

Crossing the dividing surface of transition state theory. I. Underlying symmetries and motion coordination in multidimensional systems

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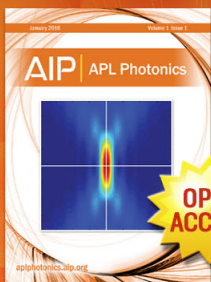
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Crossing the dividing surface of transition state theory. I. Underlying symmetries and motion coordination in multidimensional systems

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The objective of the present paper is to show the existence of motion coordination among a bundle of trajectories crossing a saddle point region in the forward direction. For zero total angular momentum, no matter how complicated the anharmonic part of the potential energy function, classical dynamics in the vicinity of a transition state is constrained by symmetry properties. Trajectories that all cross the plane $R = R_*$ at time $t = 0$ (where R_* denotes the position of the saddle point) with the same positive translational momentum P_{R_*} can be partitioned into two sets, denoted “*gerade*” and “*ungerade*,” which coordinate their motions. Both sets have very close average equations of motion. This coordination improves tremendously rapidly as the number of degrees of freedom increases. This property can be traced back to the existence of time-dependent constants of the motion. © 2014 AIP Publishing LLC. [<http://dx.doi.org/10.1063/1.4870038>]

I. INTRODUCTION

Stationary points on the potential energy surface play a fundamental role in the rationalization of molecular structure, thermodynamics, and reaction dynamics.^{1,2} Potential wells are studied by vibrational spectroscopy, which is based on models whose validity is in principle limited to displacements of infinitesimal amplitude in a harmonic force field. These restrictions are unacceptable in the study of reaction dynamics, which focuses on another kind of stationary points, namely saddle points. Therefore, one must resort to classical trajectory calculations. Unfortunately, it is usually impossible to find a system of generalized body-fixed coordinates where, after removal of the center of mass, both the kinetic and potential parts of energy have a simple expression. Therefore, a closed-form expression of Hamilton’s canonical equations cannot be obtained for realistic potential energy surfaces.

That interesting dynamical properties nevertheless exist in the neighborhood of saddle points has been demonstrated by several authors.

Marcus³ advocated the use of the concept of adiabaticity and pointed out that a slow dissociation mode can be expected to be decoupled from fast vibrational modes at least in a limited region around the saddle point. The quantum numbers of transverse vibrations (i.e., perpendicular to the reaction coordinate) are then approximate constants of the motion. The adiabaticity of vibrational motions has also been exploited by Truhlar.⁴

Berry and Wales^{5–9} investigated the classical motion near saddle points by calculating Liapunov exponents and Kolmogorov entropies and found evidence for regular dynamics at least in some cases. They discussed the role played by such factors as extent of coupling among degrees of freedom, type of motion, flatness of the saddle,¹⁰ and influence of the internal energy.

Miller^{11–14} demonstrated the existence of locally conserved action variables associated with a transition state even when the Hamiltonian involves a non-separable potential energy function. Conservation properties were shown to be a direct consequence of the dichotomy between imaginary and real frequencies because there can be no local Fermi resonances between the two.

Wiggins^{15–17} and, independently, Komatsuzaki and Berry^{18–25} reformulated the problem in terms of a new set of coordinates denoted “normal form coordinates,” which, in the neighborhood of the saddle point, locally decouple the dynamics into a reaction coordinate and bath modes even if the potential is anharmonic. The method is valid for high dimensional Hamiltonian systems. The degree of freedom associated with the reaction coordinate remains essentially regular through the region of the transition state even to moderately high energies. At higher energies, regularity turns to chaos.

The objective of the present paper is to show the existence of motion coordination among a bundle of trajectories crossing the saddle point region in the forward direction. Coordination is shown to exist irrespective of the magnitude of anharmonicity and to improve as the number of degrees of freedom increases. It is a direct consequence of the existence of local constraints in the vicinity of a saddle point.

II. DIAGONAL KINETIC ENERGY

Our aim is the detection of symmetry properties that exist irrespective of the shape of the potential energy surface. Therefore, the expression of the latter is left unspecified. In addition, we choose to work in the Hirschfelder system of body-fixed coordinates,²⁶ where the kinetic energy is diagonal and independent of spatial coordinates. Then, the kinetic and potential parts are neatly separated and only the latter can

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contain couplings of all kinds. The Hamiltonian has the form

$$H = \frac{P_R^2}{2M} + \frac{1}{2} \sum_j^N \frac{p_j^2}{m_j} + V(R, q_1, \dots, q_j, \dots, q_N), \quad (2.1)$$

where R and P_R denote the reaction coordinate and its conjugate momentum, respectively. Nothing is known on the potential energy surface, except that there exists an extremum, in our case a saddle point, at coordinates $(R_*, q_{1*}, \dots, q_{j*}, \dots)$.

Local analytic solutions, valid in the neighborhood of the saddle point, can be derived as a formal series solution by repeated application of the Poisson bracket equation, which gives the rate of change of any dynamical variable X . Assuming initial conditions $(R_0, P_{R_0}, \dots, q_{j_0}, p_{j_0}, \dots)$ at time $t = 0$, the equation of motion of the reaction coordinate R can be formulated as follows:²⁷

$$\begin{aligned} R(t) &= R_0 + t [R, H]_0 + \left(\frac{t^2}{2!}\right) [[R, H], H]_0 \\ &\quad + \left(\frac{t^3}{3!}\right) [[[R, H], H], H]_0 + \dots \\ &= R_0 + c_1 t + c_2 \left(\frac{t^2}{2!}\right) + c_3 \left(\frac{t^3}{3!}\right) + \dots, \end{aligned} \quad (2.2)$$

where the subscript zero refers to the initial conditions at time $t = 0$.

Taking into account the symmetry properties inherent in a stationary point, it makes sense to consider a bundle of forward trajectories that all begin at time $t = 0$ at $R_0 = R_*$, with the same translational momentum oriented in the forward direction, denoted by $P_{R_0} = +P_{R_*}$, and with all of the possible sign combinations in the set $\{q_{1*} \pm \delta q_1, \pm p_1, \dots, q_{j*} \pm \delta q_j, \pm p_j, \dots\}$ for the other variables. (The initial elongations δq_j and momenta p_j are defined as positive quantities.) For a system of N degrees of freedom in addition to the reaction coordinate, the bundle consists of 2^{2N} trajectories. The objective of the present paper is to demonstrate the existence of motion coordination among members of the bundle.

To do this, it proves convenient to split the bundle into two sets distinguished by the parity of the initial conditions. Adopting the German nomenclature in current use in chemical physics, we denote as “*gerade*” the set of trajectories that all have an even number of minus signs in the specification of their initial conditions (i.e., $\{q_{1*} + \delta q_1, +p_1, \dots, q_{j*} + \delta q_j, +p_j, \dots\}$, $\{q_{1*} - \delta q_1, -p_1, \dots, q_{j*} + \delta q_j, +p_j, \dots\}$, $\{q_{1*} - \delta q_1, +p_1, \dots, q_{j*} - \delta q_j, +p_j, \dots\}$, etc.). The other set of trajectories whose initial conditions contain an odd number of minus signs is referred to as the “*ungerade*” set. We wish to prove that both sets have an extremely similar average equation of motion in the vicinity of the saddle point, i.e.,

$$\langle R(t) \rangle_g \approx \langle R(t) \rangle_u. \quad (2.3)$$

More precisely, we consider the averages $\langle c_j \rangle_g$ and $\langle c_j \rangle_u$ of the coefficients of Eq. (2.2), where the average is taken over the set of 2^{2N} initial conditions, i.e., over both spatial coordinates and conjugate momenta. We wish to prove the equality $\langle c_j \rangle_g = \langle c_j \rangle_u$ up to a certain value of j that depends

on the dimensionality of the Hamiltonian (i.e., on the value of N), and a near equality $\langle c_j \rangle_g \approx \langle c_j \rangle_u$ beyond that value.

In other words, we wish to determine the conditions under which the expansion

$$\begin{aligned} \langle \Delta c_j \rangle &= \langle c_j \rangle_g - \langle c_j \rangle_u = \left\langle \sum_k c_{jk} \right\rangle_g - \left\langle \sum_k c_{jk} \right\rangle_u \\ &= \left\langle \sum_k (-1)^{p_{jk}} c_{jk} \right\rangle \end{aligned} \quad (2.4)$$

reduces to a value close to zero. In this expression, the symbol p_{jk} is equal to 0 or to +1, depending on whether the k th nest of Poisson brackets derives from an even or odd set of initial conditions.

The first Poisson bracket $[R, H]_0$ is equal to P_{R_*} / M and is the same for all trajectories of the bundle, as it should. Therefore, $\langle \Delta c_1 \rangle = 0$, in every case.

The second coefficient,

$$c_2 = [[R, H], H]_0 = -\frac{1}{M} \left. \frac{\partial V}{\partial R} \right|_0, \quad (2.5)$$

measures the acceleration and depends on spatial coordinates only. Thus, $\langle \Delta c_2 \rangle$ vanishes after averaging over all possible values of momenta.

The cubic term, c_3 , involves momenta and second-order derivatives of the potential:

$$c_3 = -\frac{P_{R_*}}{M^2} \left. \frac{\partial^2 V}{\partial R^2} \right|_0 - \frac{1}{M} \sum_j^N \frac{p_j}{m_j} \left. \frac{\partial^2 V}{\partial R \partial q_j} \right|_0. \quad (2.6)$$

The first term of the right-hand side of Eq. (2.6) is the same for all trajectories of the bundle and makes no contribution to $\langle \Delta c_3 \rangle$. However, the contribution of the second term depends on the value of N , and this has an incidence on the dynamics.

A. $N = 1$

The case $N = 1$ describes, e.g., the dissociation of a fictitious triatomic molecule constrained to remain collinear. The bundle consists of two *gerade* and two *ungerade* trajectories leading to the average quantity

$$\langle \Delta c_3 \rangle = \frac{p_1}{M m_1} \left(\left. \frac{\partial^2 V}{\partial R \partial q_1} \right|_{R_*, q_{1*} - \delta q_1} - \left. \frac{\partial^2 V}{\partial R \partial q_1} \right|_{R_*, q_{1*} + \delta q_1} \right). \quad (2.7)$$

A more concrete expression is obtained if the potential energy is expanded as a Taylor series about the saddle point at coordinates (R_*, q_{1*}) . Then, Eq. (2.7) reduces to

$$\langle \Delta c_3 \rangle = -\frac{2}{3} \frac{\delta q_{1*} p_1}{M m_1} \left(k_{12}^3 + \frac{1}{10} k_{14}^5 \delta q_{1*}^2 + \dots \right) \quad (2.8)$$

which involves the force constant of high-order anharmonic terms in the expansion of the potential, namely, $(1/6)k_{12}^3(R - R_*)(q_1 - q_{1*})^2$ and $(1/120)k_{14}^5(R - R_*)(q_1 - q_{1*})^4$. These force constants may be reasonably assumed to be small, at least in some instances. Moreover, the presence of two heavy nuclear masses in the denominator of

Eqs. (2.7) and (2.8) reduces the magnitude of $\langle \Delta c_3 \rangle$. The next terms, $\langle \Delta c_4 \rangle$ and $\langle \Delta c_5 \rangle$ do not vanish either, but their expressions contain terms cubic in masses in the denominator. Thus, *gerade* and *ungerade* trajectories coordinate their motion, at least to some extent. The coordination improves as the number of degrees of freedom increases, as will be shown presently.

B. $N = 2$

In this case, the bundle consists of 16 trajectories whose initial conditions correspond to four possible choices for the momenta and four possible points in configuration space. At each one of these points, i.e., at a given value of the elongations, the second derivatives that appear in Eq. (2.6) have the same value. Hence, the contribution of that point to $\langle \Delta c_3 \rangle$ vanishes after averaging over the momenta.

This is not the case for the quartic coefficient, c_4 . It contains terms where a single momentum p_j is raised to the power 0, or 1, or 2. These terms give a vanishing contribution to $\langle \Delta c_4 \rangle$ when averaged over all possible values of momenta. But the expansion also contains a cross-term that induces a nonzero contribution equal to

$$\langle \Delta c_4 \rangle = -2 \frac{p_1 p_2}{M m_1 m_2} \left. \frac{\partial^3 V}{\partial R \partial q_1 \partial q_2} \right|_0. \quad (2.9)$$

A more concrete expression is obtained if the potential energy is expanded as a Taylor series about the saddle point at coordinates (R_*, q_{1*}, q_{2*}) . Then, Eq. (2.9) reduces to an expansion whose leading term is

$$\langle \Delta c_4 \rangle = -\frac{2}{15} \left(k_{122}^5 + \frac{1}{21} k_{142}^7 \delta q_1^2 + \frac{1}{21} k_{124}^7 \delta q_2^2 \right) \times \frac{p_1 p_2 \delta q_1 \delta q_2}{M m_1 m_2} \quad (2.10)$$

which involves the force constant of, e.g., the very high-order anharmonic term $(1/120)k_{122}^5 (R - R_*)(q_1 - q_{1*})^2 (q_2 - q_{2*})^2$.

Similar calculations can be done for the quintic term. One finds

$$\langle \Delta c_5 \rangle = -\frac{2}{15} k_{222}^6 \frac{P_{R_*} p_1 p_2 \delta q_1 \delta q_2}{M^2 m_1 m_2} + \dots \quad (2.11)$$

C. $N = 3$

The cubic term $\langle \Delta c_3 \rangle$ vanishes for the same reasons as in the previous case and so does also the quartic term $\langle \Delta c_4 \rangle$. The reason is that the cross terms

$$-\frac{2}{M} \sum_{j,k} \frac{p_j p_k}{m_j m_k} \left. \frac{\partial^3 V}{\partial R \partial q_j \partial q_k} \right|_0 \quad (2.12)$$

contained in the term c_4 now give a vanishing contribution when averaged over the whole set of momenta $\{p_1, p_2, \dots, p_N\}$ if N is larger than 2. The first nonzero contribution is provided by the quintic term, whose expression is

$$\langle \Delta c_5 \rangle = -\frac{2}{105} k_{1222}^7 \frac{p_1 p_2 p_3 \delta q_1 \delta q_2 \delta q_3}{M m_1 m_2 m_3}. \quad (2.13)$$

Here again, the presence of four nuclear masses in the denominator greatly reduces its magnitude.

D. Conclusions

Similar calculations have been carried out up to $N = 4$, i.e., for a five-dimensional Hamiltonian. The difference between the two average trajectories is obtained by substituting Eqs. (2.8), (2.10), and (2.13), plus the result derived for $N = 4$ into Eqs. (2.2) and (2.4). Retaining the leading term only leads to a general expression

$$\begin{aligned} \langle R(t) \rangle_g - \langle R(t) \rangle_u \\ = -\frac{2}{(N+2)!(2N+1)!!} k_{12\dots 2}^{2N+1} \frac{1}{M} \prod_{i=1}^N \frac{p_i \delta q_i}{m_i} t^{N+2} \\ + O(t^{N+3}), \end{aligned} \quad (2.14)$$

where the symbol $n!!$ denotes the double factorial (e.g., $5!! = 1 \cdot 3 \cdot 5$).

This equation shows that the two sets of trajectories, *gerade* and *ungerade*, coordinate their motion, at least to some extent. The lack of coordination, which is measured by the quantity $\langle R(t) \rangle_g - \langle R(t) \rangle_u$, can be traced back to mode-mode coupling, which appears in Eq. (2.14) in the form of a high-order interaction force constant in the molecular force field. Particularly noteworthy is the influence of the number of degrees of freedom, which improves the quality of motion coordination tremendously rapidly for several reasons: First, the denominator contains two factorials, $(N+2)!$ and $(2N+1)!!$; second, it also contains the product of $(N+1)$ heavy nuclear masses; third, the first nonzero term involves the $(N+2)$ th power of time, which amounts to saying that the discrepancy between $\langle R(t) \rangle_g$ and $\langle R(t) \rangle_u$ fades away as N increases.

Similar relations are also valid for the bounded degrees of freedom, i.e., for coordinates q_1, q_2 , etc., and for their conjugate momenta.

In practice, Hirschfelder coordinates are not often used in dynamical calculations. Nevertheless, the previous results are meaningful because the physical significance of a conclusion should not depend on the choice of a coordinate system. To check this, we now consider in more detail the triatomic case studied in Jacobi coordinates.

III. THE TRIATOMIC CASE

The Hamiltonian describing an atom-diatom interaction for a body-fixed rotationless study has been derived by several authors:^{15,24,28-32}

$$\begin{aligned} H = \frac{1}{2M} P_R^2 + \frac{1}{2\mu} p_r^2 + \frac{1}{2} \left(\frac{1}{M R^2} + \frac{1}{\mu r^2} \right) p_\theta^2 \\ + V(R, r, \theta), \end{aligned} \quad (3.1)$$

where R is the distance between the atom and the center of mass of the diatomic, r is the internuclear distance of the latter, θ is the angle between the two position vectors, P_R, p_r, p_θ are the conjugate momenta, μ is the reduced mass of the diatomic, and M is that of the atom-diatom system.

When the Hamiltonian is given by Eq. (3.1), the Poisson brackets that appear in Eq. (2.2) are equal to

$$c_1 = \frac{P_{R_0}}{M}, \quad (3.2)$$

$$c_2 = \frac{p_{\theta_0}^2}{M^2 R_0^3} - \frac{1}{M} \left. \frac{\partial V}{\partial R} \right|_0, \quad (3.3)$$

$$c_3 = -3 \frac{P_{R_0} p_{\theta_0}^2}{M^3 R_0^4} - 2 \frac{p_{\theta_0}}{M^2 R_0^3} \left. \frac{\partial V}{\partial \theta} \right|_0 - \frac{P_{R_0}}{M^2} \left. \frac{\partial^2 V}{\partial R^2} \right|_0 - \frac{p_{r_0}}{M \mu} \left. \frac{\partial^2 V}{\partial R \partial r} \right|_0 - \frac{p_\theta}{M} \left(\frac{1}{M R_0^2} + \frac{1}{\mu r_0^2} \right) \left. \frac{\partial^2 V}{\partial R \partial \theta} \right|_0. \quad (3.4)$$

Now, assume that the potential energy surface is characterized by a saddle point at coordinates (R_*, r_*, θ_*) . The bundle of trajectories now consists of 16 forward trajectories that all begin at time $t = 0$ at $R_0 = R_*$, with the same translational momentum normal to the dividing surface denoted

$P_{R_0} = P_{R_*}$, and with the 16 possible sign combinations in the set $\{r_* \pm \delta r, \pm p_{r_0}, \theta_* \pm \delta \theta, \pm p_{\theta_0}\}$ for the other variables. They can be partitioned into two sets, *gerade* and *ungerade*.

Calculations entirely similar to those carried out in Sec. II lead to $\langle \Delta c_1 \rangle = \langle \Delta c_2 \rangle = \langle \Delta c_3 \rangle = 0$. The fourth term $\langle \Delta c_4 \rangle$ does not vanish and its evaluation leads to

$$\begin{aligned} \langle R(t) \rangle_g - \langle R(t) \rangle_u &= \left(-\frac{\delta r \delta \theta p_r p_\theta}{36 M \mu} \right) \left(6 \frac{k_{102}^3}{\mu r_*^4} - \frac{3 k_{112}^4}{2 \mu r_*^3} + \frac{k_{022}^4}{M R_*^3} \right) t^4 + \dots \end{aligned} \quad (3.5)$$

As a consequence, the averages of *g* and *u* trajectories have the same equation of motion, up to and including terms cubic in time. The divergence between the two stems from quartic and higher terms. However, due to the heaviness of the nuclear masses, it can be expected to be quite small.

A similar relation is also valid for the other two coordinates, *r* and θ , and for their conjugate momenta:

$$\langle r(t) \rangle_g - \langle r(t) \rangle_u = \left(-\frac{\delta r \delta \theta p_r p_\theta}{18 \mu^3 r_*^3} \right) \left(72 \frac{k_{002}^2}{r_*^2} - 6 \frac{k_{012}^3}{r_*} - k_{022}^4 + 12 k_{004}^4 \left(\frac{\delta \theta_*}{r_*} \right)^2 \right) t^4 + \dots, \quad (3.6)$$

$$\langle \theta(t) \rangle_g - \langle \theta(t) \rangle_u = \left(\frac{\delta r \delta \theta p_r p_\theta}{3 \mu^2 r_*^4} \right) \left(\frac{9 k_{011}^2}{\mu r_*} - 2 k_{003}^3 \left(\frac{3}{M R_*^2} + \frac{5}{\mu r_*^2} \right) - \frac{2 k_{021}^3}{\mu} \right) t^4 + \dots, \quad (3.7)$$

$$\langle P_R(t) \rangle_g - \langle P_R(t) \rangle_u = \left(-\frac{\delta r \delta \theta p_r p_\theta}{3 \mu} \right) \left(\frac{2 k_{102}^3}{\mu r_*^4} - \frac{k_{112}^4}{2 \mu r_*^3} + \frac{k_{022}^4}{3 M R_*^3} \right) t^3 + \dots, \quad (3.8)$$

$$\langle p_r(t) \rangle_g - \langle p_r(t) \rangle_u = \left(-\frac{2}{9} \frac{\delta r \delta \theta p_r p_\theta}{\mu^2 r_*^3} \right) \left(\frac{72 k_{002}^2}{r_*^2} - \frac{6 k_{012}^3}{r_*} - k_{022}^4 \right) t^3 + \dots, \quad (3.9)$$

$$\langle p_\theta(t) \rangle_g - \langle p_\theta(t) \rangle_u = \left(-\frac{\delta r \delta \theta p_r p_\theta}{2 \mu^2 r_*^3} \right) \left(\frac{4 k_{003}^3}{r_*} - k_{013}^4 \right) t^3 + \dots \quad (3.10)$$

IV. FOUR DEGREES OF FREEDOM

Four degrees of freedom systems can only be obtained when constraints are introduced into tetra-atomic molecules. A typical example is hydrogen peroxide in a body-fixed rotationless system of coordinates under the constraint that the two OH bond lengths are fixed. Its classical Hamiltonian has been derived by Schinke and Staemmler:³³

$$H = \frac{P_R^2}{2M} + \sum_{i=1}^2 B \left(p_{\theta_i}^2 + \frac{P_{\phi_i}^2}{\sin^2 \theta_i} \right) + V(R, \theta_1, \theta_2, \varphi), \quad (4.1)$$

where *R* is the distance between the centers of mass of the two OH fragments, θ_1 and θ_2 are the polar angles of these fragments with respect to *R*, φ is the torsional dihedral angle ($\varphi = \varphi_1 - \varphi_2$), and *B* is the rotational constant of the two frozen fragments. Initial conditions are constrained by the condition

$p_{\varphi_1} = -p_{\varphi_2} = p_\varphi$ to ensure zero angular momentum. In this case, the leading term of the equation that expresses motion coordination between *g* and *u* trajectories is equal to

$$\langle R(t) \rangle_g - \langle R(t) \rangle_u = -\frac{32}{5! 7!!} k_{1222}^7 \frac{B^3 p_{\theta_1} p_{\theta_2} p_\varphi \delta \theta_1 \delta \theta_2 \delta \varphi}{\sin^2 \theta_{eq}} t^5 \quad (4.2)$$

which is in line with Eqs. (2.13) and (2.14) with $N = 3$.

V. DISCUSSION

A. Synopsis

The symmetry detected here by elementary means is a direct consequence of the existence of the approximate constants of the motion brought to the fore by the systematic and detailed analysis of phase space structure carried out by Wiggins, Komatsuzaki, Berry, and their co-workers.¹⁵⁻²⁵

This structure is independent of the system of coordinates that is being chosen and a glimpse of it already shows up in conventional coordinates without carrying out an unwieldy symplectic transformation to normal form coordinates.

Our aim is the detection of symmetry properties that exist when the form of the potential energy surface is unspecified: thus, as general as possible and containing couplings of all kinds. Therefore, we choose to work in coordinate systems where the kinetic energy is diagonal and independent of spatial coordinates; kinetic and potential parts are then neatly separated. Getting together the conclusions derived from Eqs. (2.14), (3.5), and (4.2), we end up with a result where the influence of the anharmonic coupling on motion coordination is characterized by four properties. First, it is seen to derive from particular high-order interaction force constants. Second, its magnitude is considerably reduced by the heaviness of nuclear masses. Third, it is prominent at long times only, when the system has wandered far away from the saddle point region. Fourth, it rapidly fades away as the number of degrees of freedom increases.

Two conclusions emerge. First, motion coordination spectacularly depends on the number of degrees of freedom, much more than on the shape and anharmonicity of the potential energy surface (i.e., on mode-mode coupling).

The second conclusion is that it is best to restrict consideration to low energies. The product $\prod_i^N p_i \delta q_i$ that appears in the numerator of Eq. (2.14) increases with the internal energy. Even more important is the fact that the concept of a bundle of closely related trajectories makes sense only if the initial points have at least comparable energies. Since initial conditions are arranged symmetrically with respect to the stationary point, this will be the case if the anharmonicity of the motions perpendicular to the reaction coordinate is not too important and if the elongations are not too large. Thus, the implications for the dynamics in the neighborhood of a saddle point can be expected to be relevant at not too high internal energies.

To get further insight, it is best to study a particular example where the expression of the potential energy surface has been specified. This will be done in Paper II,³⁴ where a numerical calculation of the average trajectories $\langle R(t) \rangle_g$ and $\langle R(t) \rangle_u$ will be presented.

B. Motion coordination and time-dependent constants of the motion

The fact that averages over g and u trajectories remain very close in the vicinity of the saddle point has been described in Secs. II and III as motion coordination.

Ever since the work by Goldstein,²⁷ dynamical constraints and conservation laws have been related to symmetry properties of the system. (See, e.g., Ref. 27, pp. 589.) Symmetry should be understood as invariance under a particular transformation group of either the Hamiltonian or of the equations of motion of the system.³⁵ In the latter case, the connection is accounted for by the concept of time-dependent constant of the motion.³⁶

For a given Hamiltonian involving N degrees of freedom (now including the reaction coordinate), a classical trajectory is completely characterized by its initial conditions,

i.e., by two N -dimensional vectors $\mathbf{q}(0)$ and $\mathbf{p}(0)$. At each time, the trajectory remembers its $2N$ initial conditions, as a time-reversal calculation would show. Therefore, as noted by Levine and co-workers,^{36–38} at any time t and for any point of the trajectory, one can in principle invert the trajectory and write formally

$$\mathbf{q}(0) = Q(\mathbf{q}(t), \mathbf{p}(t), t),$$

$$\mathbf{p}(0) = P(\mathbf{p}(t), \mathbf{q}(t), t).$$

Although in most cases, except in the simplest examples, the functions Q and P remain unknown, they can nevertheless be termed time-dependent constants of the motion,^{36–38} because their value does not change along the trajectory.

Since the bundle of trajectories has been defined by a highly symmetrical set of initial conditions, it is quite easy to set up linear combinations of $\mathbf{q}(0)$ and $\mathbf{p}(0)$ that result in a value of zero. The six particular ones that have been considered in the case of the triatomic system are specified on the left-hand sides of Eqs. (3.5)–(3.10). When they are evaluated at time $t = 0$, they vanish identically, by construction. However, their special virtue is that they reveal the simplicity of the unknown functions Q and P , which are found to be nearly separable in the neighborhood of the transition state. Furthermore, either their time expansion lacks the first few terms, or, more probably, these terms must also have symmetry properties in order to vanish in the linear combination.

Motion coordination is characteristic of harmonic force fields. Here, we present an example where, at low energies, the concept keeps its validity in an arbitrarily anharmonic potential including cross-terms.

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¹D. J. Wales, *Energy Landscapes* (Cambridge University Press, Cambridge, UK, 2003).

²D. J. Wales, *Philos. Trans. R. Soc., A* **370**, 2877 (2012).

³R. A. Marcus, *Science* **256**, 1523 (1992).

⁴D. G. Truhlar, *J. Chem. Phys.* **53**, 2041 (1970).

⁵D. J. Wales and R. S. Berry, *J. Phys. B: At., Mol. Opt. Phys.* **24**, L351 (1991).

⁶R. J. Hinde, R. S. Berry, and D. J. Wales, *J. Chem. Phys.* **96**, 1376 (1992).

⁷R. J. Hinde and R. S. Berry, *J. Chem. Phys.* **99**, 2942 (1993).

⁸J. R. Green, T. S. Hofer, R. S. Berry, and D. J. Wales, *J. Chem. Phys.* **135**, 184307 (2011).

⁹J. R. Green, T. S. Hofer, D. J. Wales, and R. S. Berry, *Mol. Phys.* **110**, 1839 (2012).

¹⁰J. C. Lorquet, *J. Phys. Chem. A* **115**, 4610 (2011).

¹¹W. H. Miller, *Faraday Discuss. Chem. Soc.* **62**, 40 (1977).

¹²W. H. Miller, R. Hernandez, N. C. Handy, D. Jayatilaka, and A. Willets, *Chem. Phys. Lett.* **172**, 62 (1990).

¹³R. Hernandez and W. H. Miller, *Chem. Phys. Lett.* **214**, 129 (1993).

¹⁴S. Keshavamurthy and W. H. Miller, *Chem. Phys. Lett.* **205**, 96 (1993).

¹⁵H. Waalkens, A. Burbanks, and S. Wiggins, *J. Chem. Phys.* **121**, 6207 (2004).

¹⁶H. Waalkens, R. Schubert, and S. Wiggins, *Nonlinearity* **21**, R1 (2008).

¹⁷A. Goussev, R. Schubert, H. Waalkens, and S. Wiggins, *Adv. Quantum Chem.* **60**, 269 (2010).

¹⁸T. Komatsuzaki and R. S. Berry, *J. Chem. Phys.* **110**, 9160 (1999).

¹⁹T. Komatsuzaki and R. S. Berry, *Phys. Chem. Chem. Phys.* **1**, 1387 (1999).

- ²⁰T. Komatsuzaki and R. S. Berry, *J. Mol. Struct.: THEOCHEM* **506**, 55 (2000).
- ²¹T. Komatsuzaki and R. S. Berry, *Proc. Natl. Acad. Sci. U.S.A.* **98**, 7666 (2001).
- ²²T. Komatsuzaki and R. S. Berry, *J. Phys. Chem. A* **106**, 10945 (2002).
- ²³T. Komatsuzaki and R. S. Berry, *Adv. Chem. Phys.* **123**, 79 (2002).
- ²⁴C. B. Li, Y. Matsunaga, M. Toda, and T. Komatsuzaki, *J. Chem. Phys.* **123**, 184301 (2005).
- ²⁵S. Kawai and T. Komatsuzaki, *Phys. Rev. Lett.* **105**, 048304 (2010).
- ²⁶J. O. Hirschfelder, *Int. J. Quantum Chem.* **3**(S3a), 17 (1969).
- ²⁷H. Goldstein, C. Poole, and J. Safko, *Classical Mechanics* (Addison Wesley, San Francisco, 2002).
- ²⁸A. O. Cohen and R. A. Marcus, *J. Chem. Phys.* **49**, 4509 (1968).
- ²⁹W. H. Miller, *J. Chem. Phys.* **53**, 1949 (1970).
- ³⁰W. H. Miller, *J. Chem. Phys.* **54**, 5386 (1971).
- ³¹N. Smith, *J. Chem. Phys.* **85**, 1987 (1986).
- ³²S. C. Farantos and J. Tennyson, *J. Chem. Phys.* **84**, 6210 (1986).
- ³³R. Schinke and V. Staemmler, *Chem. Phys. Lett.* **145**, 486 (1988).
- ³⁴J. C. Lorquet, *J. Chem. Phys.* **140**, 134304 (2014).
- ³⁵J. M. Lévy-Leblond, *Am. J. Phys.* **39**, 502 (1971).
- ³⁶R. D. Levine, *Chem. Phys. Lett.* **79**, 205 (1981).
- ³⁷R. D. Levine and C. E. Wulfman, *Chem. Phys. Lett.* **87**, 105 (1982).
- ³⁸R. D. Levine, in *New Horizons of Quantum Chemistry*, edited by P. O. Löwdin and B. Pullman (D. Reidel, Dordrecht, 1983).