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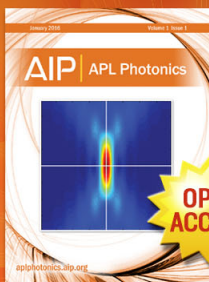
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## Adiabatic invariance along the reaction coordinate

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In a two-dimensional space where a point particle interacts with a diatomic fragment, the action integral  $\oint p_\theta d\theta$  (where  $\theta$  is the angle between the fragment and the line of centers and  $p_\theta$  its conjugate momentum) is an adiabatic invariant. This invariance is thought to be a persistent dynamical constraint. Indeed, its classical Poisson bracket with the Hamiltonian is found to vanish in particular regions of the potential energy surface: asymptotically, at equilibrium geometries, saddle points, and inner turning points, i.e., at remarkable situations where the topography of the potential energy surface is locally simple. Studied in this way, the adiabatic decoupling of the reaction coordinate is limited to disjoint regions. However, an alternative view is possible. The invariance properties of entropy (as defined in information theory) can be invoked to infer that dynamical constraints that are found to operate locally subsist everywhere, throughout the entire reactive process, although with a modified expression. © 2009 American Institute of Physics.

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### I. INTRODUCTION

Theories of chemical dissociation assume a statistical distribution of energy over all internal degrees of freedom resulting from strong coupling among participating modes.<sup>1</sup> However, studies of energy disposal in the products<sup>2</sup> indicate deviations from the behavior predicted by purely statistical models. The presence of a certain degree of selectivity in the measured product energy distributions proves the existence of dynamical constraints. The purpose of the present paper is to investigate the nature and properties of these constraints.

In 1939, Hirschfelder and Wigner<sup>3</sup> drew an analogy with the Born–Oppenheimer separation and suggested that the motion along the reaction path should be expected to be adiabatically decoupled from a fast vibrational motion. This proposal has found many interesting applications.

- (i) Several statistical theories, which explicitly exploit the concept of adiabaticity, have been proposed, in particular, the statistical adiabatic channel model<sup>4–6</sup> and the adiabatic capture centrifugal sudden approximation.<sup>7</sup> These theories have been shown to be equivalent.<sup>8</sup>
- (ii) The propensity rule detected in the vibrational predissociation of van der Waals complexes is accounted for by the principle of adiabatic invariance of the action.<sup>9</sup>
- (iii) As shown by Miller *et al.*,<sup>10</sup> the dynamics is also constrained by adiabaticity when the potential energy surface assumes the shape of a harmonic valley about a slightly curved reaction path. The development of a reaction path Hamiltonian is based on this property.<sup>10,11</sup> The breakdown of vibrational adiabaticity resulting from curvature plays an important role in studies of tunneling<sup>12</sup> and of population inversion.<sup>13,14</sup>

- (iv) The adiabatic approximation was also extensively used by Marcus in his effort to go beyond the simple assumptions of the statistical theory of unimolecular reactions and in his study of product energy distributions.<sup>15–17</sup>
- (v) A detailed study of the exchange of a light particle between two heavy atoms (HLH reactions) has been carried out by Skodje and co-workers,<sup>18–20</sup> resulting in a picture of piecewise adiabatic invariance.
- (vi) The present paper is especially concerned with an assertion due to Bates<sup>21</sup> that the dynamics of ion-permanent dipole and ion-quadrupole interactions is dominated by the invariance of the action integral

$$\langle p_\theta \rangle = [\theta_2(r) - \theta_1(r)]^{-1} \int_{\theta_1(r)}^{\theta_2(r)} p_\theta d\theta = \oint p_\theta d\theta, \quad (1.1)$$

where  $\theta$  is the angle between the dipole or quadrupole and the line of centers,  $p_\theta$  its conjugate momentum, and  $\theta_1(r)$  and  $\theta_2(r)$  are the turning points of the hindered rotation of the neutral fragment at a fixed value of the reaction coordinate  $r$ . When the rotation is free, the boundaries  $\theta_1$  and  $\theta_2$  should be replaced by 0 and  $2\pi$ .

Kern and Schlier<sup>22</sup> used this simplification to reduce the dynamics of an ion-molecule reaction (constrained to take place in a plane) to a one-dimensional (1D) motion in an effective potential. Djebri *et al.* developed a three-dimensional (3D) adiabatic separation of the rotational and radial motions at the semiclassical level for ion-molecule reactive collisions at very low energies.<sup>23</sup>

The aim of the present work is to demonstrate the presence of dynamical constraints deriving from the properties of Eq. (1.1) for a variety of interaction potentials. We use classical dynamics<sup>24–26</sup> to detect them locally, as a function of the reaction coordinate. The action integral  $\langle p_\theta \rangle$  is invariant if its Poisson bracket (PB) with the Hamiltonian (denoted as

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$[\langle p_\theta \rangle, H]$  is equal to zero. It is of interest to determine the locus in phase space where the latter quantity vanishes, i.e., where the adiabatic approximation applies.

We could recently demonstrate the adiabatic invariance of the action integral for long-range electrostatic potentials.<sup>27</sup> The PB is found not to vanish. However, for the ion-permanent dipole and ion-quadrupole interactions, it is found to decrease 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, the more reliable is the adiabatic approximation, as expected from the usual argumentation.<sup>25,26,28</sup> This study indicates that, for an ion-molecule reaction, the reaction path coordinate is asymptotically adiabatically separable from the perpendicular degrees of freedom.

The derivation of the previous results was greatly facilitated by the mathematical simplicity of electrostatic potentials. However, there is no reason why adiabatic invariance should be limited to ion-molecule reactions or to the asymptotic range of the reaction coordinate. In the present contribution, we wish to extend the previous results and to examine the adiabatic separation of the reaction coordinate at shorter values of the reaction coordinate.

The classical Hamiltonian used in this study is presented in Sec. II with an overview of the method. The results in Sec. III and IV show that the reaction coordinate is adiabatically decoupled in its asymptotic range for any dissociation (or association) reaction even those involving neutral species. Those derived in Sec. V and VI apply to minima, saddle points, and turning points. Section VII is devoted to a brief analysis of phase space partitioning. Two opposite concepts are confronted: piecewise invariance<sup>19,20</sup> and entropy (as defined in information theory) conservation.<sup>29,30</sup>

## II. CLASSICAL HAMILTONIAN

For the sake of simplicity, our treatment is restricted to a two-dimensional (2D) space, under conditions where the total angular momentum is equal to zero. Using the Jacobi system of coordinates, the interaction between a point particle and a diatomic fragment is represented by the following classical Hamiltonian:<sup>22,27,31</sup>

$$H(r, p_r, \theta, p_\theta) = \frac{1}{2m_{\text{red}}} \left[ p_r^2 + \frac{p_\theta^2}{r^2} \right] + \frac{p_\theta^2}{2I(r)} + V(r, \theta), \quad (2.1)$$

where  $r$  denotes the separation between the centers of mass of the two moieties, while  $\theta$  specifies the orientation of the diatom with respect to the line joining these centers of mass.  $I(r)$  denotes the moment of inertia of the fragment, seen as a parametric function of  $r$ , and  $m_{\text{red}}$  is the reduced mass of the point-diatom system. The rotation of the fragment is free if  $r$  is large enough and is restricted otherwise.

In the following sections, a number of model potentials will be considered. For each one, the value of  $p_\theta$  is extracted from the equation  $H=E$ ,

$$p_\theta(r, p_r) = r \left[ \frac{2m_{\text{red}}I(r)}{m_{\text{red}}r^2 + I(r)} \right]^{1/2} \left[ E - \frac{p_r^2}{2m_{\text{red}}} - V(r, \theta) \right]^{1/2} \quad (2.2)$$

and is then integrated over the whole range where the integrand is real to derive an expression of the action integral [Eq. (1.1)]. The PB of the latter is then calculated as

$$[\langle p_\theta \rangle, H] = \frac{\partial H}{\partial p_r} \frac{\partial \langle p_\theta \rangle}{\partial r} - \frac{\partial H}{\partial r} \frac{\partial \langle p_\theta \rangle}{\partial p_r}. \quad (2.3)$$

The locus where this expression vanishes determines the regions of adiabaticity.

## III. ASYMPTOTIC RANGE OF ION-MOLECULE REACTIONS

Consider a potential having the form

$$V_n(r, \theta) = -Cr^{-n}\varphi(\theta), \quad (3.1)$$

where  $n$  is a positive integer and  $C$  is a constant. The anisotropy function  $\varphi(\theta)$  is assumed to be expandable as a Fourier series

$$\varphi(\theta) = a_0 + \sum_{j=1} a_j \cos(j\theta) + \sum_{k=1} b_k \sin(k\theta). \quad (3.2)$$

Note the relationship between the coefficient  $a_0$  and the average value of the potential,

$$\langle V_n \rangle = (2\pi)^{-1} \int_0^{2\pi} V_n(r, \theta) d\theta = -a_0 Cr^{-n}. \quad (3.3)$$

The action integral (evaluated for a free rotation of the fragment) is expanded about  $r \rightarrow \infty$ . The result is

$$\begin{aligned} \langle p_\theta \rangle &= \sqrt{2I(r \rightarrow \infty)E} \\ &\times \left[ 1 - \frac{I(r \rightarrow \infty)}{2m_{\text{red}}r^2} \dots - \frac{p_r^2}{4m_{\text{red}}E} \dots - \frac{\langle V_n \rangle}{2E} \dots \right] \end{aligned} \quad (3.4)$$

and the PB is found to be equal to

$$[\langle p_\theta \rangle, H] = n \frac{p_r}{m_{\text{red}}r} \sqrt{\frac{I(r \rightarrow \infty)}{2E}} [\langle V_n \rangle - V_n(r, \theta)]. \quad (3.5)$$

The PB is seen to decrease with  $r$  faster than the potential  $V_n(r, \theta)$ , whatever the value of  $n$  and no matter how complicated the angular dependence is.

The same is true for a nonseparable potential

$$V(r, \theta) = -Cr^{-2}\varphi(\theta) - C'r^{-3}\varphi'(\theta), \quad (3.6)$$

which generates a PB expressed by Eq. (3.5) with  $n=2$ .

The adiabatic approximation is thus an excellent approximation for all ion-molecule reactions studied in their asymptotic range even if the anisotropy function is complicated and even if the variables  $r$  and  $\theta$  are not separated in the potential.

#### IV. LONG-RANGE MORSE POTENTIAL

The asymptotic part of the potential energy function describing the dissociation of a neutral molecule is often adequately described by Eq. (3.1) with  $n=6$ . Nevertheless, for the sake of completeness, we now consider a separable potential where the radial part is the asymptotic expansion of a Morse function. The angular part is reduced to a cosine function,

$$V(r, \theta) = -2D \exp[-\beta(r - r_{eq})] \cos \theta. \quad (4.1)$$

The action integral (evaluated for a free rotation of the fragment) is expressed in terms of elliptic integrals, which are expanded about  $r \rightarrow \infty$ . The resulting expression is very similar to the previous equation (3.4) since the average potential  $\langle V \rangle$  now vanishes,

$$\begin{aligned} \langle p_\theta \rangle, H &= \sqrt{2I(r \rightarrow \infty)E} \\ &\times \left[ 1 - \frac{I(r \rightarrow \infty)}{2m_{\text{red}}r^2} \cdots - \frac{p_r^2}{4m_{\text{red}}E} + \cdots \right]. \end{aligned} \quad (4.2)$$

The PB is found to vanish as the inverse fifth power of the interfragment separation

$$\langle p_\theta \rangle, H = \frac{3}{\sqrt{2}} \frac{p_r I(r \rightarrow \infty)^{5/2} \sqrt{E}}{r^5 m_{\text{red}}^3}. \quad (4.3)$$

This result provides an additional justification for the use of the adiabatic separation in the asymptotic range.

#### V. EQUILIBRIUM GEOMETRIES AND SADDLE POINTS

We now calculate the PB around a stationary point, i.e., around a minimum of the potential energy surface or around a first-order saddle point. Locally, the potential surface can be represented by a quadratic function,

$$V(r, \theta) = a_{rr}(r - r_e)^2 + b_{\theta\theta}(\theta - \theta_e)^2 + c_{r\theta}(r - r_e)(\theta - \theta_e). \quad (5.1)$$

The force constant  $b_{\theta\theta}$  is always positive (as a consequence, the rotation of the fragment is hindered), whereas  $a_{rr}$  is positive if we study a stable structure and is negative for a saddle point. In the first case, the function  $V(r, \theta)$  generates a paraboloid that is symmetrical if the coupling constant  $c_{r\theta}$  vanishes and slanted if  $c_{r\theta} \neq 0$ . If  $a_{rr} < 0$ , the function  $V(r, \theta)$  describes a transition state. The reaction coordinate coincides with  $r$  if  $c_{r\theta} = 0$  and has nonzero components both on  $r$  and  $\theta$  if  $c_{r\theta} \neq 0$ . The graph representing the potential  $V$  is slanted in a direction or another, depending on the sign of  $c_{r\theta}$ .

The action integral  $\langle p_\theta \rangle$  is now calculated according to Eqs. (1.1) and (2.2). The diatomic fragment undergoes hindered rotation and the turning points  $\theta_1$  and  $\theta_2$  determine the range where  $p_\theta$  is real. Close to a stationary point, the fragment approaches a stable structure and it is a good approximation to neglect  $(\partial I / \partial r)_{r=r_e}$  in the calculation of  $\langle p_\theta \rangle$  and of the PB.

The PB is found to vanish exactly at the stationary point. Its expansion about the point  $(r_e, \theta_e)$  for small values of  $c_{r\theta}$  is reported in an abbreviated form,

$$\begin{aligned} \langle p_\theta \rangle, H &= K_1 p_r [2c_{r\theta} r_e (\theta - \theta_e) - K_2 (r - r_e)^2 + 6K_3 c_{r\theta} \\ &\times (r - r_e)(\theta - \theta_e) + 4K_3 b_{\theta\theta} (\theta - \theta_e)^2 + \cdots], \end{aligned} \quad (5.2)$$

where  $K_1$  and  $K_2$  are two positive constants that depend on the values of  $I(r_e, \theta_e)$ ,  $E$ ,  $p_r$ ,  $m_{\text{red}}$ ,  $r_e$ , and  $a_{rr}$ , while  $K_3$  stands for  $I(r_e, \theta_e) / [I(r_e, \theta_e) + m_{\text{red}} r_e^2]$ . From the theory of conic sections, the locus where the PB vanishes is deduced to be a hyperbola if  $c_{r\theta} \neq 0$ , which reduces to two straight lines crossing at point  $(r_e, \theta_e)$  when  $c_{r\theta}$  vanishes. Adiabatic behavior is therefore to be expected in the neighborhood of stationary points.

#### VI. TURNING POINTS

In the previous derivations, the PB is found to be proportional to  $p_r$ , in conformity with the usual derivations of the principle of adiabatic invariance.<sup>25,26,28</sup> Denote the coordinates of the inner turning point of the radial motion as  $r_t$  and  $\theta_t$ . Therefore, when the system evolves along the reaction coordinate, the PB should vanish at  $r=r_t$ .

This conclusion is confirmed by a direct calculation. The potential function  $V(r, \theta)$  is assumed to be linear with a negative slope in the neighborhood of  $r_t$ .

$$V(r, \theta) = -C(r - r_t)\varphi(\theta). \quad (6.1)$$

Nothing is assumed about the angular function  $\varphi(\theta)$  except that its first derivative vanishes at  $r=r_t$ . The rotation is now hindered. The expression of the action integral is fairly awkward but the PB can be written as

$$\langle p_\theta \rangle, H = p_r [K_r (r - r_t)^2 + K_\theta (\theta - \theta_t)^2], \quad (6.2)$$

where  $K_r$  and  $K_\theta$  are functions of  $C$ ,  $m_{\text{red}}$ ,  $E$ ,  $I(r_t)$ ,  $\varphi(\theta_t)$ , and  $\varphi''(\theta_t)$ .

The PB is a third-order quantity because  $p_r$ ,  $(r - r_t)$ , and  $(\theta - \theta_t)$  tend to zero as the system approaches the turning point. Therefore, adiabaticity is expected to be a good approximation in the neighborhood of a turning point even if the anisotropy function is complicated.

#### VII. DISCUSSION

In this paper, we have considered a particular constraint derived from a unique Hamiltonian (more exactly, a unique kinetic energy part but with different interaction potentials). The PB of the action integral [Eq. (1.1)] can be expressed as

$$\langle p_\theta \rangle, H = p_r \Phi(r, \theta). \quad (7.1)$$

The function  $\Phi$  is found to vanish in numerous but disjoint regions of the potential energy surface: asymptotically, at inner turning points, in the neighborhood of equilibrium geometries and saddle points, i.e., at remarkable situations, whenever the topography of the potential energy surface is locally simple.

A central question emerges. What happens between these disjoint regions? Are they islands of adiabaticity in a sea of chaos? The question can also be formulated in a slightly different way: Is the mathematical simplicity of the potential responsible for adiabatic invariance or does it simply make possible an explicit calculation of the necessary PBs? Unfor-

tunately, no clear answer can be given at the present time. The discursive nature of the following discussion clearly indicates the need for future, more detailed, studies focusing on the connectedness of phase space.

### A. The separatrix problem

A separatrix is a dividing surface in phase space that separates two distinctly different types of motion. For example, in the pendulum problem, it separates oscillation and rotation. Similarly, in the long-range part of the reaction coordinate, it separates libration and perturbed rotation of the fragments.

In an extensive series of papers, Skodje and co-workers<sup>18–20,32</sup> showed that the adiabatic approximation is not valid for trajectories in the vicinity of a separatrix. The reason is that adiabatic theory is based on a large difference between time scales. However, at the separatrix, the frequency of the coordinate that has previously been assumed to depict the fast motion suddenly goes to zero. The resulting theory has been applied to an analysis of HLH reactions.

The picture presented by Skodje and co-workers is that of “a uniform analysis of piecewise adiabatic invariant dynamics defined in disjoint adiabatic regions of phase space which are bounded by separatrices.” Adiabaticity is assumed to hold only during the time interval where the trajectory stays on one side of the separatrix but breaks down thereafter. The action integral is approximately constant as long as the separatrix is not crossed. Similar results were obtained by Kern and Schlier in their 2D study of ion-molecule collisions.<sup>22</sup>

### B. Adiabatic channel potential curves

The calculation of adiabatic channel potential curves is particularly simple for ion-molecule reactions. The adiabats are given by the eigenvalues of a Schrödinger equation at a fixed interfragment separation  $r$ .<sup>6,7</sup> The equation to be solved is identical to that describing the Stark effect on a linear dipole molecule, which admits two different power series expansions: one about  $r \rightarrow 0$  and one about  $r \rightarrow \infty$ .<sup>6</sup> Thus, this piecewise construction is characterized by a discontinuity that is reminiscent of the separatrix problem. Moreover, at some point, a transition must be introduced between two regimes.<sup>7</sup> In the long-range region, the adiabatic approximation is quite reasonable. By contrast, at small values of  $r$ , the channels are strongly coupled. Here, the transition between the two regimes is not sharp: it is measured by the value of a Massey parameter.<sup>33,34</sup>

### C. Entropy

However, in spite of this forceful argumentation in favor of a partitioning of phase space, attention should be drawn to an unexpected conclusion derived from the invariance properties of the entropy.

Consider a time-dependent system described either by a classical distribution in phase space or by a density operator, both being denoted as  $\rho(t)$ . In the maximum entropy method (MEM),<sup>2,29,30,35</sup> i.e., in the method where energy randomiza-

tion is as extensive as possible subject to the dynamical constraints on the system, this state is expressed as an expansion

$$\rho(t) = \exp \left[ - \sum_{r=0} \lambda_r(t) A_r \right], \quad (7.2)$$

where the  $A_r$ 's are a set of operators associated with the constraints and the  $\lambda_r$ 's are Lagrange multipliers. The entropy corresponding to this state is

$$S[\rho(t)] = - \text{Tr}[\rho(t) \ln \rho(t)] = \sum_{r=0} \lambda_r(t) \langle A_r \rangle(t). \quad (7.3)$$

In a time-dependent problem,  $S$  remains constant during the entire evolution.

These views are supported by explicit quantum dynamical calculations of reactive scattering. Clary and Nesbet calculated the population of internal states as a function of the reaction coordinate.<sup>36–38</sup> The entropy of the calculated distributions is found to maintain its maximum value subject only to dynamical constraints throughout the entire reaction process and not just in regions where the topography of the potential energy surface is particularly simple.

### D. The variable nature of the constraints

As shown by Levine and co-workers,<sup>2,29,30,35</sup> information theory can be used to define measures of the lack of energy randomization in an activated molecule. A nonzero value of them indicates that energy exchange among degrees of freedom is restricted by dynamical constraints. These measures, termed surprisal and entropy deficiency, are constants of the motion and are experimentally measurable. The surprisal is simply defined as  $-\ln p$ . The entropy is thus the average value of the surprisal.

This means that the influence of a constraint detected in a particular region (e.g., asymptotically) subsists in other regions. However, as emphasized by Levine and co-workers, the nature of the constraint is expected to vary considerably during the lifetime of the molecule (i.e., along the reaction path): it might be simple asymptotically but dispersed on many degrees of freedom at short values of the reaction coordinate, in the strong coupling region.

The skill, in a MEM analysis, lies in the choice of the set of operators to be used in expansions (7.2) and (7.3). They should be associated with the observables measured or playing a role in the reaction. It may happen that some of the Lagrange multipliers are equal to zero at particular times. For example, it is often observed in studies of translational distributions that at very long times (i.e., at asymptotically large values of the reaction coordinate), the set reduces to a single operator, namely, the translational momentum  $p_r$  or, equivalently, the square root of the translational kinetic energy  $\varepsilon^{1/2}$ .<sup>39,40</sup> This has been taken as an evidence of adiabatic decoupling of the reaction coordinate.<sup>27</sup> The reason is that if the dynamics reduces to a 1D motion in an effective potential  $V(s)$ , then Jacobi's form of the least-action principle is particularly simple. It requires the minimization of the integral  $\int_{s_1}^{s_2} \varepsilon^{1/2} ds$ . Because of its analogy with Fermat's principle of geometrical optics, the translational momentum  $\varepsilon^{1/2}$  is seen to play a fundamental role in the dynamics that takes place

asymptotically. However, at shorter values of the reaction coordinate, the translational momentum loses its relevance. Expansions (7.2) and (7.3) then no longer reduce to a single term, i.e., many dynamical constraints operate. It might happen that in another range, the topography of the potential energy surface again becomes simple. Then, the dynamical constraints might again be described by a simple model that makes them few in number and readily identifiable if expanded in another set of appropriate operators. Nevertheless, as shown by Levine and co-workers,<sup>29,30</sup> the surprisal and entropy deficiency are constants of the motion, i.e., the lack of energy randomization persists during the entire lifetime of the reacting molecule. Thus, in contradistinction to summary sketches of statistical theories, the system never forgets its previous history.

## E. Conclusion

A final element of the problem must be pointed out. A great difference between the results of 2D and 3D studies has been observed by Skodje in his study of HLH reactions.<sup>19,20</sup> In the collinear problem, the nuclear trajectories are found not to sample phase space in a uniform way, thereby indicating the presence of dynamical constraints. By contrast, in the 3D study, trajectories that cross the separatrix are found to quickly separate from one another, i.e., to exhibit chaotic features and thus to behave statistically, which implies the absence of constraints.

Therefore, to sum up, a fully satisfactory discussion of the presence of adiabatic constraints requires a joint discussion of 3D dynamics and of the invariance properties of entropy. It is hoped to address this point in a future research.

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