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Adiabatic invariance treatment of reactive collisions between ions and polar molecules at low temperatures

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Abstract. A new semiclassical adiabatic invariance treatment of ion-molecule reactive collisions is proposed to investigate the influence of the molecular rotation on the cross-sections and rate constants at very low temperatures. Within the domain of validity of the adiabatic separation of the ion-molecule radial motion and the molecular rotation, the method is applicable to linear or symmetric-top molecules, for which the system is integrable. The correspondence principle is then used to partition the space of the classical action space into quantum "bins", each of which corresponds to a specific quantum state. The procedure differs from the more usual Einstein-Brillouin-Keller (EBK) semiclassical quantization, where each quantum state is represented by a single point of action space. The results for the linear rigid rotor case, obtained using this modified semiclassical adiabatic invariance model, are in excellent agreement with the quantum mechanical methods, even for low rotational levels of the molecule, where the EBK semiclassical quantization fails.

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1 Introduction

At very low (meV) energies, the cross-sections for exoergic ion-molecule reactive collisions with no activation barrier are strongly influenced by the anisotropy of the long-range multipolar ion-molecule interaction. The non-isotropic component of the interaction couples the rotational states of the colliding molecule at ion-molecule distances well beyond those for which the chemical reaction occurs and, as a consequence, reactive rate constants may exhibit a strong dependence on temperature in the range from 1 to 100 K.

Of the various theoretical approaches used to take account of rotational mixing during the collision, the most successful are those based on the adiabatic separation of the molecular rotation and the radial ion-molecule motion. In a quantum mechanical representation of the system, this leads to the notion of an adiabatic rotational state and if non-adiabatic coupling can be assumed negligible, a great simplification of the theoretical model is achieved. Amongst the methods, which exploit this approach, are the Perturbed Stationary State (PRS) method [1,2], the statistical adiabatic capture channel model (SACM) [3–5] and the adiabatic capture centrifugal sudden approximation (ACCSA) [6]. It has been subsequently shown [7] that the ACCSA and SACM methods are identical.

When a semi-classical description of the system is used, a similar adiabatic separation of the rotational and radial motion can be achieved by the introduction of adiabatic invariance [8,9]. Indeed, the notion of adiabatic invariance is the classical equivalent of the adiabatic representation used in quantum mechanics. This approach was first proposed by Bates [10] and Sakimoto [11] and successfully applied by them [12–14] using a semiclassical (EBK) quantization of the rotational levels to investigate reactions involving both linear and symmetric top molecules.

For temperatures greater than about 100 K, there is excellent agreement between the semiclassical [12–14] and ACCCSA [6,15] calculations, but at lower temperatures the semiclassical method becomes rapidly unsatisfactory and gives inaccurate results at typical interstellar temperatures of 10–20 K. The failure of the standard semiclassical method is directly related to the defect of the EBK semiclassical quantization for low rotational quantum states, especially for $j = 0$, 1. These defects are not serious if many excited rotational states of the molecule are populated initially (such as for molecules with low rotational constants). But in dilute astrophysical environments typical of the interstellar molecular clouds,

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local thermodynamic equilibrium is rarely attained and most molecules are likely to be in low rotational states. In this case, the semi-classical methods [10,11] of Bates and Sakimoto are unreliable at very low temperatures.

The aim of the present work is to remove the major defect of the EBK quantization in a way consistent with the classical description of the system. Rather than assume that each initial quantum state of the molecule corresponds to some unique classical value of the angular momentum, we propose to partition phase space in such a way that each quantum state is represented by a distribution of classical angular momentum (both in magnitude and direction).

2 Classical treatment

First of all, we recall briefly how the notion of adiabatic invariance in an ion-molecule system can be used to simplify the dynamics. The starting point (as in the quantum adiabatic approximation) is the Hamiltonian of the system at some fixed ion-molecule distance r:

$$H(r,\theta) = T(\theta) + \frac{D}{r^2}\cos\theta \tag{1}$$

where D is the molecular dipole moment and $T(\theta)$, the rotational kinetic energy, is given by

$$T(\theta) = \frac{1}{2I}(\dot{\theta}^2 + \dot{\varphi}^2\sin^2\theta) \tag{2}$$

I being the moment of inertia and (θ,φ) the Euler angles describing the orientation of the molecular axis. We may remark that, under these conditions the Hamiltonian depends parametrically on r but is constant of the motion for fixed r. That is to say we may write

$$H(r,\theta) = \varepsilon(r). \tag{3}$$

Introducing the conjugate angular momentum p_θ, p_φ and taking account of the fact that φ is a cyclic coordinate, $p_\varphi = \text{constant} = M$, equation (2) may be written as

$$T(\theta) = \frac{B}{\hbar^2}\left(p_\theta^2 + \frac{p_\varphi^2}{\sin^2\theta}\right) = \frac{B}{\hbar^2}\left(p_\varphi^2 + \frac{M^2}{\sin^2\theta}\right) \tag{4}$$

where $B = \hbar^2/2I$ is the rotational constant.

The determination of $\varepsilon(r)$ as a function of r is achieved by imposing the condition of adiabatic invariance, which is valid if the rotation period is short compared to the time for appreciable changes in the radial motion. In the present case, where the molecule is assumed to behave as a rigid linear rotor, there are two adiabatic invariants, I_θ, I_φ:

$$I_\theta(r) = \frac{1}{2\pi}\oint p_\theta(r)\mathrm{d}\theta = \frac{1}{\pi}\int\limits_{\theta_1}^{\theta_2} p_\theta(r)\mathrm{d}\theta = I_\theta(\infty) \tag{5}$$

$$I_\varphi(r) = \frac{1}{2\pi}\oint p_\varphi(r)\mathrm{d}\varphi = M \tag{6}$$

where $\theta_1 < \theta_2$ are the classical turning points of the molecular libration when only a restricted range of angles is accessible. Of course, if the energy is such that all angles are classically accessible, the range of integration over θ extends from 0 to π. Using (3) and (4) we may express p_θ in terms of r, θ by the relation

$$p_\theta = \hbar\left[\frac{\varepsilon(r)}{B} - \frac{D\cos\theta}{Br^2} - \frac{M^2}{\hbar^2\sin^2\theta}\right]^{1/2}\cdot \tag{7}$$

Introducing the dimensionless quantities

$$\rho = \cos\theta \qquad x = r\sqrt{\frac{B}{D}} \tag{8}$$

we may then write (5) in the form

$$I_\theta = \frac{\hbar}{\pi x}\int\limits_c^b \left(\frac{\sqrt{f(\rho)}}{1-\rho^2}\right)\mathrm{d}\rho \tag{9}$$

where

$$\begin{aligned} f(\rho) &= \rho^3 - \frac{\varepsilon(r)}{B}x^2\rho^2 - \rho + x^2\left(\frac{\varepsilon(r)}{B} - \frac{M^2}{\hbar^2}\right) \\ &\equiv (\rho-a)(\rho-b)(\rho-c). \end{aligned} \tag{10}$$

In the asymptotic limit ($x \to \infty$), the integration (9) can be carried out analytically to give

$$I_\theta = \hbar\sqrt{\frac{\varepsilon(\infty)}{B}} - |M|. \tag{11}$$

It is then seen that for a given initial rotational energy $\varepsilon(\infty)$ and a given constant M, we may associate a specific adiabatic energy $\varepsilon(r)$ for a given r. Classically the energy of a rotor with angular momentum J is $\varepsilon(\infty) = (B/\hbar^2)J^2$. So we designate the adiabatic energies as $\varepsilon_{JM}(r)$. The method to evaluate (9) was first proposed by Sakimoto [11], who showed that for finite r, the integral (9) can be expressed in terms of complete elliptic integrals of the first, second and third kind [16]

$$\begin{aligned} \frac{\varepsilon_{JM}(r)}{B} = \frac{\pi}{\hbar}(J-|M|)\frac{\sqrt{(a-c)}}{2xK(q)} - \frac{(a-c)E(q)}{x^2K(q)} + \frac{a}{x^2} \\ + \left[\frac{\Pi(p_1,q)}{1-c} + \frac{\Pi(p_2,q)}{1+c}\right]\frac{M^2}{2K(q)\hbar^2} \end{aligned} \tag{12}$$

where

$$q = \frac{b-c}{a-c}, \qquad p_1 = \frac{b-c}{1-c}, \qquad p_2 = \frac{c-b}{1+c}\cdot \tag{13}$$

It may be remarked at this stage that this classical theory of adiabatic invariants does not yet take account of the quantization of the initial molecular states. It is therefore necessary to address the problem of semiclassical quantization of the molecular rotation.

3 Semiclassical quantization

There is no unique way of describing stationary states in a semiclassical approximation. Two approaches are usually followed. The first (and commonest) way of adapting classical dynamics is to treat the discrete nature of molecular rotation is the EBK semiclassical quantization (equivalent to Bohr-Sommerfeld quantization in the case of one degree of freedom) of the action variables [17,18]. This approach is adopted by Bates [10] and Sakimoto [11] who assume that the adiabatic invariants in ion-molecule collisions are quantized according to:

$$I_\theta = \frac{1}{\pi}\int_{\theta_1}^{\theta_2} p_\theta \mathrm{d}\theta = J - |M| = (n_\theta + 1/2)\hbar \qquad n_\theta = 0,1,2,... \quad (14)$$

$$I_\varphi = \frac{1}{2\pi}\oint p_\varphi \mathrm{d}\varphi = M = n_\varphi\hbar \qquad |n_\varphi| = 0,1,2,... \quad (15)$$

A correct spacing of the rotational energies (albeit with an error in their absolute energy) is obtained. This semiclassical quantization gives an excellent representation of highly excited rotational states, but it is less satisfactory for the ground and low-lying states. In what follows, we shall designate the rotational states by the quantum numbers j, m.

One of the main weaknesses of the EBK semiclassical quantization becomes apparent if we compare the adiabatic potentials derived from the classical adiabatic invariants with the adiabatic potentials obtained from the quantum mechanical calculations. For example, in a typical system such as He$^+$/HCl, the EBK semiclassical adiabatic potential corresponding to (J, M) associated with the ground state ($n_\theta = 0$, $n_\varphi = 0$) exhibits a weak long distance activation barrier which hinders the reaction at very low temperatures. On the other hand, the quantum adiabatic potential associated with ($j = 0$, $m = 0$) [15] exhibits no such barrier and the reaction can proceed rapidly for all temperatures.

It is clear that the major defect of the EBK quantization comes from the attribution of a unique classical angular momentum to each given quantum state. Indeed, it is well-known from classical trajectory Monte-Carlo methods [19,20] in ion-Rydberg atom collisions that to obtain meaningful results, it is necessary to use a distribution over all classical phase space with a partitioning into bins corresponding to the quantum states. In the following section, we investigate how the partitioning of phase space can be achieved in an optimal way.

Let us consider a dynamical system with N degrees of freedom, described by a Hamiltonian $H(\mathbf{p},\mathbf{q})$ where $(\mathbf{p},\mathbf{q}) \equiv (p_1,...p_N;q_1,...q_N)$ are canonically conjugate variables. According to the semiclassical approximation [21], the number of quantum states with energy less than E is given by the volume of phase space within the energy hypersurface divided by $(2\pi\hbar)^N$

$$N^{sc}(E) = \frac{1}{(2\pi\hbar)^N}\int_{H(\mathbf{p},\mathbf{q})<E} \mathrm{d}^N p\,\mathrm{d}^N q. \quad (16)$$

For integrable systems, it is always possible to find a canonical transformation to action angle variables [9,17,21]

$$(\mathbf{p},\mathbf{q}) \leftrightarrow (\mathbf{I},\boldsymbol{\theta}) \quad (17)$$

where

$$I_i^{\min} < I_i < I_i^{\max}, \quad 0 \le \theta_i < 2\pi, \quad i = 1,2,...N. \quad (18)$$

Since the Hamiltonian function depends then only on the action variables, (16) can be written as

$$N^{sc}(E) = \frac{1}{(\hbar)^N}\int_{H(\mathbf{I})<E} \mathrm{d}^N I. \quad (19)$$

Expression (19) suggests that to each quantum state, there is a corresponding volume of $\hbar^N$ in action space.

At this stage we may remark that the semiclassical (EBK or tori) quantization [17,21] gives a discrete set of action variables which correspond to quantum states

$$\mathbf{I} = \left(\mathbf{n} + \frac{\boldsymbol{\alpha}}{4}\right)\hbar \quad (20)$$

where n_i are quantum numbers and α_i are the Maslov indices. This discretization of the action variables corresponds to the approach [10,11].

The procedure followed here is different. Action space is partitioned into "bins" (mutually exclusive subspaces) $D(\mathbf{n})$, each of which contains a single point of the type (20) and has a volume of $\hbar^N$; that is to say, the following condition is satisfied

$$g_{\mathbf{n}} \equiv \frac{1}{\hbar^N}\int_{D(\mathbf{n})} \mathrm{d}^N I = 1. \quad (21)$$

Of course, even if condition (21) is satisfied there is no unique way of partitioning phase space and in many CTMC calculations an empirical approach is often adopted. In what follows, we propose a way of determining the most reasonable division of action space. Here we shall only treat the case of the rigid linear rotor, which has two degrees of freedom. For completeness, the case of the rigid symmetric-top rotor (three degrees of freedom) is given in the appendix.

4 Partitioning of phase space

The Hamiltonian of the free linear rigid rotor, using (4) is given by

$$H = \frac{BJ^2}{\hbar^2} = \frac{B}{\hbar^2}\left(p_\theta^2 + \frac{p_\varphi^2}{\sin^2\theta}\right) \quad (22)$$

where $\mathbf{J}$, the angular momentum, is a constant of motion. The generating function for the canonical transformation to action-angle variables is obtained from the solution of the Hamilton-Jacobi equation [17]

$$S(\theta,\varphi,J,M) = J\arccos\frac{J\cos\theta}{\sqrt{J^2-M^2}} - |M|\arccos\frac{|M|\cot\theta}{\sqrt{J^2-M^2}} + M\varphi. \quad (23)$$

It then follows that the action-angle variables are (J, M, θ_J, θ_M) where $J = |\mathbf{J}|$, $M = J_z$ obey the restrictions

$$0 \le J < \infty \tag{24}$$

$$-J \le M \le J. \tag{25}$$

The EBK quantization conditions read:

$$J = (j + 1/2)\hbar \qquad j = 0, 1, 2, ... \tag{26}$$

$$M = m\hbar \qquad m = 0, \pm 1, \pm 2, ... \pm j. \tag{27}$$

In order to determine the bin boundaries in action space, we introduce two functions $F(m, j, J)$ and $G(j)$, which, although not strictly defined, are subject to certain constraints. The condition (21) can then be written as

$$g_{jm} \equiv \frac{1}{\hbar^2} \int_{G(j)}^{G(j+1)} \mathrm{d}J \int_{F(m,j,J)}^{F(m+1,j,J)} \mathrm{d}M = 1 \tag{28}$$

where, because of (24) and (25), we must impose the additional constraints

$$G(0) = 0 \tag{29}$$

$$F(-j, j, J) = -J \qquad F(j + 1, j, J) = J. \tag{30}$$

Making the simplest possible assumption that $F(m, j, J)$ is a linear function of m,

$$F(m, j, J) = (m - \beta)A \tag{31}$$

where β and A are constants (depending on j and J) we deduce from (30) that

$$A = \frac{2J}{2j + 1}, \qquad \beta = \frac{1}{2} \tag{32}$$

yielding

$$F(m, j, J) = \left(m - \frac{1}{2}\right) \frac{2J}{2j + 1}\cdot \tag{33}$$

The equation (28) gives

$$\frac{1}{\hbar^2} \int_{G(j)}^{G(j+1)} \mathrm{d}J \int_{\frac{(2m-1)J}{2j+1}}^{\frac{(2m+1)J}{2j+1}} \mathrm{d}M =$$

$$\frac{1}{\hbar^2} \int_{G(j)}^{G(j+1)} \frac{2J}{2j + 1} \mathrm{d}J = \frac{G^2(j + 1) - G^2(j)}{(2j + 1)\hbar^2} = 1. \tag{34}$$

Taking account of the condition (29), the solution of (34) in the form of a linear function is

$$G(j) = j\hbar. \tag{35}$$

Therefore the boundaries of the bins $D(jm)$ are defined by

$$j\hbar \le J < (j + 1)\hbar \tag{36}$$

$$\frac{(2m - 1)J}{2j + 1} \le M < \frac{(2m + 1)J}{2j + 1}\cdot \tag{37}$$

With this choice we find the mean values per bin are given by

$$\bar{J}^2 = (2j + 1)^2 \frac{\hbar^2}{4} \left[1 + \frac{1}{(2j + 1)^2}\right] = \hbar^2 \left[j(j + 1) + \frac{1}{2}\right] \tag{38}$$

$$\bar{J} = (j + 1/2)\hbar \left[1 + \frac{1}{3(2j + 1)^2}\right] \tag{39}$$

$$\bar{M} = m\hbar \left[1 + \frac{1}{3(2j + 1)^2}\right]\cdot \tag{40}$$

The solution (36, 37) is not unique. It is easy to verify that functions

$$G(j) = j\hbar \tag{41}$$

$$F(m, j, J) = \begin{cases} (m + j)\hbar - J & \text{for } -j \le m \le 0 \\ (m - j - 1)\hbar + J & \text{for } 0 < m \le j \end{cases} \tag{42}$$

also satisfy (28). The bins $D(jm)$ then correspond to:

$$j\hbar \le J < (j + 1)\hbar \tag{43}$$

$$(m + j)\hbar - J \le M < (m + j + 1)\hbar - J \qquad \text{for} \quad -j \le m < 0 \tag{44}$$

$$j\hbar - J \le M < -j\hbar + J \qquad \text{for } m = 0 \tag{45}$$

$$(m - j - 1)\hbar + J \le M < (m - j)\hbar + J \qquad \text{for } 0 < m \le j. \tag{46}$$

Instead of (38–40) we now have

$$\bar{J}^2 = \begin{cases} (2j + 1)^2 \dfrac{\hbar^2}{4} \left[1 + \dfrac{1}{3(2j + 1)^2}\right] = \\ \qquad \hbar^2 \left[j(j + 1) + \dfrac{1}{3}\right] & m \ne 0 \\ (2j + 1)^2 \dfrac{\hbar^2}{4} \left[1 + \dfrac{4j + 3}{3(2j + 1)^2}\right] = \\ \qquad \hbar^2 \left[j(j + 1) + \dfrac{j}{3} + \dfrac{1}{2}\right] & m = 0 \end{cases} \tag{47}$$

$$\bar{J} = \begin{cases} \left(j + \dfrac{1}{2}\right)\hbar & m \ne 0 \\ (2j + 1)\dfrac{\hbar}{2} \left[1 + \dfrac{1}{3(2j + 1)}\right] & m = 0 \end{cases} \tag{48}$$

$$\bar{M} = m\hbar. \tag{49}$$

We may remark that the bin definition of (36, 37) corresponds to that used in CTMC calculations [22] for charge transfer reactions. To our knowledge, no previous demonstration of this result has been given. We may note that the averaged energy gives (as the EBK semiclassical) the correct rotational spacing. On the other hand, the bin definition of (43–46) only gives the correct rotational spacing for the non-zero m levels.

Table 1. Parameters in atomic units of molecular systems.

System	Mass μ	Rotational constant B	Polarizability	Dipole moment
He$^+$/HCl	6575	4.825×10^{-5}	17.75	0.4363
H$_3^+$/HCN	4922	6.739×10^{-6}	17.27	1.1729

5 Applications

To test the validity of the semiclassical partitioning of phase space, we have carried out a series of calculations for a number of simple ion-molecule systems with different B/D ratios. These are assembled in the following Table 1.

We shall not present the results for adiabatic states (j, m) with $j > 2$, since there is excellent agreement between the quantum and EBK semiclassical quantization in that case for all collision energies. It is only for states with low quantum numbers $j \leq 2$, for which the EBK semiclassical quantization becomes increasingly unreliable as j decreases. In the following we shall compare results obtained by our semiclassical partitioning of action space with both the quantum and EBK semiclassical quantization.

The first (and most difficult) stage of the calculations is the determination of the classical adiabatic potential $\varepsilon_{JM}(r)$ using equation (12) for a given initial set of classical J, M. We may note that the quantities $\{a, b, c, q, p_1, p_2\}$ depend on $\varepsilon_{JM}(r)$ in quite a complex way *via* the parameters of elliptic integrals. However, these latter can be computed using standard library subroutines [23]. It is found that an iterative solution of (12) is satisfactory. Besides, since the solution is known analytically at $r \to \infty$, it is simplest to begin by using the solution $\varepsilon_{JM}(r)$ as the first order approximation to $\varepsilon_{JM}(r - \delta r)$. To compute the reactive cross-section, two approaches are possible. The first involves making an average over a bin of $\varepsilon_{JM}(r)$ to yield a classically averaged adiabatic potential $\bar{\varepsilon}_{jm}(r)$

$$\bar{\varepsilon}_{jm}(r) = \frac{1}{\hbar^2} \int\limits_{D_{jm}} \bar{\varepsilon}_{JM}(r) \mathrm{d}J \, \mathrm{d}M \qquad (50)$$

and then to determine the cross-section as in the ACCSA method. The second is to compute the classical cross-section σ_{JM} and then make an average over the cross-sections

$$\sigma_{jm} = \frac{1}{\hbar^2} \int\limits_{D_{jm}} \sigma_{JM} \mathrm{d}J \, \mathrm{d}M. \qquad (51)$$

Both procedures give very similar results. The first procedure facilitates the comparison with the quantum and the EBK semiclassical method. We designate by ε_{jm}^{Q}, the adiabatic rotational energy of the quantum ACCSA or SACM methods by ε_{jm}^{sc}, the EBK semiclassical adiabatic potential energy used in both [10,11].

We have partitioned action-space in two ways: first according to (36, 37) and secondly according to (43–46). The details of this partition are given in Table 2.

Table 2. Partitioning of action space.

j	m	Limits of $J/\hbar$	Limits of M according to (36, 37)	Limits of M according to (43–46)
0	0	$(0, 1)$	$(-J, J)$	$(-J, J)$
1	-1	$(1, 2)$	$\left(-J, -\frac{J}{3}\right)$	$(-J, -J + \hbar)$
1	0	$(1, 2)$	$\left(-\frac{J}{3}, \frac{J}{3}\right)$	$(-J + \hbar, J - \hbar)$
1	1	$(1, 2)$	$\left(\frac{J}{3}, J\right)$	$(J - \hbar, J)$
2	-2	$(2, 3)$	$\left(-J, -\frac{3J}{5}\right)$	$(-J, -J + \hbar)$
2	-1	$(2, 3)$	$\left(-\frac{3J}{5}, -\frac{J}{5}\right)$	$(-J + \hbar, -J + 2\hbar)$
2	0	$(2, 3)$	$\left(-\frac{J}{5}, \frac{J}{5}\right)$	$(-J + 2\hbar, J - 2\hbar)$
2	1	$(2, 3)$	$\left(\frac{J}{5}, \frac{3J}{5}\right)$	$(J - 2\hbar, J - \hbar)$
2	2	$(2, 3)$	$\left(\frac{3J}{5}, J\right)$	$(J - \hbar, J)$

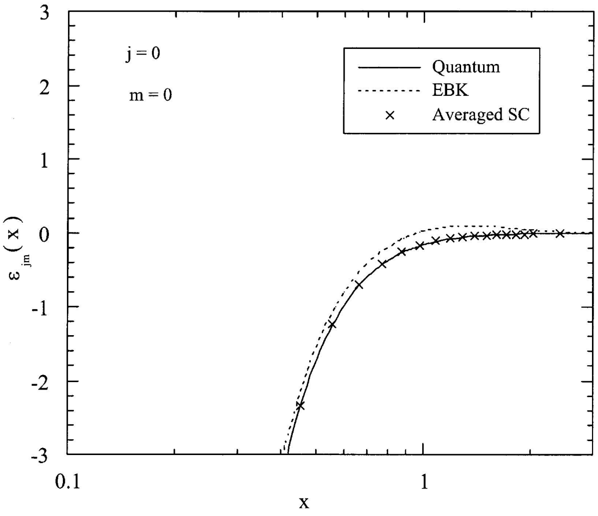

Fig. 1. Adiabatic rotational potential curves (in units of B) as a function of the reduced ion-molecule distance x (in units of $\sqrt{D/B}$) for the $(j = 0, m = 0)$ dissociation limit. The solid line corresponds to the quantum mechanical (ACCSA) method, the dashed line to the adiabatic invariant method with EBK quantification. The crosses designate the adiabatic invariant averaged semi-classical methods with action space partitioned according to (36, 37) or (43, 45).

6 Results and discussion

Typical results of the adiabatic potentials are presented in Figures 1, 2, 3 for $j = 0$, 1, 2 (for all possible values of m), where a comparison is made of $\bar{\varepsilon}_{jm}(r)$, ε_{jm}^{Q} and ε_{jm}^{sc}. While there is excellent agreement for all values of x

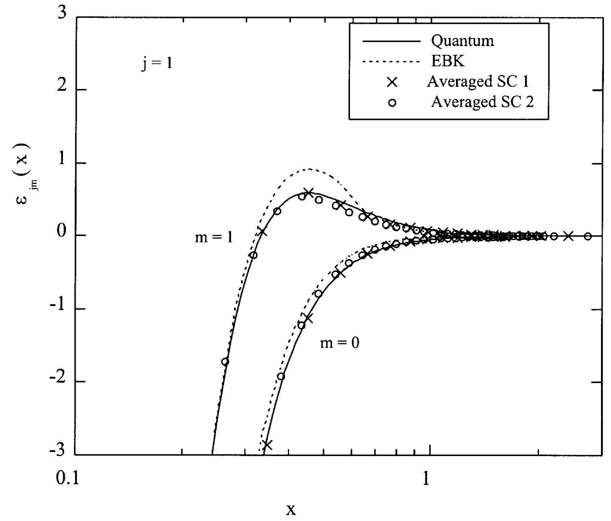

Fig. 2. Adiabatic rotational potential curves (in units of B) as a function of the reduced ion-molecule distance x (in units of $\sqrt{D/B}$) for the ($j = 1$, $m = 0$) and ($j = 1$, $m = 1$) dissociation limits. The solid and dashed lines are as in Figure 1. The crosses and circles designate the adiabatic invariant averaged semiclassical methods, the crosses with action space partitioned according to (36, 37), the circles with action space partitioned according to (43–46).

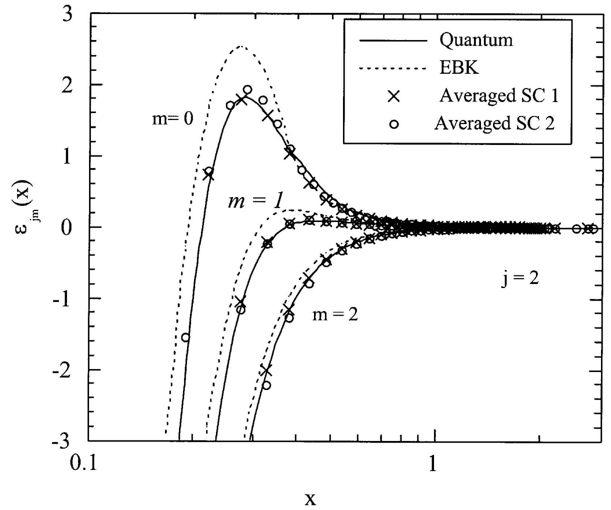

Fig. 3. Adiabatic rotational potential curves (in units of B) as a function of the reduced ion-molecule distance x (in units of $\sqrt{D/B}$) for the ($j = 2$, $m = 0$), ($j = 2$, $m = 1$) and ($j = 2$, $m = 2$) dissociation limits. The solid and dashed lines, the crosses and circles are as in Figure 2.

between our calculated $\bar{\varepsilon}_{jm}(r)$ and ε^{Q}_{jm}, there are very significant differences with ε^{sc}_{jm}. This difference is especially striking for the $j = 0$, $m = 0$ where the EBK semiclassical potential exhibits a repulsive barrier around $x = 1$, which does not exist in $\bar{\varepsilon}_{jm}(r)$ and ε^{Q}_{jm}. This explains the failure of the EBK semiclassical method at very low temperatures where the reaction is dominated by molecules in their ground rotational state. Similar discrepancies also occur for $j = 1$ and 2, especially when $m = 0$, although the consequences on the cross-sections are not so dramatic as for ground state molecules.

Cross-sections are computed (as in the ACCSA and SACM methods) according to the Langevin capture model, in which it is assumed that a reaction occurs if the impact parameter is smaller than the critical value b_c for which orbiting occurs. The conditions for orbiting ($\dot{r} = 0$) are given by

$$E = \frac{Eb_c^2}{r_{\max}^2} + V_{jm}(r_{\max}) \tag{52}$$

where $V_{jm}(r)$ designates the adiabatic potential $\bar{\varepsilon}_{jm}(r)$, ε^{Q}_{jm} or ε^{sc}_{jm} and $r_{\max}$ is determined by

$$\frac{2Eb_c^2}{r_{\max}^3} = \left(\frac{\mathrm{d}V_{jm}(r)}{\mathrm{d}r}\right)_{r=r_{\max}} \cdot \tag{53}$$

In the case of the adiabatic potentials $\bar{\varepsilon}_{jm}(r)$ and ε^{sc}_{jm}, the derivative of the potential required in (53) can easily be derived from relation (12)

$$\frac{\mathrm{d}V_{jm}}{\mathrm{d}x} = 2x^{-3}\left[(a-c)E(q)/K(q) - a\right] \cdot \tag{54}$$

Rather than compute the critical orbiting parameter b_c for a given energy, it is more convenient to generate an array of (b_c, E) from an arbitrary set of values of $r_{\max}$. It is then straightforward to obtain by inverse interpolation the value of b_c (and consequently the cross-section $\sigma_{jm}(E) = \pi b_c^2$) for any given E. The energy range covered by this investigation lies in the interval $[0.01B, 250B]$. The rate constants $k(T)$ are obtained by averaging over a thermal (Maxwellian) distribution of the reactants.

The reactive cross-sections

$$Q_j(E) = \frac{1}{2j+1} \sum_{m=-j}^{j} \sigma_{jm}(E) \tag{55}$$

for an ion-dipole system are presented in Figure 4. As in most previous publications, the cross-sections presented in Figure 4 give the ratio of the calculated value to the Langevin isotropic value obtained by taking account of the dipole polarizability term in the potential (but neglecting the anisotropic contribution). This scaling procedure allows us to plot the cross-sections of all ion-dipole systems on one single curve. The most striking results are for $j = 0$ and $j = 1$. As we have already remarked in our discussion of the adiabatic potentials, the existence of the long range activation barrier in the EBK semiclassical potential leads to negligibly small reaction rates when $E/B < 1$. On the other hand, our partitioning of classical action-space into quantum bins yields cross-section in excellent agreement with the quantum calculations for all j. There is no significant difference between the two types of partitioning action space.

The calculated rate constants for the system $\mathrm{He}^+/\mathrm{HCl}$ (Fig. 5) and $\mathrm{H}_3^+/\mathrm{HCN}$ (Fig. 6) also show that, even after

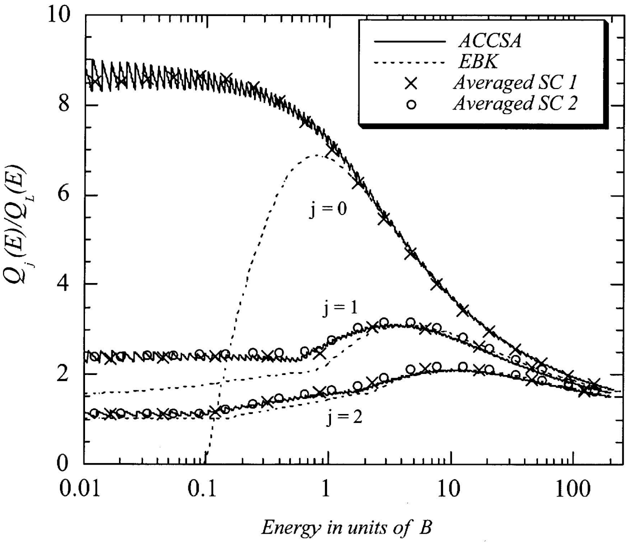

Fig. 4. Calculated (state selective) reactive cross-sections $Q_j(E)$, (j = 0, 1 and 2) scaled with the Langevin cross-section $Q_L(E)$, for an ion-dipole system as a function of energy (in units of B). The solid and dashed lines, the crosses and circles are as in Figure 2.

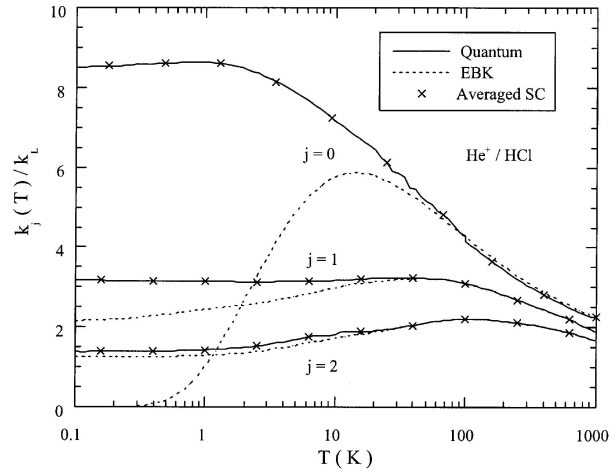

Fig. 5. Calculated (state selective) reactive rate constants $k_j(T)$, (j = 0, 1 and 2) scaled with the Langevin rate constant k_L for the He$^+$/HCl system as a function of temperature (in units of K). The solid and dashed lines are as in Figure 2. The crosses designate the adiabatic invariant averaged semi-classical methods with action space partitioned according to (36, 37).

thermal averaging, the EBK semiclassical method is not satisfactory at low temperatures. This is especially true of molecules with large rotational constants like HCl, where the EBK semi-classical results are only reliable for $T > 50$ K. On the other hand, for molecules with small rotation constants (for example HCN), the EBK semiclassical method is satisfactory for temperatures down to about 10 K.

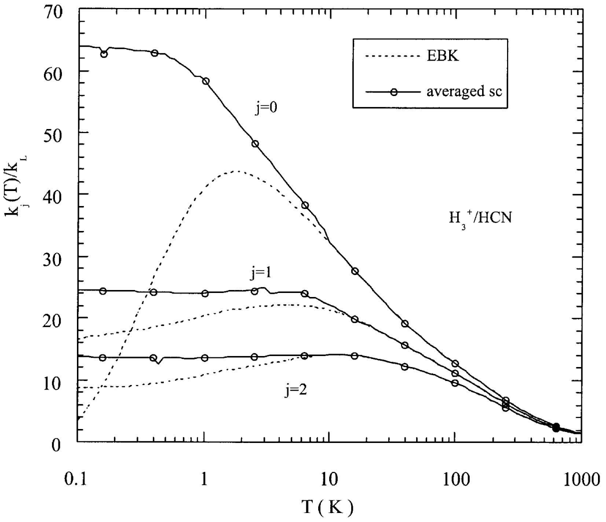

Fig. 6. Ratio of calculated (state averaged) reactive rate constant to Langevin reactive rate constant for the H^{3+}/HCN system as a function of temperature (in units of K). The dashed lines are as in Figure 5, while the circles designate adiabatic invariant averaged semiclassical results.

7 Conclusion

The main conclusion of this work is that the semi-classical adiabatic invariance method is only satisfactory provided the molecular rotation is partitioned into quantum bins in action space. Agreement with quantum calculations is excellent (both for the adiabatic potentials and the reaction cross-sections) for all values of the quantum number and at all collision energies. This is in contrast to the EBK semiclassical method, which fails for low quantum numbers.

Our semiclassical quantization method of phase space should have applications to more general types of classical trajectory calculations (such as CTMC) involving state-to-state reactions.

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Appendix: Partitioning of phase space for a symmetric top rotor

The Hamiltonian of the free symmetric rigid rotor is given by

$$H = B(J_x^2 + J_y^2) + CJ_z^2 = BJ^2 - (B - C)J_z^2 \qquad (56)$$

$$= B\left[p_\theta^2 + \frac{p_\psi^2 + p_\varphi^2 - 2p_\varphi p_\psi \cos\theta}{\sin^2\theta}\right]^2 - (B - C)p_\psi^2 \qquad (57)$$

where $J_{x,y,z}$ are the projections of the angular momentum on the body fixed axis and $\{\varphi, \theta, \psi\}$ are the Euler angles specifying the orientation of the molecule with respect to a space-fixed axis. The canonical transformation to action-angle variables is given by Augustin and Millar [24] and Child [17] from which it is deduced that the action-angle variables are $\{J, M, K, \theta_J, \theta_M, \theta_K\}$, where $K = J_z$ and $M = J_{z'}$, the projection of $\mathbf{J}$ on the space-fixed axis with the following constraints

$$0 \le J < \infty \tag{58}$$

$$-J \le M \le J \tag{59}$$

$$-J \le K \le J. \tag{60}$$

The EBK semiclassical quantization is as follows

$$J = \left(j + \frac{1}{2}\right)\hbar \qquad j = 0, 1, 2, ... \tag{61}$$

$$M = m\hbar, \qquad m = 0, \pm 1, \pm 2, ... \pm j \tag{62}$$

$$K = k\hbar, \qquad k = 0, \pm 1, \pm 2, ... \pm j. \tag{63}$$

In order to determine the bin size, we introduce three functions $F_1(m, j, J)$, $F_2(k, j, J)$ and $G(j)$. The condition (21) can then be written as

$$g_{jmk} \equiv \frac{1}{\hbar^3} \int\limits_{G(j)}^{G(j+1)} \mathrm{d}J \int\limits_{F_1(m,j,J)}^{F_1(m+1;j,J)} \mathrm{d}M \int\limits_{F_2(k,j,J)}^{F_2(k+1;j,J)} \mathrm{d}K = 1 \tag{64}$$

with the additional conditions

$$G(0) = 0 \tag{65}$$

$$F_1(-j, j, J) = -J, \quad F_1(j+1, j, J) = J \tag{66}$$

$$F_2(-j, j, J) = -J, \quad F_2(j+1, j, J) = J. \tag{67}$$

As for the case of the linear rotor, it is easily deduced from conditions of (65) and (66) (and assuming a linear dependence in m) that

$$F_1(m, j, J) = \frac{(2m-1)J}{2j+1} \tag{68}$$

$$F_2(k, j, J) = \frac{(2k-1)J}{2j+1}\cdot \tag{69}$$

Substitution of (67) and (68) in (63) gives

$$\frac{G^3(j+1) - G^3(j)}{3(2j+1)^2\hbar^3} = \frac{1}{4}\cdot \tag{70}$$

Taking account of (64) we can try the polynomial solution

$$G^3(j) = Aj(j-\gamma)(j-\delta)\hbar^3. \tag{71}$$

Substitution of (70) in (69) gives

$$A = 1, \quad \gamma = 1/2, \quad \delta = -1/2. \tag{72}$$

So that we have

$$G(j) = \left[\frac{(2j-1)j(2j+1)}{4}\right]^{1/3} \hbar. \tag{73}$$

The bins $D(j, k, m)$ are then given by

$$\left[\frac{(2j-1)j(2j+1)}{4}\right]^{1/3} \hbar \le J \le \left[\frac{(2j+1)(j+1)(2j+3)}{4}\right]^{1/3} \hbar \tag{74}$$

$$\frac{(2m-1)J}{2j+1} \le M \le \frac{(2m+1)J}{2j+1} \tag{75}$$

$$\frac{(2k-1)J}{2j+1} \le K \le \frac{(2k+1)J}{2j+1}\cdot \tag{76}$$

The mean values per bin are

$$\bar{J}^2 = \frac{\hbar^2}{2^{1/3}10(2j+1)^{1/3}} \times \left[(j+1)^{5/3}(2j+3)^{5/3} - j^{5/3}(2j-1)^{5/3}\right] \tag{77}$$

$$\bar{K}^2 = \frac{2^{2/3}(12k^2+1)\hbar^2}{60(2j+1)^{7/3}} \times \left[(j+1)^{5/3}(2j+3)^{5/3} - j^{5/3}(2j-1)^{5/3}\right]\cdot \tag{78}$$

For large values of j, (76) and (77) behave as

$$\bar{J}^2 \approx \left(j + \frac{1}{2}\right)^2 \hbar^2 \left[1 + \frac{1}{(2j+1)^2} + ...\right] \tag{79}$$

$$\bar{K}^2 \approx \left(k^2 + \frac{1}{12}\right) \hbar^2 \left[1 + \frac{1}{(2j+1)^2} + ...\right]\cdot \tag{80}$$

By analogy with the alternative solution (50–53) for the linear rotor, we might try the second partition

$$j\hbar \le J < (j+1)\hbar \tag{81}$$

$$\begin{cases} (m+j)\hbar - J \le M < (m+j+1)\hbar - J & \text{for } -j \le m < 0 \\ j\hbar \le M < -j\hbar + J & \text{for } m = 0 \\ (m-j-1)\hbar + J \le M < (m-j)\hbar + J & \text{for } 0 < m \le j \end{cases} \tag{82}$$

$$\begin{cases} (k+j)\hbar - J \le K < (k+j+1)\hbar - J & \text{for } -j \le k < 0 \\ j\hbar \le K < -j\hbar + J & \text{for } k = 0 \\ (k-j-1)\hbar + J \le K < (k-j)\hbar + J & \text{for } 0 < k \le j \end{cases}. \tag{83}$$

However (80–82) do not satisfy the condition (63). One finds that

$$g_{jmk} = \begin{cases} 1 & \text{for } k \ne 0 \text{ and } m \ne 0 \\ \dfrac{4}{3} & \text{for } k = 0 \text{ and } m = 0 \end{cases}. \tag{84}$$

So the bins for $\{j, m = 0, k = 0\}$ have too large a statistical weight. Only the solution (73–75) should therefore be retained.

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