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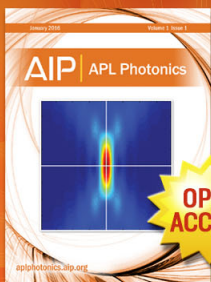
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# Adiabatic and diabatic invariants in ion-molecule reactions

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A point charge interacting with a dipole (either induced or permanent) constitutes a completely integrable dynamical subsystem characterized by three first integrals of the motion ( $E$ ,  $p_\phi$ , and either  $\ell^2$  or a Hamilton–Jacobi separation constant  $\beta$ ). An ion-molecule reaction (capture or fragmentation) can be seen as an interaction between such a subsystem and a bath of oscillators. This interaction is a perturbation that destroys some of the first integrals. However, the perturbation depends on the separation between the fragments and the destruction is gradual. The mathematical simplicity of the long-range electrostatic interaction potential leads to useful simplifications. A first-order perturbation treatment based on the structured and regular nature of the multipole expansion is presented. The separating integrals valid in the asymptotic limit are found to subsist at intermediate distances, although in a weaker form. As the reaction coordinate decreases, i.e., as the fragments approach, the asymptotic range is followed by an outer region where (i) the azimuthal momentum  $p_\phi$  remains a constant of the motion; (ii) the square angular momentum  $\ell^2$  or the separation constant  $\beta$  transform into a diabatic invariant in regions of phase space characterized by a high value of the translational momentum  $p_r$ ; (iii) for low values of  $p_r$ , it is advantageous to use the action integral  $\oint p_\phi d\theta$ , which is an adiabatic invariant. The conditions under which an effective potential obtained by adding centrifugal repulsion to an electrostatic attractive term can be validly constructed are specified. In short, the dynamics of ion-molecule interactions is still regular in parts of phase space corresponding to a range of the reaction coordinate where the interaction potential deviates from its asymptotic shape. © 2009 American Institute of Physics. [doi:10.1063/1.3276446]

## I. INTRODUCTION

The study of reaction dynamics is often based on one-dimensional (1D) models, which aim at representing the dynamics by an equation of motion in the direction of the reaction path of a particle in a 1D space governed by an effective potential energy curve.

The usual justification is based on a suggestion, originally due to Hirschfelder and Wigner,<sup>1</sup> according to which the principle of adiabatic invariance can be used to separate the slow motion along the reaction coordinate from other motions. The quantum numbers (or the classical action) of the latter are assumed to be adiabatic invariants, that is, quantities that do not change if the motion along the reaction coordinate is slow enough. This idea is at the heart of reaction dynamics. Some theories, such as the statistical adiabatic channel model<sup>2–4</sup> and the adiabatic capture centrifugal sudden approximation<sup>5–7</sup> build directly on the construction of a set of effective potential energy curves. These theories have been shown to be equivalent.<sup>8</sup> But even the well-known transition state theory greatly benefits by the adiabatic approximation.<sup>9–11</sup> Many useful concepts are derived from these considerations: the reaction path Hamiltonian model,<sup>12–14</sup> the study of product energy distributions,<sup>7,10,14–23</sup> the mechanism of population inversion,<sup>24,25</sup> the concept of “corner cutting” to describe the exchange of a light particle between two heavy atoms,<sup>26–29</sup> and subtleties in low-temperature chemistry.<sup>30,31</sup>

The present work is based on the following sequence of considerations.

- (1) Consider a unimolecular reaction that consists in expelling an atom or a diatomic fragment, or the reverse recombination reaction. To study the reaction dynamics, the smallest really satisfactory subsystem should describe interplay among three degrees of freedom: a stretching motion along the reaction coordinate and two orthogonal bending vibrations. This set will be referred to as the three-dimensional (3D) subsystem. The remainder of the molecule is seen as a bath formed by a collection of oscillators. Neat separation between the two subsystems is achieved only at asymptotically large values of the reaction coordinate. Then, the total Hamiltonian splits into two parts
- $$H^{\text{Tot}} = H_{3\text{D}}^{\text{asympt}} + H_{\text{bath}}. \quad (1.1)$$
- (2) We aim at understanding the validity of approximate methods (such as the adiabatic separation) as a function of the reaction coordinate and, more generally, in different regions of phase space. This requires simultaneous specification of position and momenta. Therefore, in order to develop a “local” approach, classical mechanics will be used throughout.
  - (3) To proceed further, it is necessary to specify the potential energy function that enters into the Hamiltonian. In this respect, the study of ion-molecule reactions is especially interesting because of the mathematical simplicity of the long-range electrostatic interaction poten-

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tial, which is accurately described by a multipole expansion.<sup>32</sup>

- (4) Attention is focused on two particular examples of interactions that are known to be exactly soluble in classical mechanics. They both concern the interaction between a point charge and a dipole, either induced or permanent. In both cases, three first integrals of the motion can be found.<sup>33–35</sup> Thus, at extremely large values of the reaction coordinate, the small 3D subsystem is both well separated from the bath and exactly soluble.
- (5) As the magnitude of the reaction coordinate decreases, i.e., as the fragments approach, the system is perturbed away from this ideal situation. Additional terms must be introduced into the multipole expansion. Furthermore, the long-range forces are no longer decoupled from the vibrational motion of the interacting fragments. An exact description of the overall system is no longer possible. However, the magnitude of the perturbation depends on the interfragment separation. This suggests that the separating integrals valid in the asymptotic limit should not suddenly vanish. At intermediate distances, their influence can be expected to subsist, although in a weaker form. The purpose of the present paper is to study this gradual transition.
- (6) To examine whether the quantities that are strict constants of the motion in the asymptotic limit are still approximately invariant at smaller values of the reaction coordinate, their Poisson bracket (PB) with the perturbed Hamiltonian will be calculated. The PB between a Hamiltonian  $H$  and an expression  $g$  (both depending on the same set of conjugate variables  $\{q_j, p_j\}$ ) is defined as<sup>33–35</sup>

$$[g, H] = \sum_j \left( \frac{\partial H}{\partial p_j} \frac{\partial g}{\partial q_j} - \frac{\partial H}{\partial q_j} \frac{\partial g}{\partial p_j} \right). \quad (1.2)$$

The magnitude of this quantity determines the rate of change in  $g$  with respect to time along the path of the system in phase space. If the PB vanishes, then  $g$  is a constant of the motion.

- (7) The scope of the present treatment is limited by two severe restrictions. First, overall rotation is ignored in the present model. The use of two distinct frames of reference (space-fixed and body-fixed) is outside the range of the present study. Second, only weak interactions can be considered. Chemical processes taking place in the tight range of the reaction coordinate cannot be considered.<sup>36–38</sup>

Summing up, the question we wish to examine concerns the presence of interactions between the 3D subsystem and the bath during capture or fragmentation. This question can be formulated as follows. As the magnitude of the reaction coordinate decreases, and as the two fragments interact, does the resulting perturbation transform the first integrals of motion into, e.g., adiabatic invariants or into another kind of dynamical constraint? Knowledge of such constraints would be very useful in the study of exit-channel effects that determine product energy distributions.<sup>7,10,14–25,39,40</sup>

In Sec. II, ion-molecule reactions taking place in a central force field are examined, with particular reference to the ion-induced dipole interaction (Langevin problem<sup>16,17</sup>). The anisotropic ion-permanent dipole is dealt with in Sec. III. Adiabatic invariants are discussed in Sec. IV. Concluding remarks are presented in Sec. V.

## II. CENTRAL POTENTIALS

### A. The asymptotic Hamiltonian

A particularly simple example is to be found in the motion in a central force field. For more generality and for further use in the perturbed model, we ignore the simplification resulting from the planarity of the motion and we write the Hamiltonian of the 3D subsystem in terms of three spherical polar coordinates  $(r, \theta, \varphi)$  with the polar axis oriented along the line joining the centers of mass of the two fragments.<sup>33–35</sup>

$$H_{\text{central}}^{\text{asympt}} = \frac{1}{2m} \left( p_r^2 + \frac{p_\theta^2}{r^2} + \frac{p_\varphi^2}{r^2 \sin^2 \theta} \right) + \frac{C}{r^n}. \quad (2.1)$$

For example, for an ion-induced dipole interaction,  $C = -\alpha q^2/2$ , where  $\alpha$  is the polarizability of the neutral,  $q$  the elementary charge, and  $n=4$ .

The dynamics of this 3D subsystem is simplified to the extreme by the presence of three first integrals of the motion: the energy  $E$ , the angular momentum  $p_\varphi$  about the polar axis (which is conjugate to the cyclic coordinate  $\varphi$ ), and the total angular momentum  $\ell$ , whose square is expressed as

$$\ell^2 = p_\theta^2 + \frac{p_\varphi^2}{\sin^2 \theta}. \quad (2.2)$$

### B. The perturbed Hamiltonian

At finite values of the reaction coordinate, the expression of the 3D Hamiltonian is no longer given by Eq. (2.1). The expelled or approaching atom recognizes that its partner is not a point charge. Taking into account the main sources of nonseparability, we propose to represent the perturbation induced by the contraction of the reaction coordinate by (i) changing the effective masses to take into account any curvature of the reaction path (as derived by Marcus<sup>10</sup> and by Miller *et al.*<sup>12</sup>), (ii) introducing cross terms between momenta, and (iii) adding a short-range contribution to the potential. Since the correct Hamiltonian should smoothly transform into  $H_{\text{central}}^{\text{asympt}}$  as  $r \rightarrow \infty$ , the perturbative terms necessarily die out more rapidly than the potential. We therefore assume the following ansatz for the Hamiltonian of the 3D subsystem valid in the inner range of the reaction coordinate:

$$H_{\text{central}}^{\text{inner}} = \frac{p_r^2}{2m} \left( 1 + \frac{\kappa_\theta}{r^{k_\theta}} \theta + \frac{\kappa_\varphi}{r^{k_\varphi}} \varphi \right)^{-2} + \frac{p_\theta^2}{2mr^2} + \frac{p_\varphi^2}{2mr^2 \sin^2 \theta} + \lambda_{r\theta} \frac{p_r p_\theta}{r^2} \frac{\Omega_{r\theta}(\theta)}{r^{k_{r\theta}}} + \lambda_{r\varphi} \frac{p_r p_\varphi}{r^2} \frac{\Omega_{r\varphi}(\varphi)}{r^{k_{r\varphi}}} + \lambda_{\theta\varphi} \frac{p_\theta p_\varphi}{r^2} \frac{\Omega_{\theta\varphi}(\theta, \varphi)}{r^{k_{\theta\varphi}}} + \frac{C}{r^n} + \lambda_{\text{pot}} \frac{\Psi(\theta, \varphi)}{r^{k_{\text{pot}}}}. \quad (2.3)$$

The coordinates  $\theta$  and  $\varphi$  now represent transitional modes.

The values of the curvatures  $\kappa$ , of the coupling parameters  $\lambda$ , and the expression of the anisotropy functions  $\Omega$  and  $\Psi$  are left unspecified. The exponents  $k_{\text{pot}}$ ,  $k_\theta$ , and  $k_\varphi$  that control the rate of decrease in the different perturbative terms are necessarily larger than  $n$  because  $H_{\text{central}}^{\text{inner}} \rightarrow H_{\text{central}}^{\text{asympt}}$  as  $r \rightarrow \infty$ . A similar property holds for  $k_{r\theta}$ ,  $k_{r\varphi}$ , and  $k_{\theta\varphi}$ , as will be seen later on.

To get further insight, it is useful to examine the expression of the potential energy in the important particular case of an ion-induced dipole interaction between a polyatomic ion and a neutral atom. The latter is assumed to be in a  $S$  state. Otherwise, it possesses an electrostatic quadrupole moment that contributes an anisotropic term in  $r^{-3}$ .<sup>32</sup>

The induction energy is given by a series expansion whose first two terms are<sup>32</sup>

$$V(r, \theta) = -\frac{\alpha q^2}{2r^4} - \frac{2\alpha q\mu}{r^5} \cos \theta, \quad (2.4)$$

where  $\mu$  denotes the magnitude of the dipole moment of the ionized polyatomic fragment. Higher-order terms are proportional to  $r^{-6}$ . They correspond to charge-induced quadrupole and dispersion terms.<sup>32,41</sup>

Therefore, if the perturbation treatment is limited to its first order, it is appropriate to define an outer region, intermediate between the asymptotic range governed by Hamiltonian (Eq. (2.1)) and the inner range defined by Hamiltonian (Eq. (2.3)). In this region,  $\Psi(\theta, \varphi)$  reduces to  $\Psi(\theta)$ , in conformity with Eq. (2.4). If the potential part is an even function of  $\theta$  alone, then the kinetic part should also be required to have the same parity and to be independent of  $\varphi$ . As shown by examining the explicit expression of the six Hamilton canonical equations derived from Eq. (2.3), this leads to the following simplifications: the curvature terms disappear; the function  $\Omega_{\theta\varphi}$  is independent of  $\varphi$ ;  $\Omega_{r\varphi}$  reduces to a constant that is included in  $\lambda_{r\varphi}$ ;  $\Omega_{\theta\varphi}$  and  $\Omega_{r\theta}$  are even functions of  $\theta$ . With these simplifications, the Hamiltonian valid in the outer range is, to the first order

$$H_{\text{central}}^{\text{outer}} = H_{\text{central}}^{\text{asympt}} + \lambda_{r\theta} \frac{p_r p_\theta}{r^{2+k_{r\theta}}} \Omega_{r\theta}(\theta) + \lambda_{r\varphi} \frac{p_r p_\varphi}{r^{2+k_{r\varphi}}} + \lambda_{\theta\varphi} \frac{p_\theta p_\varphi}{r^{2+k_{\theta\varphi}}} \Omega_{\theta\varphi}(\theta) + \lambda_{\text{pot}} \frac{\Psi(\theta)}{r^{k_{\text{pot}}}}. \quad (2.5)$$

According to Eq. (2.4),  $k_{\text{pot}}=5$  for an ion-induced dipole interaction. However, we leave it as such to keep track of it in what follows.

### C. Invariance of the former first integrals

In the outer range,  $\varphi$  remains a cyclic variable and the azimuthal momentum  $p_\varphi$  remains a constant of the motion.

The PB of  $p_\theta^2 + p_\varphi^2 / \sin^2 \theta$  has been calculated

$$\begin{aligned} & \left[ H_{\text{central}}^{\text{outer}} p_\theta^2 + \frac{p_\varphi^2}{\sin^2 \theta} \right] \\ &= 2\sqrt{2m} \sqrt{E - \frac{p_r^2}{2m}} \left\{ \lambda_{\text{pot}} \frac{d\Psi}{d\theta} r^{1-k_{\text{pot}}} \right. \\ & \quad \left. + 2\lambda_{\theta\varphi} m \left( E - \frac{p_r^2}{2m} \right) \right. \\ & \quad \left. \times \left[ \Omega_{\theta\varphi}(\theta) \cos \theta + \frac{d\Omega_{\theta\varphi}}{d\theta} \sin \theta \right] r^{1-k_{\theta\varphi}} \right\} + O(r^{-k_{r\theta}}). \end{aligned} \quad (2.6)$$

Because this expression must vanish as soon as  $r$  is in its asymptotic range, the unknown exponent  $k_{\theta\varphi}$  must have the same order of magnitude as  $k_{\text{pot}}$  (i.e.,  $n+1$ ). Since the PB is not proportional to the translational momentum  $p_r$ , the quantity  $p_\theta^2 + p_\varphi^2 / \sin^2 \theta$  is not an adiabatic invariant in the outer range. It is just the opposite: the factors  $(E - p_r^2 / 2m)^{1/2}$  or  $(E - p_r^2 / 2m)^{3/2}$  provide a reduction in the magnitude of the PB in the regions of phase space characterized by a high value of the translational momentum  $p_r$ . It may thus be said that the dynamical constraint that subsists as remembrance of the conservation of the total angular momentum in the unperturbed situation provides an example of diabatic invariance.

The concept of diabatic invariance finds confirmation in the classical trajectory calculations performed by Hase and co-workers<sup>18-21</sup> for several reactions. The magnitude of the orbital angular momentum was observed to be conserved as the trajectory proceeds from the potential energy barrier to products. Interestingly enough, the calculations reveal that the higher the internal energy (i.e., the higher the magnitude of the translational momentum  $p_r$ ), the better the conservation. This observation is in complete agreement with our findings.

The PB (Eq. (2.6)) also vanishes at particular values of  $\theta$ . Consider a simple example. As suggested by Eq. (2.4), assume  $\Psi(\theta) = \cos \theta$ , and, furthermore,  $\Omega_{\theta\varphi}(\theta) = \cos \theta$ ,  $k_{\text{pot}} = k_{\theta\varphi} = 5$ . Then the PB (Eq. (2.6)) becomes

$$\left[ H_{\text{central}}^{\text{outer}} p_\theta^2 + \frac{p_\varphi^2}{\sin^2 \theta} \right] \propto (2mE - p_r^2)^{1/2} (A \cos 2\theta - \sin \theta) \quad (2.7)$$

with the introduction of the dimensionless parameter  $A$

$$A = \frac{\lambda_{\theta\varphi}}{\lambda_{\text{pot}}} (2mE - p_r^2) \quad (2.8)$$

the sign of  $A$  is undetermined.

When  $p_r$  is close to its maximum value  $(2mE)^{1/2}$ ,  $A$  is small in modulus, and the PB vanishes at values of  $\theta$  equal to  $A$  or to  $\pm(\pi - A)$  (i.e., for the collinear approach). For  $p_r$  close to zero, the PB vanishes at four values of  $\theta$ :  $-3\pi/4 + (2\sqrt{2A})^{-1}$ ,  $-\pi/4 - (2\sqrt{2A})^{-1}$ ,  $\pi/4 - (2\sqrt{2A})^{-1}$ , and  $3\pi/4 + (2\sqrt{2A})^{-1}$ . Figure 1 shows a contour plot of  $A \cos 2\theta - \sin \theta$  as a function of  $A$  and  $\theta$ . The locus where the PB vanishes is represented as a thick line.

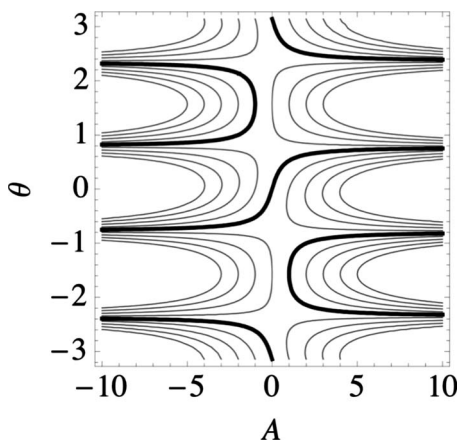


FIG. 1. Locus where  $p_r^2 + p_\varphi^2 / \sin^2 \theta$  is a constant of the motion, represented as a thick line in a contour plot in phase space, as a function of  $A$  [Eq. (2.8)] and  $\theta$ .

This result can be interpreted as follows. In the asymptotic region, the two partners are separated and the angular momentum  $\ell$  of the 3D subsystem is conserved. The approach of the partners creates a torque that destroys conservation of  $\ell$ . However, the torque is inefficient along the specified loci in phase space.

This analysis sheds light on the validity of a widespread reactivity criterion. A centrifugal potential can be defined<sup>16–21,42</sup> only if the angular momentum of the relative motion is conserved. Therefore, an effective potential obtained by adding centrifugal repulsion to an electrostatic attractive potential is reliable only where the PB (Eq. (2.6)) [or (Eq. (2.7))] vanishes. This is strictly true at high values of  $p_r$  and for a collinear alignment. However, even when this is not the case, centrifugal barriers are still meaningful along the loci represented in Fig. 1. In addition, note that at the intermediate values of the reaction coordinate that characterize the outer region, rotation is hindered and it is not certain that  $\theta$  can reach the amplitudes  $-\pi/4$  and  $\pi/4$ .

### III. ION-PERMANENT DIPOLE REACTIONS

#### A. A separable Hamiltonian

The motion of a charged particle in the field of two charges fixed in space is easily analyzed by the Hamilton–Jacobi method.<sup>33,34</sup> The equation is separable in a system of elliptic coordinates. If the orientation in space of the dipole is no longer fixed, the solution has been shown<sup>34</sup> to remain valid provided that the distance  $d$  between the two charges of the dipole is small with respect to the distance  $r$  between the center of the dipole and the charged particle. Then, the elliptic coordinates reduce to spherical polar coordinates  $(r, \theta, \varphi)$  as in the previous example. Specifically, the approximation is valid when  $\sinh \xi \approx \cosh \xi$  with  $\xi = 2r/d$ .<sup>34</sup> This should be a good approximation in the outer region considered in the paper.

Thus, in the asymptotic region, the Hamiltonian of the 3D subsystem is

$$H_{\text{iondip}}^{\text{asympt}} = \frac{p_r^2}{2m} + \frac{p_\theta^2}{2mr^2} + \frac{p_\varphi^2}{2mr^2 \sin^2 \theta} - \frac{q\mu \cos \theta}{r^2}, \quad (3.1)$$

where  $\mu$  is the strength of the electric dipole.

The azimuthal angle  $\varphi$  is a cyclic variable and its conjugate momentum  $p_\varphi$  is a constant of the motion. The equation  $H_{\text{iondip}}^{\text{asympt}} = E$  can be split into two equations

$$E - \frac{p_r^2}{2m} = \frac{\beta}{2mr^2}, \quad (3.2)$$

$$p_\varphi^2 = \sin^2 \theta (\beta - p_\theta^2 + 2mq\mu \cos \theta). \quad (3.3)$$

The motion is separable, with three first integrals of the motion: the total energy  $E$ , the momentum  $p_\varphi$ , and the separation constant  $\beta$ , which determines the partitioning of the internal energy between radial and angular motions.

$$\beta = p_\theta^2 + \frac{p_\varphi^2}{\sin^2 \theta} - 2mq\mu \cos \theta. \quad (3.4)$$

#### B. The perturbed Hamiltonian

Here again, as in Sec. II B, we look for an expression of the 3D Hamiltonian valid for finite values of the reaction coordinate, when the dipole recognizes the presence of additional multipole moments in the charge distribution of the approaching partner.

We therefore assume the following ansatz for the Hamiltonian valid in the inner range of the reaction coordinate:

$$H_{\text{iondip}}^{\text{inner}} = \frac{p_r^2}{2m} \left( 1 + \frac{\kappa_\theta}{r^{k_\theta}} \theta + \frac{\kappa_\varphi}{r^{k_\varphi}} \varphi \right)^{-2} + \frac{p_\theta^2}{2mr^2} + \frac{p_\varphi^2}{2mr^2 \sin^2 \theta} + \lambda_{r\theta} \frac{p_r p_\theta}{r^2} \frac{\Omega_{r\theta}(\theta)}{r^{k_{r\theta}}} + \lambda_{r\varphi} \frac{p_r p_\varphi}{r^2} \frac{\Omega_{r\varphi}(\varphi)}{r^{k_{r\varphi}}} + \lambda_{\theta\varphi} \frac{p_\theta p_\varphi}{r^2} \frac{\Omega_{\theta\varphi}(\theta, \varphi)}{r^{k_{\theta\varphi}}} - \frac{q\mu \cos \theta}{r^2} + \lambda_{\text{pot}} \frac{\Psi(\theta, \varphi)}{r^{k_{\text{pot}}}}. \quad (3.5)$$

The last term results from the charge-quadrupole and dipole-dipole interactions. The former depends on  $\theta$  alone. The latter depends on both angles. However, the dependence on  $\varphi$  vanishes if the presence of a symmetry element in the partner of the dipole annuls the dipole-dipole contribution. If this is the case,  $\Psi(\theta, \varphi)$  reduces to  $\Psi(\theta)$ . Then, if the potential part is an even function of  $\theta$ , the kinetic part should also have the same parity and should be required to be independent of  $\varphi$  [as already argued in the derivation of Eq. (2.5)]. Here again, the curvature terms disappear; the functions  $\Omega_{r\varphi}$  and  $\Omega_{\theta\varphi}$  are independent of  $\varphi$ ; therefore the former reduces to a constant that is included in  $\lambda_{r\varphi}$ . With these simplifications, the Hamiltonian valid in the outer range is, to the first order

$$H_{\text{iondip}}^{\text{outer}} = H_{\text{iondip}}^{\text{asympt}} + \lambda_{r\theta} \frac{P_r P_\theta}{r^{2+k_r\theta}} \Omega_{r\theta}(\theta) + \lambda_{r\varphi} \frac{P_r P_\varphi}{r^{2+k_r\varphi}} + \lambda_{\theta\varphi} \frac{P_\theta P_\varphi}{r^{2+k_\theta\varphi}} \Omega_{\theta\varphi}(\theta) + \lambda_{\text{pot}} \frac{\Psi(\theta)}{r^{k_{\text{pot}}}}. \quad (3.6)$$

For an ion-permanent dipole interaction,  $k_{\text{pot}}$  should be equal to 3.

### C. Invariance of the former first integrals

In the outer range,  $\varphi$  remains a cyclic variable and the azimuthal momentum  $p_\varphi$  remains a constant of the motion.

The PB of the separation constant  $\beta$  [Eq. (3.4)] has been calculated

$$[H_{\text{iondip}}^{\text{outer}}, \beta] = 2\sqrt{2m} \sqrt{E - \frac{p_r^2}{2m}} \left\{ \lambda_{\text{pot}} \frac{d\Psi}{d\theta} r^{1-k_{\text{pot}}} + 2\lambda_{\theta\varphi} m \times \left( E - \frac{p_r^2}{2m} \right) \left[ \Omega_{\theta\varphi}(\theta) \cos \theta + \frac{d\Omega_{\theta\varphi}}{d\theta} \sin \theta \right] \times r^{1-k_{\theta\varphi}} \right\} + O(r^{-k_r\theta}). \quad (3.7)$$

The result is seemingly identical with Eq. (2.6), but the equality is not strict. The expansion of the PB (Eq. (3.7)) reveals the presence of additional high-order terms. At a low-order, the agreement between Eqs. (2.6) and (3.7) results from the fact that the expansion of  $[H_{\text{iondip}}^{\text{outer}}, \beta]$  generates two canceling terms, because  $\cos \theta$  and  $p_\theta^2 + p_\varphi^2 / \sin^2 \theta$  both appear in the two partners of the PB.

The discussion given in Sec. II C about the diabatic nature of the invariant applies to the present case. However, as far as the validity of centrifugal barriers is concerned, an important modification should be noted.

To describe the perturbation induced by the approach of the two partners in an ion-permanent dipole interaction, a quadrupolar term should be introduced into the potential. Namely, one assumes  $\Psi(\theta) = P_2(\cos \theta) = (3 \cos^2 \theta - 1)/2$ , where  $P_2$  denotes the second-order Legendre polynomial. In the present case, the potential term introduced by the perturbation cannot distinguish between both ends of the molecule. (Remember that the partner of the permanent dipole has been assumed to have no dipole moment.) Therefore, the corresponding kinetic term must be of the same type, i.e.,  $\Omega_{\theta\varphi}(\theta) = P_2(\cos \theta)$ . Furthermore, we assume  $k_{\text{pot}} = k_{\theta\varphi} = 3$ . Then the PB (Eq. (3.7)) becomes

$$[H_{\text{iondip}}^{\text{outer}}, \beta] \propto (2mE - p_r^2)^{1/2} \cos \theta (9A \cos 2\theta - 12 \sin \theta - 5A). \quad (3.8)$$

The locus where this expression vanishes is represented as a thick line in Fig. 2. There are now six real roots, i.e., six values of  $\theta$  in the range  $[-\pi, +\pi]$  at which the torque created by the approach of the partners is inefficient and at which the concept of centrifugal barrier is reliable. Two roots are found at  $\pm \pi/2$  (exactly). For large values of  $A$ , the other four are at  $-2.6507 + (\sqrt{7A})^{-1}$ ,  $-0.4909 - (\sqrt{7A})^{-1}$ ,  $0.4909 - (\sqrt{7A})^{-1}$ , and  $2.6507 + (\sqrt{7A})^{-1}$ .

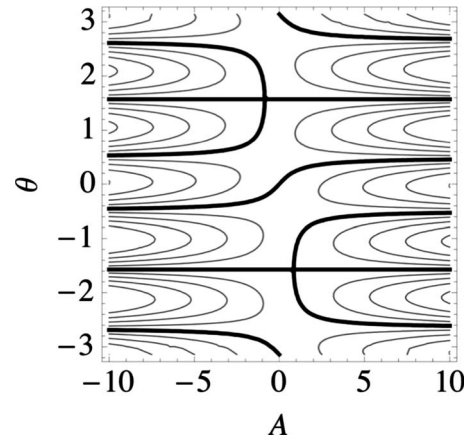


FIG. 2. Locus where the Hamilton–Jacobi separation constant  $\beta$  of the 3D subsystem [Eq. (3.4)] is a constant of the motion, represented as a thick line in a contour plot in phase space, as a function of  $A$  [Eq. (2.8)] and  $\theta$ .

Therefore, for the ion-permanent dipole interaction, an effective potential obtained by adding centrifugal repulsion to an electrostatic attractive potential<sup>16,17,42</sup> is reliable at these six particular values of the angle  $\theta$  even if  $p_r$  is small. This result offers better prospects than in the case of an ion-induced dipole interaction, where the invariance of  $\ell^2$  was guaranteed at only four values of  $\theta$ .

### IV. ADIABATIC INVARIANCE OF THE ACTION INTEGRAL $\langle p_\theta \rangle = \oint p_\theta d\theta$

In a study of ion-dipole and ion-quadrupole reactions, Bates<sup>43</sup> has suggested that the dynamics should be dominated by the invariance of the action integral  $\oint p_\theta d\theta$  (see also Refs. 23 and 44). Obviously, this property would be a welcome addition to the previous results. We thus examine its validity for a general Hamiltonian that describes both the ion-induced and ion-permanent dipole interactions studied in the outer range as particular cases

$$H_{\text{gen}}^{\text{outer}} = \frac{p_r^2}{2m} + \frac{p_\theta^2}{2mr^2} + \frac{p_\varphi^2}{2mr^2 \sin^2 \theta} + \lambda_{r\theta} \frac{P_r P_\theta}{r^{2+k_r\theta}} \Omega_{r\theta}(\theta) + \lambda_{r\varphi} \frac{P_r P_\varphi}{r^{2+k_r\varphi}} + \lambda_{\theta\varphi} \frac{P_\theta P_\varphi}{r^{2+k_\theta\varphi}} \Omega_{\theta\varphi}(\theta) + \frac{V(\theta)}{r^n} + \lambda_{\text{pot}} \frac{\Psi(\theta)}{r^{k_{\text{pot}}}}. \quad (4.1)$$

The rotation is hindered in the outer region because the potential is no longer central, even in the ion-induced dipole case. Therefore, the action integral has to be calculated over a limited range of the polar angle  $\theta$ . Since  $H_{\text{gen}}^{\text{outer}}$  is an even function of  $\theta$ , one has

$$\langle p_\theta \rangle = \frac{1}{\theta_{\text{lim}} - 0} \int_0^{\theta_{\text{lim}}} p_\theta d\theta, \quad (4.2)$$

where the value of  $p_\theta$  is extracted from the equation  $H_{\text{gen}}^{\text{outer}} = E$  and expanded as a power series about  $r \rightarrow \infty$ .

The following expression is derived for the low-order terms of the PB:

$$[H_{\text{gen}}^{\text{outer}}, \langle p_\theta \rangle] = p_r \left\{ (n-2)r^{-n} \frac{1}{\sqrt{2m}} \left( E - \frac{p_r^2}{2m} \right)^{-1/2} [V(\theta) - \langle V \rangle_\theta] + \lambda_{\text{pot}}(k_{\text{pot}} - 2) \frac{1}{\sqrt{2m}} \left( E - \frac{p_r^2}{2m} \right)^{-1/2} r^{-k_{\text{pot}}} [\Psi(\theta) - \langle \Psi \rangle_\theta] \right. \\ \left. + \lambda_{\theta\varphi} \sqrt{2m} \left( E - \frac{p_r^2}{2m} \right)^{1/2} k_{\theta\varphi} r^{-k_{\theta\varphi}} \sin \theta [\Omega_{\theta\varphi}(\theta) - \langle \Omega_{\theta\varphi} \rangle_\theta] \right\} + O(r^{-k_r\sigma-1}) + O(r^{-k_r\varphi-1}), \quad (4.3)$$

where, e.g.,  $\langle V \rangle_\theta$  denotes the average  $\theta_{\text{lim}}^{-1} \int_0^{\theta_{\text{lim}}} V(\theta) d\theta$ .

The PB is proportional to the translational momentum  $p_r$ . The action integral  $\oint p_\theta d\theta$  is thus an adiabatic invariant, as expected, and the invariance can be assigned to a separation of time scales, in conformity with the usual argumentation.<sup>33–35,45</sup> The first term between curly brackets vanishes, either when  $V(\theta)$  is a constant (ion-induced dipole case), or when  $n=2$  (ion-permanent dipole case). It subsists for the ion-quadrupole interaction. Note furthermore the role played by the singularity in one of the terms: the quantity  $r^{-1}(E - p_r^2/2m)^{-1/2}$  tends asymptotically to  $\sqrt{2m}\ell^{-1}$  (as shown by expanding  $r^{-1}(H_{\text{gen}}^{\text{outer}} - p_r^2/2m)^{-1/2}$  about  $r \rightarrow \infty$ ). This is understandable:  $\ell$  cannot be zero because enough internal energy must remain available for rotation if the concept of cyclic integral is to retain its meaning.

The PB (Eq. (4.3)) also vanishes at particular values of  $\theta$ . Consider first the same particular case as the one studied in Sec. II C for the central force field interaction [i.e.,  $\Psi(\theta) = \Omega_{\theta\varphi}(\theta) = \cos \theta$ ,  $k_{\text{pot}} = k_{\theta\varphi} = 5$ ]. Then the PB (Eq. (4.3)) contains the product of three factors

$$[H_{\text{gen}}^{\text{outer}}, \langle p_\theta \rangle] \propto p_r (1 - A \sin \theta) \left( \cos \theta - \frac{\sin \theta_{\text{lim}}}{\theta_{\text{lim}}} \right) \quad (4.4)$$

with  $A$  given by Eq. (2.8). For small values of  $p_r$  (i.e., large values of  $A$ ), Eq. (4.4) vanishes when  $\theta$  is close to  $A^{-1}$ ,  $\pi - A^{-1}$ ,  $-\pi - A^{-1}$ . It also vanishes at two additional values given by the roots of the equation  $\cos \theta - \sin \theta_{\text{lim}}/\theta_{\text{lim}} = 0$ . Whatever the value of  $p_r$ , there always exist four particular values of  $\theta$  in the range  $[-\pi, +\pi]$  at which the action integral is invariant.

Consider now the particular case studied in Sec. III C for the ion-permanent dipole interaction [i.e.,  $\Psi(\theta) = \Omega_{\theta\varphi}(\theta) = P_2(\cos \theta)$ ,  $k_{\text{pot}} = k_{\theta\varphi} = 3$ ]. Then, the PB (Eq. (4.3)) contains the product of three factors

$$[H_{\text{gen}}^{\text{outer}}, \langle p_\theta \rangle] \propto p_r (1 - A \sin \theta) \left( 2 \cos 2\theta - \frac{\sin 2\theta_{\text{lim}}}{\theta_{\text{lim}}} \right). \quad (4.5)$$

For small values of  $p_r$  (i.e., large values of  $A$ ), Eq. (4.4) vanishes when  $\theta$  is close to  $A^{-1}$ ,  $\pi - A^{-1}$ ,  $-\pi - A^{-1}$ . It also vanishes at four additional values given by the roots of the equation  $2 \cos 2\theta - \sin 2\theta_{\text{lim}}/\theta_{\text{lim}} = 0$ . Thus, for the ion-permanent dipole interaction, as a result of the more complicated nature of the perturbation, six particular values of  $\theta$  can be found in the range  $[-\pi, +\pi]$  at which the action integral is always an invariant.

## V. CONCLUDING REMARKS AND SUMMARY

The Rice–Ramsperger–Kassel–Marcus (RRKM) theory<sup>16,17</sup> is the best-known model of unimolecular kinetics. However, non-RRKM behavior has been detected, e.g., in the study of  $S_N2$  reactions.<sup>36–38</sup> The difficulty results from an oversimplified view of the dynamics that takes place in the tight range of the reaction coordinate where the potential energy can only be determined via *ab initio* calculations.

An alternative approach based on a search for dynamical constraints and adiabatic variables is possible. The assumption of orbital angular momentum conservation has played a major role in unimolecular reaction dynamics, especially in the study of product energy distributions. Theories known as phase space theory, orbiting transition state theory, and statistical adiabatic channel model have greatly contributed to our understanding,<sup>16,17</sup> at least for processes that take place in the loose region of the reaction coordinate.

The present contribution belongs to the second approach. It can be summarized as follows.

The study of reaction dynamics is on much safer ground for ionized than for neutral systems (compare Refs. 2 and 4, or Refs. 5 and 6, and see Ref. 42). The simplicity and the systematic regularities of the multipole expansion can be turned to great advantage. The first-order perturbation treatment presented here is based on this structure. A point charge recognizes the existence of an approaching electric dipole before it can detect the presence of a quadrupole moment. A similar hierarchy exists for the angular dependence of electrostatic interactions, at least if, for an ion-permanent dipole reaction, the charged partner of the dipole is required to have a center of symmetry. Then, the low-order terms depend on  $\theta$  alone, with the variable  $\varphi$  appearing only at shorter distances.<sup>32</sup>

Several authors have developed theories where transitional modes are assumed to be nonadiabatic at short values of the reaction coordinate and adiabatic beyond a certain extension.<sup>14,15,24,25,46</sup> The strategy adopted here has been to start from the asymptotic region, where a 3D Hamiltonian is completely integrable and where the three first integrals of the motion ( $E$ ,  $p_\varphi$ , and  $\ell^2$  or  $\beta$ ) are known. Then, the perturbation induced by the approach of the fragments has been analyzed, in order to discern the general trends that result from the expression of the perturbed Hamiltonians.

The asymptotic range has been seen to be followed by an outer region where the perturbation maintains cylindrical symmetry. As a result,  $\varphi$  is still a cyclic variable and  $p_\varphi$  continues to be invariant. The third constraint must subsist in some form because conservation of angular momentum results from the isotropy of space,<sup>47</sup> which remains valid in the

perturbed system. The method adopted here shows that  $p_\theta^2 + p_\varphi^2/\sin^2 \theta$  (or  $\beta$ ) remain invariant in the outer space for large values of the translational momentum. For this reason, they can be termed diabatic invariants. This conclusion is supported by previous classical trajectory calculations.<sup>18–21</sup>

In the other part of phase space (low values of  $p_r$ ), the action integral  $\oint p_\theta d\theta$  (which is adiabatically invariant, as expected) can be used to advantage as a third constraint.

In other words, for dynamical systems studied at low values of the translational momentum, the appropriate approximation is to postulate conservation of the action integral (conveniently interpreted as a quantum number). In the opposite case (high values of  $p_r$ ), it is advisable to argue in terms of a centrifugal barrier. However, outside the appropriate range of  $p_r$ , both angular momentum and action integral are still invariant along particular loci in phase space. The concept of centrifugal barrier is particularly useful for an ion-permanent dipole interaction because its construction is always valid at high values of  $p_r$  and remains useful otherwise at six particular values of  $\theta$ .

The efficiency of these invariants does not depend on physicochemical parameters, e.g., the polarizability  $\alpha$  or the dipole moment  $\mu$  of the neutral fragment. An unexpected and noteworthy conclusion is that, among the six perturbative terms initially introduced into Eqs. (2.3) and (3.5), only two are really efficient in the outer region, namely those containing  $\lambda_{\text{pot}}$  and  $\lambda_{\theta\varphi}$ , as shown by Eqs. (2.6), (3.7), and (4.3).

Too many unknown parameters appear in Eqs. (2.3), (2.5), (3.5), and (3.6) to consider doing numerical calculations. A specific application should be preceded by *ab initio* computations. Examples of these can be found in the literature.<sup>48–50</sup> Klippenstein<sup>48</sup> has started such a study for the halogen loss reaction from halogenobenzene ions. The transition between the outer and the asymptotic regions is found to take place at about 7–8 Å. A similar range was also found in a study of the  $\text{CH}_3^+ + \text{H}_2$  reaction.<sup>49</sup> Information on the anisotropy functions  $\Psi(\theta, \varphi)$  or  $\Psi(\theta)$  can also be derived in this way.

Summing up, the dynamics of ion-molecule interactions is still regular in parts of phase space corresponding to a range of the reaction coordinate where the interaction potential deviates from its asymptotic shape. Just as in the case studied by Kolmogorov, Arnold, and Moser (see, e.g., Ref. 35) perturbation of a simple integrable dynamical system leads to a division of phase space into regions of regular and irregular motion.

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