectors in the Hilbert space of electron states. The presented approach is demonstrated on the practical example of pericyclic reactions for which its results correctly reproduce the conclusions of Woodward–Hoffmann rules.

One of the first attempts at the formulation of selection rules in chemical reactivity is represented by the old intuitive idea that chemical reactions prefer those reaction paths along which the reacting molecules undergo minimal structural changes. Stimulated by this idea, Rice and Teller introduced the so-called least-motion principle (LMP) in which the criterion of minimal structural changes was identified with the requirement of minimal changes in nuclear and electron configurations of reacting molecules[1−2]. In spite of simplicity and conceptual attractiveness of the above intuitive formulation, its impact on the formulation of practically applicable selection rules has been so far rather limited. This is apparently due to the fact that the principle is difficult to quantify. The first attempts at the systematic exploitation of the LMP[3−7] were based on the model of the so-called harmonic distortions which, however, expressed the requirements of the principle only from the point of view of the minimization in the positions of nuclei, without taking into account the second, more abstract criterion of minimal changes in electron configurations. Although the applications of such simplified models were quite successfull in a number of cases, their failure in some instances (several examples demonstrating the failure of the so-called principle least nuclear motion are given in ref.[8]), as well as the complete universality of purely electronic Woodward–Hoffmann rules[9] suggest that a satisfactory LMP cannot be formulated without taking into account just the neglected electronic part of the LMP criterion.

A few studies attempting at the satisfactory solution of this problem were already

reported from which we note the recent report by Igawa and Fukutome[10] and also our own studies[11-13] in which a simple topological approach was introduced, characterizing the electron reorganization in terms of the so-called similarity index. Despite remarkable success of this simple approach in rationalization of various aspects of pericyclic reactivity, the proposed model has, however, one important conceptual limitation. This limitation consists in the complete lack of the variational character which normally is one of the fundamental attributes of the LMP. Our aim in this study is just to remedy this important limitations and to propose a new, truly variational formulation of the LMP. The basis of our approach is a simple idea identifying the criterion of minimal changes in electron configurations with the requirement of minimal changes of state vectors in the Hilbert space of electron states of the system. Using this approach we demonstrate that the above abstract criterion of minimal structural change is equivalent to the search for the line of the shortest length connecting the reactant and the product in the above space. In connection with this simple model it is necessary to stress that the complete neglect of atomic nuclei represents, of course, a certain simplification, but since the similar topological approximation[14,15] was successful in the complete reproduction of Woodward--Hoffmann rules[9], we believe it to be satisfactory for our purpose as well.

THEORETICAL

Let us consider the real Hilbert space $\mathcal{H}$ of electron states of the system. Assuming the separability of the space, an arbitrary vector $|\psi\rangle$ can be expressed in terms of Einstein sum-convention over the pair of corresponding co- and contravariant indices as

$$|\psi\rangle = x^i|\psi_i\rangle ,\qquad (1)$$

where $|\psi_i\rangle$ are basis vectors and x^i the contravariant coordinate components. Moreover, let the norm on $\mathcal{H}$ be defined in terms of scalar product $\langle\psi|\psi\rangle$ by the usual relation

$$\|\psi\| = (\langle\psi|\psi\rangle)^{1/2} .\qquad (2)$$

As a consequence of the induction of the metrics by this norm, the length element dl can be expressed in the form

$$dl \equiv \|d|\psi\rangle\| ,\qquad (3)$$

where

$$d|\psi\rangle = \frac{\partial}{\partial x^i}|\psi\rangle\, dx^i .\qquad (4)$$

Using the relations *(1)*, *(2)* and *(4)* the Eq. *(3)* can be finally rewritten in terms of metric tensor g_{ij} as

$$\mathrm{d}l^2 = g_{ij}\,\mathrm{d}x^i\,\mathrm{d}x^j\,, \tag{5}$$

where

$$g_{ij} \equiv \langle \psi_i | \psi_j \rangle\,. \tag{6}$$

Because it is convenient to work with unit vectors we will further require them to fulfill the identity

$$\|\psi\| \equiv 1\,. \tag{7}$$

This can be most simply achieved by using the transformation into the coordinates ξ^i satisfying transformation relations

$$x^i = \xi^1 x^i(\xi^2, \ldots, \xi^n, \ldots)\,. \tag{8}$$

Using this relation, the condition *(7)* can be fulfilled identically when setting

$$\xi^1 = \frac{1}{(\langle \phi | \phi \rangle)^{1/2}}\,, \tag{9}$$

where

$$|\phi\rangle = x^i(\xi^2, \ldots, \xi^n, \ldots)\,|\psi_i\rangle\,. \tag{10}$$

As a consequence of the transformation *(8)*, the length element $\mathrm{d}l$ can be rewritten in the form analogous to the relation *(5)*:

$$\mathrm{d}l^2 = h_{ij}\,\mathrm{d}\xi^i\,\mathrm{d}\xi^j\,, \tag{11}$$

in which the metric tensor h_{ij} in the coordinates ξ^i is defined as

$$h_{ij} = \langle \nabla_i \psi | \nabla_j \psi \rangle \tag{12}$$

and where ∇_k denoting the partial derivative $\partial/\partial\xi^k$ is, for convenience, included into both bra and ket.

   After having introduced these fundamental relations it is possible to start the formulation of the LMP. This formulation originates from the scalar product of two different vectors, one with the coordinates ξ^i and the other with parametric coordinates η^j:

$$K = \langle \psi(\xi) | \psi(\eta) \rangle\,. \tag{13}$$

On combining the Eq. (1) with relations (8−10) the number of both coordinate and parametric independent variables in this product reduces by one. This fact can be symbolically written as

$$K = K(\xi^2, ..., \xi^n, ...; \eta^2, ..., \eta^n ...) \,. \tag{14}$$

On the basis of this relation and using the prime symbol indicating the omission of the first coordinate and parametric component, the Eq. (13) can be alternatively expressed in the form

$$K = \frac{\langle \phi(\xi') | \phi(\eta') \rangle}{\| \phi(\xi') \| \, \| \phi(\eta') \|} \,. \tag{15}$$

Due to normalization in the denominator of the right part of this relation, the value of K is bound by the inequality

$$0 \le |K(\xi'; \eta')| \le 1 \tag{16}$$

attaining its maximum $K = 1$ for $\xi' = \eta'$.

Let us consider now an arbitrary ket $|\psi(\eta')\rangle$ on $\mathscr{H}$ with the parametric coordinates η' (because of the normalization condition (7) the first component η^1 is not independent, but is given analogously to Eq. (9)). The LMP can be now formulated in the form of a condition requiring the infinitesimal transformation of this ket into another neighboring ket $|\psi(\xi')\rangle$ to proceed in the direction ensuring the maximization of the scalar product (15). This requirement is equivalent to the search for the direction in which the derivative of the $K(\xi'; \eta')$ for $\xi' = \eta'$ attains its minimum. The directional derivative of the K is given by

$$\frac{\mathrm{d}}{\mathrm{d}l} K = \sigma^i \nabla_i K \,, \tag{17}$$

where the components σ^i of the unit vector characterizing the direction are given as

$$\sigma^i = \frac{\mathrm{d}\xi^i}{\mathrm{d}l} \,. \tag{18}$$

The direct calculation of the gradient of the scalar product (15) at the point $\xi' = \eta'$ demonstrates, however, that

$$\nabla_i K(\eta'; \eta') \equiv 0 \tag{19}$$

for any i. This implies that there is no direction in which the limiting first derivative of K is nonzero. This is a natural consequence of the fact that for $\xi' = \eta'$ the scalar

product K attains its local maximum. This suggests that the search of the appropriate direction satisfying the least motion criterion should be based on the second directional derivative defined by

$$\frac{\mathrm{d}^2}{\mathrm{d}l^2} K = \frac{\mathrm{d}}{\mathrm{d}l} \left(\sigma^i \nabla_i K \right), \tag{20}$$

which can be in the limiting case, taking into account the relation (19), expressed alternatively as

$$\frac{\mathrm{d}^2}{\mathrm{d}l^2} K(\eta'; \eta') = \sigma^i \sigma^j \nabla_i \nabla_j K(\eta'; \eta') . \tag{21}$$

In this connection it is, however, necessary to realize that because of above mentioned extremal properties of K the second derivative is always negative, so that the LMP will be satisfied by the infinitesimal transformation in a direction ensuring the minimal absolute value of this derivative. The direct calculation of this quantity demonstrates that the individual components of the tensor $\nabla_i \nabla_j K$ at the point $\xi' = \eta'$ are given by the elements

$$\nabla_i \nabla_j K(\eta'; \eta') = \frac{\langle \phi | \nabla_i \phi \rangle \langle \phi | \nabla_j \phi \rangle}{\langle \phi | \phi \rangle^2} - \frac{\langle \nabla_i \phi | \nabla_j \phi \rangle}{\langle \phi | \phi \rangle} . \tag{22}$$

Inspection of this relation immediately demonstrates that the corresponding quantity is in fact only the function of the parametric variables η'. Moreover, since the above consideration apparently hold for an arbitrary vector from $\mathcal{H}$, it is possible to substitute the parametric variables by the previously introduced coordinates ξ'. After performing this formal change, let us continue in the formulation of the LMP.

Most important in this connection is the fact that in spite of their generality, our considerations were rather limited. This limitation concerns primarily the fact that the above relations express the LMP criterion only locally whereas the satisfactory solution apparently requires, as already stressed in the study by Fukutome[10], the global formulation. The criterion of globality can be incorporated into the above formalism very simply by requiring not the minimization of the infinitesimal changes of the scalar product K at every individual step but the minimization of the whole process along the appropriate curve (the sequence of infinitesimally close unit vectors from $\mathcal{H}$) having $|\psi(\alpha')\rangle$ and $|\psi(\beta')\rangle$ as starting and the final point respectively. This can be done most simply by introducing the curve integral L summing up the above local quantity in the direction tangential to this curve:

$$L = \int_{\alpha'}^{\beta'} \sigma^i \sigma^j \nabla_i \nabla_j K \, \mathrm{d}l . \tag{23}$$

This integral can be further simplified by expressing alternatively the length element $\mathrm{d}l$. For this purpose it is first of all necessary to express the total differential of the variable ξ^1 as a function of the remaining variables ξ' by

$$\mathrm{d}\xi^1 = \frac{\partial\xi^1}{\partial\xi^\mu}\,\mathrm{d}\xi^\mu\,, \tag{24}$$

where the summation over Greek indices is used to denote the exclusion of unity from the whole set of these indices. Using Eqs (2) and (9) this relation can be further simplified to the alternative form

$$\mathrm{d}\xi^1 = -\frac{\langle\phi|\nabla_\mu\phi\rangle}{\|\phi\|^3}\,\mathrm{d}\xi^\mu\,. \tag{25}$$

On the basis of this relation the Eq. (11) can be rearranged as

$$\mathrm{d}l^2 = \left(h_{11}\frac{\langle\phi|\nabla_\mu\phi\rangle\,\langle\phi|\nabla_\nu\phi\rangle}{\|\phi\|^6} - 2h_{1\nu}\frac{\langle\phi|\nabla_\mu\phi\rangle}{\|\phi\|^3} + h_{\mu\nu}\right)\mathrm{d}\xi^\mu\,\mathrm{d}\xi^\nu\,. \tag{26}$$

Substituting for

$$|\nabla_1\psi\rangle = |\phi\rangle\,, \tag{27}$$

and

$$|\nabla_\mu\psi\rangle = \xi^1|\nabla_\mu\phi\rangle \tag{28}$$

in Eqs (9) and (12), the Eq. (26) can be transformed into the form

$$\mathrm{d}l^2 = \left(-\frac{\langle\phi|\nabla_\mu\phi\rangle\,\langle\phi|\nabla_\nu\phi\rangle}{\|\phi\|^4} + \frac{\langle\nabla_\mu\phi|\nabla_\nu\phi\rangle}{\|\phi\|^2}\right)\mathrm{d}\xi^\mu\,\mathrm{d}\xi^\nu\,. \tag{29}$$

If we now realize, that as a consequence of the relation (14) the only nonzero elements in the integrand of the Eq. (23) are the terms containing components of the tensor $\nabla_\mu\nabla_\nu K$, then combining the Eqs (2), (18), (22) and (29) the Eq. (23) reduces to the final form

$$L = -\int_{\alpha'}^{\beta'}\mathrm{d}l\,. \tag{30}$$

This suggests that the reaction path satisfying the LMP criterion of minimal structural changes can be naturally expressed in the form of variational condition which is equivalent to the search

$$\delta L = 0 \tag{31}$$

for the geodesic line in the space characterized by the metric relation (29).

RESULTS AND DISCUSSION

In the following part the practical exploitation of the above formalism will be demonstrated on a concrete example of the alternative reproduction of Woodward--Hoffmann rules. It will be shown that in accord with the requirements of the LMP, the "distance" of the reactant and the product in allowed reactions is indeed lower than in the forbidden ones. In order to maintain the immediate continuity with our previous studies dealing with the Woodward–Hoffmann rules and also because of topological nature of the approximation describing the structure of the reacting molecules by electron wave functions only, the whole procedure will be mathematically expressed at the simplest possible level of the so-called overlap determinant method[15]. For this purpose let us assume the two dimensional Hilbert space with the basis spanned by the approximate electron wave functions ψ_R and ψ_P describing the ground states of the reactant and the product, respectively. Expressing now, in harmony with the spirit of the overlap determinant method these wave functions in the common basis of atomic orbitals*, the general wavefunction from the above truncated Hilbert space can be expressed, using e.g. the polar coordinates, in the form of linear combination

$$\psi = \varrho(\psi_R \cos\varphi + \psi_P \sin\varphi) . \tag{32}$$

Assuming the proper normalization of the basis functions (the norm $\|\psi_R\|$ and $\|\psi_P\|$ be unity) and using the relation (9) with the definition of the overlap integral S:

$$S = \int \psi_R \psi_P \, d\tau , \tag{33}$$

the unit normalization of the arbitrary wave function (32) can be ensured by the relation

$$\varrho = \frac{1}{(1 + S \sin 2\varphi)^{1/2}} . \tag{34}$$

The square of the length element dl in this space is given as

$$dl^2 = (1 + S \sin 2\varphi) \, d\varrho^2 + 2\varrho S \cos 2\varphi \, d\varrho \, d\varphi + \varrho^2(1 - S \sin 2\varphi) \, d\varphi^2 , \tag{35a}$$

which can be, using Eq. (34), rearranged to the form

$$dl = \frac{(1 - S^2)^{1/2}}{1 + S \sin 2\varphi} \, d\varphi . \tag{35b}$$

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* The details of this transformation, introducing into the formalism the possibility of discrimination between the allowed and forbidden reactions can be found in the original studies[15,23].

Using this result, the general expression (30) for the extent of electron reorganization accompanying the concerted transformation $R \rightarrow P$ can be rewritten in the form

$$L = -\int_0^{\pi/2} \frac{(1 - S^2)^{1/2}}{1 + S \sin 2\varphi} \, \mathrm{d}\varphi \, . \qquad (36)$$

This expression is especially simple since the concerted nature of the process (32) leaves in this case no free variational parameters so that the "length" of the reaction path characterizing the global extent of electron reorganization can be calculated analytically with the result

$$L = -\arccos S \, . \qquad (37)$$

This equation is very interesting since the direct parallel between the extent of electron reorganization and the overlap integral S immediately confirms not only the mutual relation of Woodward–Hoffmann rules and overlap determinant method but also demonstrates the expected close correspondence between the Woodward––Hoffmann rules and the least motion principle. In terms of this principle the Woodward–Hoffmann rules can be thus alternatively formulated in the form of statement that the "distance" of the reactant and product $|L|$ is in allowed reactions lower than in the forbidden ones.

   This result is very interesting since the idea of representing the chemical reaction by a certain trajectory satisfying the extremum requirement of the minimal length path appears in various form in a number of different studies[10,16−22]. As an example it is possible to mention the work by Ugi[16], in which the so-called principle of minimal chemical distance was introduced and formulated. The same idea was also discussed in the studies[18,19] dealing with analogously introduced graph-metric characteristics and in ref.[22]. From a number of other related studies it is also necessary to mention the study by Igawa and Fukutome[10], in which a metric tensor was introduced in the nuclear configuration space allowing the characterization of the LMP by the geodesic line just as in our case.

   In connection with these studies it is, however, necessary to be aware of the fact that their philosophy, despite remarkable parallels with our conclusions, is nevertheless completely different. This difference manifests itself especially in that whereas the requirement to represent the LMP by the least length line was in these studies an ad hoc presumption, in our approach it naturally implies from general considerations about the global change of state vectors in the Hilbert space. The important role is played in this connection by the functional (15), since it is just the requirement of its minimal change on going from R to P which naturally results in the representation of the LMP in the form of length of line. In connection with the above "derivation" of the LMP it is perhaps interesting to remark yet another important feature of the proposed approach. This feature consists in that the same procedure of

minimization of "structural changes" can be used not only for the functional (*15*) derived from overlap, but another related quantities could be used as well. This opens the possibility of deriving the alternative forms of LMP differing only in the precise specification of what is actually meant under the vague term of "structural change". In this respect the specification of the structural change by the functional (*15*) based on overlap represents apparently only the first crudest approximation and better more realistic results could be perhaps expected from the use of other quantities derived e.g. from the density matrices. Such calculations are being performed in our laboratory and their results will be published elsewhere.

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