COMMENTS ON THE PHYSICAL MEANING OF THE MINIMUM ENERGY PATH

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The relation between the minimum energy path and the classical equations of motion is found, and conditions implying trajectories along gradient lines are analyzed. Attention is drawn to possible statistical features of the minimum energy path.

The concept of reaction path as introduced by Fukui[1] in 1970 was based on two general assumptions: (*i*) the Born–Oppenheimer separation of the electronic and nuclear degrees of freedom of a polyatomic system[2] and (*ii*) the classical description of the nuclear motion[2]. Assuming further (*iii*) an infinitely slow motion (*i.e.* within the static approach), Fukui and coworkers defined reaction path as a gradient line on a potential energy surface emanating from the saddle point and leading to the reactant and product asymptote, respectively[1,3,4]; consequently, a space curve on the potential energy surface is given, connecting smoothly the reactant and product asymptote *via* a saddle point and tracing the bottoms of the potential energy valleys. Such a concept of reaction path relates to the potential energy surface proper rather than to a dynamical evolution of a reacting system; generally, it is referred to as the minimum energy path[5,6].

The concept of minimum energy path is incorporated in treatments of reactivity based on the transition state theory[2] and it is employed to define coordinates for the reaction-path Hamiltonian dynamics[7].

Besides the immense practical use, the static concept of minimum energy path brought about much debate concerning its conceptual aspects as well as its general properties[8–15]. In this paper we attempt to continue the discussion in the two following respects: (*i*) can be the minimum energy path derived from the classical equations of motion, and, if not, (*ii*) are there any inherent statistical features contained in the concept of the minimum energy path[2].

In the next section the underlying quasiclassical treatment of the time-evolution in polyatomic systems within the Born–Oppenheimer approximation is briefly reviewed.

In section *Comparison of the Minimum Energy Path with System Point Trajectories*, conditions are found the application of which turns the minimum energy path into a special case of a classical trajectory. It is indicated, however, that the overlap between the static and dynamical treatments occurs only in particular situations.

In section *Search for Statistical Features of the Minimum Energy Path*, a possible connection between the Einstein–Smoluchowski equation and the minimum energy path is discussed.

THEORETICAL

Classical Trajectories in Configuration Space of the Nuclei

We consider a polyatomic system free of external force and containing N atoms. Under the general assumptions *sub* (*i*) and (*ii*) the nuclei are subject to a classical motion[16] in the field of an internal force the potential of which is given by the energy pertinent to one of the eigenstates of the electronic subsystem. Let $\boldsymbol{r}_\alpha$, $\alpha = 1, \ldots, N$, be the radius vector of the α-th nucleus and $f = 3N - 6$ the number of independent coordinates. Then the radius vectors $\boldsymbol{r}_\alpha$ can be expressed in terms of f generalized coordinates q^j defining the configuration space M of the nuclei:

$$\boldsymbol{r}_\alpha = \boldsymbol{r}_\alpha(q^j), \quad \alpha = 1, \ldots, N; \quad j = 1, \ldots, f. \tag{1}$$

By eliminating variables describing the motion of the center of mass and the overall rotation, the kinetic energy T of the nuclei becomes a homogeneous quadratic form in the generalized velocities $\dot{q}^j = \mathrm{d}q^j/\mathrm{d}t$:

$$T = (1/2)\, g_{jk}\dot{q}^j\dot{q}^k. \tag{2}$$

(Lower and upper latin indices denote covariant and contravariant tensor components, respectively; summation over repeating tensor indices is employed throughout this paper.) The metric tensor g_{jk} on the tangent space $T_q(M)$ (see further on) to the configuration space M takes the form:

$$g_{jk} = \sum_\alpha m_\alpha (\partial \boldsymbol{r}_\alpha/\partial q^j)\,(\partial \boldsymbol{r}_\alpha/\partial q^k), \tag{3}$$

where m_α is the mass of the α-th nucleus. The arc length element $\mathrm{d}s$ of a system point trajectory in M is given by

$$\mathrm{d}s = (g_{jk}\,\mathrm{d}q^j\,\mathrm{d}q^k)^{1/2}. \tag{4}$$

Locating the end points $q_1 = \{q_1^j\}$ and $q_2 = \{q_2^j\}$ in the reactant and product asymptote, respectively, the trajectory obtained by solving the classical equations of motion due to the given potential energy surface $V(q^j)$ represents a realistic evolution of the polyatomic system from reactants to products[17].

To get a better understanding of the problems connected with the system point trajectories in M, let us describe in a more scrupulous way some of the mathematical concepts employed.

The tangent bundle $T(M)$ associated with configuration space M (refs[18,19]) is a set of f-dimensional vector spaces T_q (fibres) with coordinates (velocities) $\{v^j\}$; each fibre T_q is a tangent space to the configuration space M at a point q. Hence the tangent bundle $T(M)$ is locally described by $2f$ coordinates $(q, v) = \{q^i, v^j\}$. (The reader not interested in details, can consider $T(M)$ simply as a set of these $2f$ variables.)

Since any transformation of coordinates q^i in M induces a linear transformation of v^j in T_q (ref.[18]), the solution of the equations of motion does not depend in the choice of the coordinate system in M.

The classical equations of motion are equivalent to a vector field $X(q, v)$ on $T(M)$, (refs[18,19])

$$X(q, v) = v^i \frac{\partial}{\partial q^i} + \left(\Gamma^j_{km} v^k v^m - g^{jm} \frac{\partial V}{\partial q^m} \right) \frac{\partial}{\partial v^j}, \tag{5}$$

where the Christoffel symbol Γ^j_{km} appears for coordinate-dependent metric tensor g_{ij} (ref.[9]); the matrix (g^{ij}) is inverse to (g_{ij}):

$$\Gamma^j_{km} = (1/2)\, g^{ij} \left(\frac{\partial g_{ik}}{\partial q^m} + \frac{\partial g_{im}}{\partial q^k} - \frac{\partial g_{km}}{\partial q^i} \right).$$

This means that evolution of any function $w(q, v)$ on $T(M)$ consistent with classical mechanics is given by $\mathrm{d}w/\mathrm{d}t = Xw$ and thus the classical equations of motion take the form $\dot{q}^i = Xq^i$, $\dot{v}^j = Xv^j$. A vector field $Y = \varkappa(q, v)\, X$ ($\varkappa$ is a scalar; $\varkappa, \varkappa^{-1} \neq 0$) yields the same set of trajectories as $X(q, v)$: to prove this, it is sufficient to introduce a parameter t', providing $\varkappa\, \mathrm{d}t' = \mathrm{d}t$ along the trajectories. When, however, the condition $\varkappa, \varkappa^{-1} \neq 0$ is violated at some point of $T(M)$, a new situation occurs and the problem requires further analysis. It will be shown in the following section that we have to deal with this situation in comparing the minimum energy path with classical system point trajectories.

Comparison of the Minimum Energy Path with System Point Trajectories

The minumum energy path as defined by Tachibana and Fukui[9] (*cf.* also[5]) can be obtained in the quadratic neighbourhood $\mathrm{d}q^j$ of any point in configuration space M

by setting the velocity equal to zero at this point:

$$\mathrm{d}q^j = \dot{q}^j \,\mathrm{d}t + (1/2)\,\ddot{q}^j \,\mathrm{d}t^2\,, \quad \dot{q}^j = 0\,; \tag{6}$$

consequently,

$$\mathrm{d}s = (g_{jk}\,\mathrm{d}q^j\,\mathrm{d}q^k)^{1/2} = (1/2)\,(\ddot{q}^j\ddot{q}^k\,\mathrm{d}t^4 g_{jk})^{1/2}$$

$$\ddot{q}^j = \mathrm{d}\dot{q}^j/\mathrm{d}t = (\mathrm{d}/\mathrm{d}t)\,(g^{jk}p_k) = g^{jk}\dot{p}_k + p_k\dot{q}^m(\partial/\partial q^m)\,g^{jk} = g^{jk}\dot{p}_k\,.$$

Since the momentum p_k evolves according to the equation of motion $\dot{p}_k = -\partial V/\partial q^k$, we have:

$$\mathrm{d}q^j/\mathrm{d}s = \frac{-(1/2)\,g^{jk}(\partial V/\partial q^k)\,\mathrm{d}t^2}{(\mathrm{d}t^2/2)\,[(\partial V/\partial q^j)\,g^{jk}(\partial V/\partial q^m)\,g^{mn}g_{nk}]^{1/2}} = -\frac{g^{jk}\,\partial V/\partial q^k}{[(\partial V/\partial q^j)\,(\partial V/\partial q^k)\,g^{jk}]^{1/2}}\,. \tag{7}$$

Equation (7) is identical with the equation of minimum energy path[5].

Conditions (6) connect the concepts of minimum energy path and system point trajectory at any point of configuration space. It should be noted that these conditions do not have the character of constraints, because $v^j = 0$ can hold generally only at isolated points of a trajectory.

The impossibility of deriving equation (7) from the classical laws of motion can be seen by comparing the vector field Z (on M) equivalent to equation (7) (*i.e.* $\mathrm{d}w/\mathrm{d}s = Zw$ for any smooth function $w(q)$ on M)

$$Z = -\frac{g^{jk}\,\partial V/\partial q^k}{[g^{jk}(\partial V/\partial q^j)\,(\partial V/\partial q^k)]^{1/2}}\,\frac{\partial}{\partial q^j} \tag{8}$$

with the part X_M of the vector field X operating on M (*cf.* equation (5))

$$X_M = v^j\,\partial/\partial q^j\,; \tag{9}$$

whereas the classical equations of motion describe the evolution of both the coordinates and velocities $\{q, v\}$, equations (7), (8), and (9) deal just with the change of $\{q\}$. It is obvious by comparing equations (8) and (9) that, generally, the description of the evolution of coordinates due to Z and X_M leads to quite different results.

The origin of the difference between Z and X_M can be inspected by examining transformations of X_M leading to Z at $v = 0$; by introducing a vector field $\tilde{X}$ on $T(M)$

$$\tilde{X} = \varkappa(q, v)\,X\,, \quad \varkappa = \mathrm{d}t/\mathrm{d}s = (2T)^{-1/2}\,, \tag{10}$$

we have:

$$\tilde{X}_M(q, v = 0) = Z\,. \tag{11}$$

Equation (*11*) holds at $v = 0$ ($T = 0$) where $\tilde{X}_M$ is of indefinite form (0/0) and, therefore, one can consider that equation (7) results from the singular nature of the passage from dt to ds when $v = 0$.

A special case of a system point trajectory can be distinguished where conditions (*6*) need not necessarily be employed in order to arrive at the minimum energy path (7), *cf.* ref.[9]. If at a moment of time the velocity of the system point is parallel to the force $F^j = -g^{jk}\,\partial V/\partial q^k$, we have:

$$\mathrm{d}q^j/\mathrm{d}t \sim \mathrm{d}q^j/\mathrm{d}s = -\lambda g^{jk}\,\partial V/\partial q^k\,. \tag{12}$$

The proportionality constant λ ($\lambda \neq 0$) can be evaluated by multiplying equation (*12*) by $\mathrm{d}q^k/\mathrm{d}s$; one obtains

$$\lambda = \left[(\partial V/\partial q^j)\,(\partial V/\partial q^k)\,g^{jk}\right]^{-1/2}, \tag{13}$$

in accordance with equation (7). Equation (*12*) can hold even at a finite time interval, assuming, *e.g.* that the corresponding part of the trajectory represents a segment of a straight line in Cartesian coordinates. Favourable conditions for such a motion may be found in those regions of M where the direction of force does not change.

Search for Statistical Features of the Minimum Energy Path

It is interesting to compare equation (7) with the following statistical equation[20]:

$$\mathrm{d}r^i/\mathrm{d}t = -(\mu)^{-1}\,\partial V/\partial r^i + (\mu)^{-1} f_i(t)\,, \tag{14}$$

where r^i is the i-th component of the radius vector of a particle in a statistical ensemble, μ is the friction coefficient and $f_i(t)$ is a random (fluctuating) force with the correlation function $\langle f_i(t) f_j(t')\rangle = 2D\delta_{ij}\delta(t - t')$; $f_i(t)$ is supposed to have a Gaussian distribution at any time. The relaxation process in the ensemble is described in terms of the probability distribution $P(\boldsymbol{r}, t)$ by the Einstein–Smoluchowski equation[20–22]:

$$\partial P/\partial t = (\mu)^{-1}\,\partial/\partial r^i P\,\partial V/\partial r^i + (D/\mu^2)\,\partial^2 P/\partial r^i\,\partial r^i\,, \tag{15}$$

where $D = \mu k\tau$, k is the Boltzmann constant, τ is the absolute temperature; in deriving equation (*14*) or (*15*) it was assumed that the velocities of particles relax quickly to the Maxwell distribution. Equation (*15*) was used many years ago by Kramers[22] to treat chemical reactions.

For $\tau \cong 0$, equations (7) and (*14*) are formally similar ($f_i(t)$ are small). In principle, however, even small fluctuations acting for a long time can lead to large deviations of the solution to equation (*14*) from the solution to equation (7). Hence the analogy

of equations (7) and (*14*) may be of a superficial character. Note that despite the non-decreasing interest still paid to the Kramers' theory (*cf.*, *e.g.* ref.[23]), no attempt has been made to relate it to the Fukui's reaction path. Nevertheless, as indicated by a recently developed theory[24], equations (7) and (*14*) exhibit a close connection. The behaviour of the particles in the neighbourhood of a potential energy minimum is particularly interesting: roughly speaking, due to small fluctuations the particles diffuse with an enhanced probability near the minimum energy path in the direction of the saddle point (ref.[24], Ch. 4, § 3).

Both the minimum energy path (7) and the statistical equation (*14*) assume a mechanism leading to the damping of the particle motion (the zero velocity assumption in the former case and the non-zero friction coefficient in the latter).

SUMMARY

The physical meaning of the static concept of minimum energy path in terms of system point trajectories is analyzed. Precise conditions leading to the transformation of a dynamical path to the minimum energy path are established; in general, the Fukui's concept is found not to be physically derivable from the classical equations of motion.

A possible statistical interpretation of the minimum energy path is outlined; it deserves an independent study where particular attention should be paid to the underlying physical and mathematical assumption and to their mutual compatibility.

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