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Dynamical Constraints and Adiabatic Invariants in Chemical Reactions

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For long-range electrostatic potentials and, more generally, when the topography of the potential energy surface is locally simple, the reaction path coordinate is adiabatically separable from the perpendicular degrees of freedom. For the ion−permanent dipole and ion−quadrupole interactions, the Poisson bracket of the adiabatic invariant decreases with the interfragment distance more rapidly than the electrostatic potential. The smaller the translational momentum, the moment of inertia of the neutral fragment, and the dipole or quadrupole moments are, the more reliable the adiabatic approximation is, as expected from the usual argumentation. Closed-form expressions for an effective one-dimensional potential in an adiabatic Hamiltonian are given. Connection with a model where the decoupling is exact is obtained in the limit of an infinitely heavy dipole. The dynamics is also constrained by adiabatic invariance for a harmonic valley about a curved reaction path, as shown by the reaction path Hamiltonian method. The maximum entropy method reveals that, as a result of the invariance properties of the entropy, constraints whose validity has been demonstrated locally only subsist in all parts of phase space. However, their form varies continuously, and they are not necessarily expressed in simple terms as they are in the asymptotic region. Therefore, although the influence of adiabatic invariance has been demonstrated at asymptotically large values of the reaction coordinate only, it persists in more interesting ranges.

1. Introduction

The notion of dynamical constraint appears in the field of reaction dynamics in two different and even contradictory contexts. On the one hand, in the Rice−Ramsperger−Kassel−Marcus (RRKM) theory,[1] constraints are usually assumed to be inexistent or unable to prevent intramolecular vibrational energy redistribution, although this position is not universally accepted.[2,3] On the other hand, Hirschfelder and Wigner[4] drew attention to the great simplification that can be achieved by using the principle of adiabatic invariance to separate the slow motion in the reaction coordinate from other motions. This idea was brought to fruition in various theories: the statistical model of adiabatic channels,[5,6] the reaction path Hamiltonian (RPH) model,[7] and a refinement of the dynamical assumptions.[8] Clearly, these two opposite lines of thought concern two different regions of the potential energy surface (PES). Intramolecular vibrational energy redistribution concerns the short-range region where the potential energy is low and where the oscillators that exchange their energy are more-or-less equivalent. Adiabatic separation requires a situation where the potential energy is high and where one particular degree of freedom (the distance (r) between the centers of mass of two nearly independent fragments) is quite naturally singled out.

The present paper starts with an analysis of the second point of view, but some of its conclusions will concern the first one. The approach adopted consists of focusing attention on particular regions of a PES. Classical mechanics is used because, by making possible the simultaneous specification of position and momenta, it enables the study of different regions of configuration and phase spaces. It provides a rich arsenal of concepts: conservation laws, first integrals of the motion, cyclic coordinates, symmetry properties, separability of the equations of motion, vanishing Poisson brackets, and adiabatic invariants. For the complicated systems considered in reaction dynamics, no rigorous solution, in general, is possible. Therefore, hope is to be put on the concepts of adiabatic separation and adiabatic invariance.

We examine, in what follows, a few models where the local simplicity of the PES in a particular region of space suggests that some separation between the reaction path coordinate and the perpendicular degrees of freedom may be possible. Reactions involving charged species are of particular interest because of the great simplicity of long-range electrostatic potentials.

The ion−permanent dipole and ion−quadrupole interactions are examined in sections 2−4. The adiabatic separation of the reaction coordinate is justified, and closed-form expressions for an effective one-dimensional (1D) potential are given. The model of a harmonic valley about a curved reaction path studied by the RPH method provides a further example (section 5). In section 6, attention is drawn to the existence of an additional constant of the motion of a different kind, namely, the entropy. The maximum entropy method (MEM)[9−11] demonstrates[12,13] that any constraint that is found to occur in a particular range of the PES retains its influence during the entire reaction. Thus, even though a simplified Hamiltonian is no longer valid outside of its specific range, constraints persist (although in a modified

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form) even in a range where the simple model potential breaks down. As a corollary, this accounts for incomplete energy randomization.

2. The Charge−Dipole Interaction

A. Derivation of the Hamiltonian. When the reaction involves an ion of charge q and a neutral fragment characterized by a permanent electric dipole moment of magnitude μ, the leading term in the long-range potential between the fragments is the charge dipole interaction given by eq 2.1;

$$V(r, \theta) = -\frac{q\mu}{r^2}\cos\theta \quad r \in [r_0, \infty] \tag{2.1}$$

where θ specifies the orientation of the dipole and r_0 denotes the shortest interfragment distance at which the actual potential is reasonably well represented by eq 2.1.

For the sake of simplicity, we restrict ourselves to a two-dimensional (2D) model (i.e., to nuclear trajectories that take place in a plane). This problem has been studied by Schlier.[14] The neutral fragment consists of two masses, each equal to m, separated by a distance ($2d$), with a moment of inertia $I = 2md^2$. One degree of freedom is removed by freezing d. This leaves three degrees of freedom to describe the planar dynamics: r, the length of the segment joining the point charge of mass M to the center of mass of the dipole; ω, the polar angle of that segment; and ξ, the polar angle of the dipole. The origin of the coordinates is at the center of mass of the three bodies. The classical Hamiltonian can be written as shown in eq 2.2.[14]

$$H''(r, p_r, \omega, p_\omega, \xi, p_\xi) = \frac{1}{2}\left(\frac{M+2m}{2Mm}\right)\left(p_r^{\,2} + \frac{p_\omega^{\,2}}{r^2}\right) + \frac{p_\xi^{\,2}}{2I} - \frac{q\mu}{r^2}\cos(\omega - \xi) \tag{2.2}$$

The total angular momentum $p_\omega + p_\xi$ is a constant of the motion, as shown by a calculation of its Poisson bracket.

It is advisable to define two new coordinates:

$$\theta = \omega - \xi \qquad \gamma = \omega + \xi \tag{2.3}$$

The Hamiltonian transforms into eq 2.4.[14]

$$H'(r, p_r, p_\gamma, \theta, p_\theta) = \frac{1}{2}\left(\frac{M+2m}{2Mm}\right)\left[p_r^{\,2} + \frac{(p_\gamma + p_\theta)^2}{r^2}\right] + \frac{(p_\gamma - p_\theta)^2}{2I} - \frac{q\mu}{r^2}\cos\theta \tag{2.4}$$

The angle γ is a cyclic variable in the new Hamiltonian, and its conjugate momentum $p_\gamma = J/2$ is a constant of the motion.

Consider now the particular case where the total angular momentum $J = 2p_\gamma$ is zero. The relevant Hamiltonian becomes eq 2.5.[14,15]

$$H(r, p_r, \theta, p_\theta) = \frac{1}{2}\left(\frac{M+2m}{2Mm}\right)\left[p_r^{\,2} + \frac{p_\theta^{\,2}}{r^2}\right] + \frac{p_\theta^{\,2}}{2I} - \frac{q\mu}{r^2}\cos\theta \tag{2.5}$$

B. Validity of the Adiabatic Approximation. It has been suggested by Bates[16] that the dynamics of an ion−dipole complex is dominated by the invariance of the action integral $(2\pi)^{-1}\oint p_\theta\, d\theta$.[17−19] To study this point, we extract the value of p_θ from the equation $H(r, p_r, \theta, p_\theta) = E$, and average it over θ. The result is denoted $\langle p_\theta\rangle$. Its exact expression in terms of elliptic functions is too complicated to be given here, but we note that the value of $\langle p_\theta\rangle^2$ in the $r \to \infty$ limit is quite simply evaluated as shown in eq 2.6;

$$\lim_{r\to\infty}[(1/2\pi)\oint p_\theta\, d\theta]^2 = 2I\left[E - \left(\frac{M+2m}{2mM}\right)\frac{p_r^{\,2}}{2}\right]\left[1 - \left(\frac{M+2m}{M}\right)\frac{d^2}{r^2}\right] + O(r^{-4}) \tag{2.6}$$

which tends asymptotically to $2IE_{\mathrm{rot}}(\infty)$.

Two properties of $\langle p_\theta\rangle^2$ should be noted. First, its Poisson bracket (eq 2.7)

$$[\langle p_\theta\rangle^2, H(r, p_r, \theta, p_\theta)] = 2I\left(\frac{M+2m}{mM}\right)p_r\left(\frac{q\mu\cos\theta}{r^3}\right) + O(p_r/r^5) \tag{2.7}$$

does not vanish (the variable θ reappears during the calculation of the bracket). However, interestingly enough, it is seen to decrease with r as r^{-3} (i.e., more rapidly than the electrostatic potential (eq 2.1)).

Second, the equations of motion of the canonical variables can be calculated as an expansion in terms of Poisson brackets.[19] For the variable r, one has

$$r(t) = r_0 + t[r, H]_0 + (t^2/2!)\,[[r,H], H]_0 + (t^3/3!)\,[[[r, H], H],H]_0 + ... \tag{2.8}$$

where the subscript zero refers to the initial conditions at $t = 0$. This equation of motion is substituted into the expression of $\langle p_\theta\rangle^2$, and the result is expanded about the $r \to \infty$ limit. After some algebra we arrive at eq 2.9.

$$\langle p_\theta\rangle^2 = 2IE_{\mathrm{rot}}(\infty)\left[1 - \left(\frac{M+2m}{M}\right)\left(\frac{d}{r_0}\right)^2 + \left(\frac{M+2m}{M}\right)^2\left(\frac{d}{r_0}\right)^4 + ...\right] + O\left(\frac{t}{r_0^{\,3}}\right) \tag{2.9}$$

The terms that express the time-dependence of $\langle p_\theta\rangle^2$ decrease faster with r than the electrostatic potential.

Equations 2.7 and 2.9 show that, in the asymptotic range of the ion−permanent dipole potential, the quantity $[(1/2\pi)\oint p_\theta\, d\theta]^2$ is an invariant, which, to a good approximation, can be replaced by its asymptotic value (i.e., by $2IE_{\mathrm{rot}}(\infty)$). The smaller the translational momentum p_r, the moment of inertia I, and the dipole moment μ are, the more reliable the adiabatic approximation is, as expected from the usual argumentation on adiabatic invariance.[17−20]

C. The Effective Potential. To introduce the adiabatic approximation, we follow a procedure devised by Schlier.[14] We define a rotational Hamiltonian at a fixed value of r.

$$H_{\mathrm{rot}}(\theta, p_\theta; r) = \frac{1}{2}\left(\frac{M+2m}{2Mm}\right)\frac{p_\theta^{\,2}}{r^2} + \frac{p_\theta^{\,2}}{2I} - \frac{q\mu}{r^2}\cos\theta \tag{2.10}$$

Consider the simplest case, where the internuclear distance r between the fragments is so large that the diatomic fragment undergoes a free rotation. An r-dependent rotational energy $E_{\mathrm{rot}}(r)$ is defined by the equation $H_{\mathrm{rot}} = E_{\mathrm{rot}}$ under the constraint[16] that the cyclic integral $\oint p_\theta\, d\theta$ be a constant of the motion. The integration is to be carried out over all accessible values of θ (i.e., over the whole range where p_θ is real). Extract p_θ from the equation $H_{\mathrm{rot}} = E_{\mathrm{rot}}$, integrate it over a full cycle of θ, and divide it by 2π. The integration generates complete elliptic integrals of the second kind,[21] which can be expanded as a power series about the limit $r \to \infty$. This leads to eq 2.11.

$$[(1/2\pi)\oint p_\theta\, \mathrm{d}\theta]^2 = 2IE_{\mathrm{rot}}(r) - 2IE_{\mathrm{rot}}(r)\left(\frac{M+2m}{M}\right)\left(\frac{d^2}{r^2} - \frac{d^4}{r^4} + \frac{d^6}{r^6}\right) - \frac{I}{4E_{\mathrm{rot}}(r)}\left(\frac{q\mu}{r^2}\right)^2 + I\left(\frac{M+2m}{M}\right)\left[\frac{q^2\mu^2}{4E_{\mathrm{rot}}(r)}\right]\frac{d^2}{r^6} + \ldots \quad (2.11)$$

The asymptotic value of the adiabatic invariant coincides with eq 2.6. Equating eq 2.11 with $2IE_{\mathrm{rot}}(\infty)$ gives the expression of $E_{\mathrm{rot}}(r)$ shown in eq 2.12.

$$E_{\mathrm{rot}}(r) = E_{\mathrm{rot}}(\infty) + \left(\frac{M+2m}{M}\right)\left(\frac{d}{r}\right)^2 E_{\mathrm{rot}}(\infty) + \frac{1}{8E_{\mathrm{rot}}(\infty)}\left(\frac{q\mu}{r^2}\right)^2 - \left(\frac{M+2m}{M}\right)\left[\frac{q^2\mu^2}{8E_{\mathrm{rot}}(\infty)}\right]\frac{d^2}{r^6} + \ldots \quad (2.12)$$

Comparison between eqs 2.5 and 2.10 shows that $E_{\mathrm{rot}}(r)$ can be used as an effective potential in an adiabatic Hamiltonian that is valid in the zero-angular momentum, large-r limit shown in eq 2.13.

$$H_{\mathrm{ad}}(r, p_r) = \frac{1}{2}\left(\frac{M+2m}{2mM}\right)p_r^{\,2} + E_{\mathrm{rot}}(r) \quad (2.13)$$

D. Limitations. The adiabatic potential obtained in this way is defined for values of r that are large enough for the fragment to swing around a full rotation (i.e., for $r > [q\mu/E_{\mathrm{rot}}(\infty)]^{1/2}$). An extension to the range where the diatomic fragment undergoes a hindered rotation (usually termed libration) is difficult because the integrations over θ then generate incomplete elliptic functions for which analytical approximations are inconvenient. Furthermore, eqs 2.1, and hence 2.12, become unrealistic at short distances because additional terms in $-r^{-3}$ and $-r^{-4}$ should be included in the expression of the potential energy. For this reason, reaction cross sections cannot be calculated at energies that are too high because the orbiting barrier is shifted to small values of r. They cannot be calculated at energies that are too low either, because the classical approximation then breaks down. In that case, the semiclassical treatment of adiabatic invariance proposed by Djebri et al.[22] should be used. Finally, the difficulties encountered when attempting to extend the method to a three-dimensional (3D) calculation have been discussed by Schlier.[14]

3. The Charge-Heavy Dipole Interaction

Letting m and I tend to infinity in eq 2.5 generates an interesting particular case (eq 3.1).

$$H_{\mathrm{heavy}} = \frac{1}{2M}\left(p_r^{\,2} + \frac{p_\theta^{\,2}}{r^2}\right) - \frac{q\mu\cos\theta}{r^2} \quad (3.1)$$

This Hamiltonian describes the planar motion, studied in a system of polar coordinates (r, θ), of a charged particle in the field of a permanent dipole. The latter is assumed to be so heavy that it remains fixed in space. The angle ξ of the previous system of coordinates is fixed, its conjugate momentum p_ξ is zero, and the entire angular momentum results from the orbital motion. The model is interesting because it provides an example where an approximate method can be applied to a situation where the decoupling is exact. A 3D study is possible.[17,18] However, because the equations are separable, one is soon brought back to eq 3.1.

A. The Hamilton–Jacobi Equation. This problem is easily analyzed by the Hamilton–Jacobi method[17–19] because a separation of the variables is possible. The characteristic function can be written as eq 3.2.

$$S(r, \theta, t) = S_r(r) + S_\theta(\theta) - Et \quad (3.2)$$

The Hamilton-Jacobi equation separates into eq 3.3.[17–19]

$$r^2\left(\frac{\mathrm{d}S_r}{\mathrm{d}r}\right)^2 - 2MEr^2 = -\left(\frac{\mathrm{d}S_\theta}{\mathrm{d}\theta}\right)^2 + 2Mq\mu\cos\theta = \beta \quad (3.3)$$

The separation constant (β) determines the energy partitioning between the radial and angular motions. The larger the β, the larger the fraction of E that flows into the radial motion.

There is no particular difficulty in solving the first equation of motion (eq 3.4)

$$\partial S_r(r)/\partial E - t = \text{constant} \quad (3.4)$$

with eq 3.5.

$$S_r(r) = \int (2ME + \beta/r^2)^{1/2}\, \mathrm{d}r \quad (3.5)$$

The value of the constant is obtained by requiring $r = r_0$ at $t = 0$. Equation 3.4 then leads to eq 3.6.

$$r(t) = \left[r_0^{\,2} + \left(\frac{2t}{M}\right)\left(Et + (2MEr_0^{\,2} + \beta)^{1/2}\right)\right]^{1/2} \quad (3.6)$$

A very simple expression is obtained for the translational energy in the radial coordinate (eq 3.7).

$$M\dot{r}(t)^2/2 = E + \beta/2Mr^2 \quad (3.7)$$

B. The Adiabatic Approximation. Let us now compare the previous exact results with those derived from the adiabatic approximation. The value of p_θ is extracted from the equation $H_{\mathrm{heavy}} = E$ and then averaged over a full cycle of θ. The Poisson bracket of this average and H_{heavy} is identically equal to zero. The cyclic integral $(2\pi)^{-1}\oint p_\theta\, \mathrm{d}\theta$ and its square are thus strict constants of the motion in the heavy dipole limit.

The procedure described in section 2C is repeated for Hamiltonian 3.1 and leads to eq 3.9.

$$[(1/2\pi)\oint p_\theta\, \mathrm{d}\theta]^2 = 2Mr^2E_{\mathrm{rot}}(r)\left\{1 - \frac{1}{8}\left[\frac{q\mu}{E_{\mathrm{rot}}(r)r^2}\right]^2 - \frac{13}{512}\left[\frac{q\mu}{E_{\mathrm{rot}}(r)r^2}\right]^4 - \ldots\right\} \quad (3.9)$$

Obviously, this expression is invariant if the effective potential $E_{\mathrm{rot}}(r)$ decreases as r^{-2}. The expression of the adiabatic Hamiltonian in the heavy dipole limit becomes eq 3.10.

$$H_{\mathrm{ad}}(r, p_r) = p_r^{\,2}/2M + c/r^2 \quad (3.10)$$

The value of the constant (c) is determined by making a connection with the widely used average dipole orientation (i.e., by writing eq 3.11).[14,16,23]

$$c = -q\mu\langle\cos\theta\rangle \quad (3.11)$$

Thus, in the heavy dipole limit, the average value of the orientation cosine does not vary with r.

Furthermore, it is readily verified that the application of the Lagrange equation to the adiabatic Hamiltonian 3.10 and 3.11 generates equations of motion that are identical to those derived from the exact Hamilton–Jacobi method (eqs 3.6 and 3.7), with a value of the separation constant equal to eq 3.12.

$$\beta = 2Mq\mu\langle\cos\theta\rangle = -2Mr^2V_{\mathrm{eff}}(r) \qquad (3.12)$$

C. Discussion. In the heavy dipole limit, the adiabatic invariance method generates an average value $\langle\cos\theta\rangle$ that is r-independent because it is proportional to the strictly invariant Hamilton−Jacobi separation constant β. The decoupling between the reaction coordinate and the angular motion results from the presence of a first integral of the motion. The constant β determines the energy partitioning between the two degrees of freedom r and θ. The constraint can thus be said to be determined by the preparation of the initial state (i.e., by the nature of the activation process that makes the reaction possible).[13] In the heavy dipole limit, the initial energy partitioning holds on strictly during the entire evolution of the molecule. In contrast, in the general case studied in section 2, the energy partitioning remains constant in the adiabatic limit only.

4. The Charge−Quadrupole Interaction

The Hamiltonian for the charge−quadrupole interaction is analogous to eq 2.5;

$$H_{\mathrm{quad}}(r, p_r, \theta, p_\theta) = \frac{1}{2}\left(\frac{M+2m}{2Mm}\right)\left[p_r^{\,2} + \frac{p_\theta^{\,2}}{r^2}\right] + \frac{p_\theta^{\,2}}{2I} + \frac{qQ}{2r^3}(3\cos^2\theta - 1) \qquad (4.1)$$

where Q denotes the quadrupole moment.

The cyclic integral $\langle p_\theta\rangle^2 = [(1/2\pi)\oint p_\theta\,\mathrm{d}\theta]^2$ is calculated as described in section 2.B. Its asymptotic expansion is very similar to eq 2.6 (eq 4.2),

$$\lim_{r\to\infty}[(1/2\pi)\oint p_\theta\,\mathrm{d}\theta]^2 = 2I\left[E - \left(\frac{M+2m}{2mM}\right)\frac{p_r^{\,2}}{2} - \frac{qQ}{4r^3}\right]\left[1 - \left(\frac{M+2m}{M}\right)\frac{d^2}{r^2} + \left(\frac{M+2m}{M}\right)^2\frac{d^4}{r^4}\right] + O(r^{-6}) \qquad (4.2)$$

and its Poisson bracket with H_{quad} can be expanded about $r \to \infty$ to give eq 4.3.

$$[\langle p_\theta\rangle^2, H_{\mathrm{quad}}(r, p_r, \theta, p_\theta)] = \frac{9}{2}I\left(\frac{M+2m}{2mM}\right)p_r\frac{qQ}{r^4}\cos 2\theta + O\left(\frac{p_r}{r^6}\right) \qquad (4.3)$$

Here again, the Poisson bracket decreases faster than the ion−quadrupole potential. Thus, in the range where the Hamiltonian 4.1 is realistic, $\langle p_\theta\rangle^2$ can be replaced by its asymptotic value, equal to $2IE_{\mathrm{rot}}(\infty)$.

Just as before, a rotational Hamiltonian completely analogous to eq 2.10 is defined. The value of p_θ is extracted from the equation $H_{\mathrm{rot}} = E_{\mathrm{rot}}$, averaged over a full cycle of θ, and squared. This provides an invariant that, when equated to its asymptotic value, provides an expression for $E_{\mathrm{rot}}(r)$. Thus, in this approximation, the dynamics derives again from a 1D adiabatic Hamiltonian (eq 4.4).

$$H_{\mathrm{ad}}(r, p_r) = \frac{1}{2}\left(\frac{M+2m}{2mM}\right)p_r^{\,2} + E_{\mathrm{rot}}(\infty) + I\left(\frac{M+2m}{2mM}\right)\frac{E_{\mathrm{rot}}(\infty)}{r^2} + \frac{qQ}{4r^3} + O(r^{-6}) \qquad (4.4)$$

Here again, this adiabatic potential is defined for values of r large enough to allow unhindered rotation.

5. Libration in a Curved Harmonic Valley

The method developed in the previous sections becomes impractical outside the asymptotic range for the reasons given in Section 2.D. In more chemically interesting regions of the PES, the interfragment separation r has to be replaced by a reaction path coordinate s. It often happens that some parts of the potential surface can be described as a "harmonic valley" about the reaction path. Then, the RPH model can be expected to be valid, at least at low enough internal energies. Miller et al.[7] defined a dimensionless coupling parameter $\sigma(s)$ that, for a system limited to two degrees of freedom, is found to be equal to $2J\kappa(s)^2/\omega(s)$, where J is the classical action of the vibration perpendicular to s, ω denotes its s-dependent frequency, and $\kappa(s)$ is the curvature of the reaction path at point s. When σ is substantially lower than 1, J remains conserved. The dynamics is then again constrained by the adiabatic approximation. It has been possible[24] to elucidate the physical meaning of the coupling constant σ and to express it as $\sigma(s, J) = [x_{\mathrm{m}}(s, J)/R_{\mathrm{C}}(s)]^2$, where R_{C} denotes the radius of curvature (i.e., the inverse of κ), and x_{m} represents the amplitude of the vibrational motion.

When can the dynamical regime be expected to be adiabatic? Large values of the coupling parameter σ are found at small values of s because the reaction path is strongly curved in this region and because R_{C} is small. When s increases, so does R_{C}; as a result, σ decreases, and the adiabatic approximation becomes possible in an intermediate range of the reaction coordinate. However, when s becomes too large, the PES becomes very flat, which means that the amplitude (x_{m}) of the vibrational motion becomes very large, thereby increasing the coupling parameter σ. It can therefore be expected that σ goes through a minimum as the reaction coordinate is stretched. The deeper this minimum is, the more valid the adiabatic approximation is. At the corresponding value of s, the decoupling between the reaction coordinate and the orthogonal degrees of freedom can be expected to be most effective (i.e., the vibrational quantum numbers or the classical actions of the latter remain conserved). Under these circumstances, the dynamics is again reduced to a one-degree-of-freedom problem for the motion along the reaction coordinate.

6. The Maximum Entropy Method

A. Information Theory. In short, the various applications of the principle of adiabatic invariance studied in sections 2−5 result from a very simple local topography of the PES. It is not unreasonable to expect the potential surface of even a very complex reacting system to often be characterized by the existence of regions where the dynamics is locally constrained by adiabatic invariants. In other words, the existence of disjoint regions of phase space where the motion is not ergodic can also be expected.

However, additional constraints exist and have to be considered. A systematic approach is provided by the MEM, which is derived from information theory. Levine and co-workers have turned this theory into a method of central importance in the study of reaction dynamics.[9−11]

The state of a dynamical system can be described by a density matrix ρ, in quantum mechanics, or by a density of distribution in phase space in a classical description.[25] The MEM defines an entropy corresponding to a state ρ (eq 6.1),

$$S(\rho) = -Tr(\rho\ln\rho) \qquad (6.1)$$

and it exploits the fact that $S(\rho)$ is a constant of the motion if ρ is an exact solution of the equations of motion.[12,13,25]

In the MEM, state ρ is represented by the expansion shown in eq 6.2;

$$\rho = \exp[-\lambda_0 - \sum_{r=1}^{n} \lambda_r A_r] \tag{6.2}$$

where the A_r are physical properties that constrain the dynamics. They are therefore referred to as "informative observables" or "dynamical constraints". The quantities λ_r are Lagrange multipliers in a process that consists of maximizing the entropy (i.e., in making the dissociation dynamics as statistical as allowed by the constraint). Therefore, we arrive at eq 6.3.

$$S(\rho) = \lambda_0 + \sum_{r=1}^{n} \lambda_r \langle A_r \rangle \tag{6.3}$$

B. Flexibility in the Choice of the Constraints. The essential point to be noted is that for a given state ρ, expansions 6.2 and 6.3 are not unique. Any linear combination of the set of n constraints can be used instead of the original one. As emphasized by Levine and co-workers,[12,13] the analysis of constraints can be carried out in different regions of the reaction path. For example, one can envisage a set of Lagrange multipliers and observables appropriate to describe the reagents or, alternatively, another set appropriate to describe the products.

In the regions where the adiabatic approximation is valid, the resulting constraint reduces the dynamics to a 1D motion along the reaction coordinate in an effective 1D potential. Then, as shown in a previous study,[24] the application of Jacobi's form of the least-action principle to adiabatic Hamiltonians is particularly simple. Actual trajectories are required to minimize the integral shown in eq 6.4;

$$\int_{s_1}^{s_2} [H_{\mathrm{ad}}(s, p_s) - V_{\mathrm{eff}}(s)]^{1/2}\, \mathrm{d}s = \int_{s_1}^{s_2} \epsilon(s)^{1/2}\, \mathrm{d}s \tag{6.4}$$

where ϵ denotes the translational energy along the reaction coordinate s. In that case, the summations in eqs 6.2 and 6.3 reduce to a single term $A_1 = \epsilon^{1/2}$. In other words, the constraint identifies with the square root of the translational energy (i.e., with the momentum). Conversely, the observation that the dynamics is constrained by the momentum indicates that the bunch of classical trajectories has, at a particular moment of its history, traversed a (fairly small) portion (at the limit) of the PES characterized by a very simple topography and, hence, by the presence of dynamical constraints of the type previously studied.

C. Connection with Experiment. The analysis of product energy distributions by the MEM has been very useful in the understanding of reaction dynamics.[9−11,26] Particularly interesting for our purposes is the study of translational kinetic energy release distributions (KERDs),[27−35] which are expressed as a probability distribution $P(\epsilon|E)$ where E denotes the excess energy with respect to the dissociation asymptote. The experimental device resolves the translational energy ϵ but groups together all the final states that have the same vib-rotational energy. In that case, the actual KERD can be expressed as eq 6.5.

$$P(\epsilon|E) = P^0(\epsilon|E) \exp(-\lambda_0 - \lambda_1 A_1 - \lambda_2 A_2 - ...) \tag{6.5}$$

where $P^0(\epsilon|E)$ denotes the prior distribution (i.e., a fully statistical situation where all accessible quantum states of the pair of fragments are populated with the same probability). By its very definition, the prior distribution is proportional to the total density of states and can be calculated quite simply from a knowledge of these quantities. The sequence of multiplicative corrections derives from the expansions 6.2 and 6.3.

If the experimentally measured KERD $P(\epsilon|E)$ coincides with the prior distribution, then the reaction proceeds as expected from statistical physics (i.e., without any dynamical constraint). If they differ, a so-called surprisal can be defined[9−13] as $-\ln \rho$ (i.e., from eqs 6.2 and 6.5):

$$-\ln \rho = \lambda_0 + \sum_{r=1}^{n} \lambda_r A_r = -\ln\left[\frac{P(\epsilon|E)}{P^0(\epsilon|E)}\right] \tag{6.6}$$

From eq 6.1, the entropy is seen to be the average of the surprisal.

The latter quantity can be plotted as a function of various observables (e.g., as a function of $\epsilon^{1/2}$). If the plot is found to be linear, that is, if the KERD is represented by a simplified version of eq 6.5 (eq 6.7),

$$P(\epsilon|E) = e^{-\lambda_0}\, e^{-\lambda_1 \epsilon^{1/2}}\, P^0(\epsilon|E) \tag{6.7}$$

then the transformation of the prior into the actual KERD requires a single correcting factor only (i.e., a single constraint). (The factor $\exp(-\lambda_0)$ is determined by requiring the KERDs to be normalized to unity.) The reaction is said to be constrained by the momentum. This has been observed to be the case for many simple adiabatic barrierless bond cleavage reactions studied at energies that are not too high.[27−34] As a result of eq 6.4 and of the relevant discussion, such an observation strongly suggests the existence of a local simplicity in the PES, either in the asymptotic region or as a harmonic valley at some value of the reaction path. In more complicated cases, where the asymptotic potential cannot be described by a multipolar expansion because of the presence of a reverse activation barrier,[32] many terms are required in the expansion in the set of observables A_r that is being chosen for the analysis (e.g., $\epsilon^{1/2}$, ϵ, ϵ^2, ...). When two electronic states cross at a large value of the reaction coordinate, the constraint is again unique, but this time it is equal to ϵ.[35] Thus, the experimental determination of a surprisal plot provides information on the dynamics.

D. Persistence of the Constraints. Several arguments can be put forward to assess the reliability of the MEM and to show that its success in the analysis of product energy distributions goes beyond a mere empirical formulation.

Alhassid and Levine have shown[12,13] that expression 6.2 converges to an exact solution of the equations of motion. Classical trajectory calculations for reactive collisions were found to generate linear surprisal plots.[10] The same is true for quantum calculations.[36−38] Nesbet[39−41] has reformulated quantum dynamical calculations to provide a consistent definition of internal state populations as evolving functions of the reaction coordinate. The populations calculated at different values of the reaction coordinate were found to be in remarkable agreement with the equations of the MEM.

All this supports the basic postulate that the entropy of the internal state population distribution maintains its maximum value, subject only to dynamical constraints throughout the entire reaction process and not just in the asymptotic region. It gives credence to the claim that constraints that have been derived from the study of a model Hamiltonian, valid in a restricted region only, persist at other, chemically more interesting separations. Constraints subsist but in a modified form that might be termed “diluted” because they are partitioned over all degrees of freedom. In particular, they subsist at small values of the reaction coordinate, close to the bottom of the PES, where the RRKM theory assumes the oscillators freely exchange their energy.

7. Concluding Remarks

Theoretical chemistry was born the day Born and Oppenheimer developed their adiabatic separation theorem. Possible applications to chemical reactivity were already suspected by Hirschfelder and Wigner.[4] It has been argued here that, even if the validity of an adiabatic invariant can be demonstrated in a localized region only, its influence subsists in the whole range of the reaction coordinate.

Any discrepancy between the actual and the prior distributions indicates the existence of dynamical constraints that lead to a situation of lesser entropy (i.e., to incomplete phase space sampling).[9−13] Therefore, the MEM information derived from a KERD, although resulting from observations done for a portion of the PES characterized by a very simple topography, remains valid at any value of the reaction coordinate. When adiabatic separation is possible, the constraint is unique and simple. It identifies with the momentum $\epsilon^{1/2}$. Invariance compels the nuclear trajectories to visit regions of phase space where they are subject to constraints that, although expressed in a different and more complicated form, are equivalent to those detected in the asymptotic range or in a harmonic valley. Such dynamical constraints therefore exist for most ion−molecule reactions. The RPH model[7,24] is also thought to be of wide occurrence, even if only locally.

These views contradict summary sketches of the RRKM theory. The system never forgets its previous history, but its memory readjusts as the reaction proceeds. The analytical expression of the constraint is simple, for example, when $r \rightarrow \infty$, but the restrictions to phase space sampling and to energy randomization act everywhere along the reaction coordinate.

Other cases can be mentioned. Weakly bonded species similar to van der Waals complexes are frequently encountered as reaction intermediates, especially in the form of ion−neutral complexes.[42] Because the weak bond vibrates with a low frequency, the vibrational actions of the intramolecular modes are approximate constants of the motion.[43] In physical terms, the net result of the adiabatic invariance is to restrict the release of translational energy and to favor its channeling into the rotational and vibrational degrees of freedom of the pair of fragments with respect to a pure statistical partitioning. This effect has been known for a long time in the study of van der Waals complexes, where it is known as the momentum gap law.[43−45] Its quantum mechanical interpretation in terms of overlapping nuclear wave functions is particularly simple. In classical mechanics, the effect is known to affect energy transfer by collisions,[2] where it can be viewed as an extension of the Franck−Condon principle, which says that nuclei change their linear (translational) momentum only reluctantly.

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