Overcoming the zero-point dilemma in quasiclassical trajectories: (He,H_2^+) as a test case

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We present a new technique for circumventing the problem of the zero-point leak in classical trajectories by extending the action-billiard approach of de Aguiar and Ozorio de Almeida [Nonlinearity **5**, 523 (1992)]. In addition to demonstrating its utility in a model problem, we examine the application of various methods of overcoming the zero-point leak in the case of collinear $He+H_2^+$ collisions. We also show that *not* neglecting leaky trajectories gives, on an average, good agreement with quantal results for collinear as well as 3-dimensional collisions. © *1995 American Institute of Physics.*

I. INTRODUCTION

Despite the fact that fully converged three-dimensional (3D) quantum-mechanical (QM) solutions for a few elementary systems have become possible in recent years,[1] the quasiclassical trajectory (QCT) method[2] still remains computationally the most viable tool for a variety of molecular simulations involving atomic and molecular collisions. The method presupposes that the nuclear motion on an adiabatic potential-energy surface can be described adequately by the classical equations of motion. The initial vibrational and rotational actions of the reactant molecule(s) are usually assigned values corresponding to the quantum numbers of the initial state, but unfortunately, there is no control on the final action at the end of the collision. The corresponding quantum numbers of the product molecule(s) can therefore be nonintegral, and are usually rounded off to the nearest integers—this is the standard histogram method. Such an approach can yield results in good agreement with experimental and/or quantal results, when highly averaged reaction attributes such as rate constants or integral cross sections are computed and as long as there are no symmetry effects or strictly quantum phenomena like tunneling and resonances involved. However, discrepancies between QCT and QM results become noticeable when comparisons are made at the level of state-to-state transition probabilities or cross sections.

There is, however, an inherent deficiency in the method which is referred to as the zero-point leak[2–4] (ZPL), and this problem, as manifest in the $He–H_2^+$ reaction, is our main concern in this paper.

Many classical trajectories result in the product (or the reactant) molecule having vibrational energy *less* than the quantum mechanically allowed zero-point energy (ZPE). Such trajectories—which occur both below and above the quantal threshold for the reaction E_{th}^{QM}—are clearly unphysical, and have to be dealt with. The ZPL—which is sometimes termed the ''adiabatic leak,'' also mars attempts to study intramolecular vibrational relaxation processes[5] in polyatomic systems by the QCT method. For example, in a simulation with the minimum internal energy, i.e., the zero-point energy initially in each mode, since the various vibrational modes are coupled, energy can be redistributed, so that some modes may get all the energy while others have less than the zero-point energy. This often causes unphysical effects or yields meaningless result, and is entirely an artefact of the dynamical scheme chosen. The adiabatic leak, not surprisingly, arises in QCT studies of molecule–surface interactions as well,[6] and leads to similar problems there.

Several suggestions have been made in the past to circumvent the problem of the ZPL, and here we briefly review some of these. Since the ZPL is largely a low-energy phenomenon, one manifestation arises in the fact that often the classically computed threshold for a given process is *lower* than the quantal threshold. Thus one method of tackling the ZPL is to simply neglect all leaky trajectories when computing reaction attributes—in particular, to consider[7] all trajectories with $E_{tot}<E_{th}^{QM}$ as *nonreactive*.

Attempts to solve the problem of leaky trajectories, for energies $E_{tot}\geqslant E_{th}^{QM}$ can be viewed as either ''active'' (when steps are taken to ensure that the ZPL does not occur) or ''passive'' (which are more concerned with how leaky trajectories should be interpreted).

The first such active method to be introduced[8,9] involves monitoring internal energies in each mode, and when the energy in a particular mode decreases to below the ZPE in that mode, the momentum is reversed instantaneously. As is discussed in Sec. II below, this method is equivalent to introducing impenetrable barriers in phase space—the so-called action billiards[10]—which can seriously interfere with the classical dynamics. Almost invariably this leads to chaotic behavior,[11] even in otherwise nonchaotic systems.

One other active method circumvents the ZPL by a partial quantization procedure,[6] wherein the mode that is most susceptible to leakage is treated quantally, while the others are classical. However, the additional effort involved in such partial schemes vitiates the operational simplicity of the QCT approach; a more serious drawback is that the success of the

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method is strongly dependent on the choice of the mode that is quantized.

Recently, Ben Nun and Levine[12] have suggested another procedure to prevent the ZPL in classical trajectory computations. Their method starts with the quantal Hamiltonian corresponding to the original classical system, and is based on then taking the classical limit in a manner so as to ensure that the zero-point energy is always maintained in each mode. This yields a classical limit different from the (original) classical system, but one where the resulting dynamics does not suffer from the zero point leak.

The most commonly used *passive* approach is to neglect all trajectories which lead to vibrational energy of the product (or the reactant) below the ZPE. Justification, to a large extent, is made by invoking the nonphysical nature of the ZPL or by comparing 3D QCT results with available experimental results.[13,14] Refinements of this simple-minded approach have also been attempted,[15] and include:

(i) neglecting trajectories which result in *internal* energy (vibration+rotation) less than the ZPE,
(ii) neglecting trajectories which result in *vibrational* energy less than the ZPE,
(iii) neglecting trajectories which result in vibrational energy less than a fixed fraction of ZPE although the internal energy *per se* may equal or exceed the ZPE, and
(iv) replacing trajectories with internal (or vibrational) energy less than the ZPE with trajectories which do not leak but are computed for the same initial conditions of key variables like translational energy, internal energy, impact parameter, etc.

Two other methods are worthy of mention in this context, although strictly speaking they do not approach the problem of ZPL directly. The reverse QCT histogram method[16] makes use of trajectories computed for the reverse reaction in conjunction with the principle of microscopic reversibility. In one application, while computing state-to-state integral cross sections for the reaction

$$\mathrm{H}+\mathrm{H}_2(0,0)\rightarrow \mathrm{H}_2(0,j')+\mathrm{H}, \tag{1}$$

Mandy and Martin[17] showed that the reverse QCT method fared better than the standard QCT method near the threshold and for higher j'. Thus one can imagine employing reverse trajectories if the forward ones suffer the ZPL. Obviously, if the reverse trajectories also have the ZPL they are no more dependable than forward trajectories, from a formal point of view.

Moment methods[18] rely on Ehrenfest's theorem relating classical and quantal averages, coupled with the use of information theory[19] or scaling analysis,[20] or cross-correlation methods[21] to obtain transition probabilities. The contention here is that even though individual trajectories may show unphysical behavior, the averaged information coming from an ensemble of trajectories is more likely to be accurate. Indeed, this technique yields accurate results, although applications have mainly been made to collinear collisions or systems with few degrees of freedom.[18,20,21]

In earlier 3D QCT studies[12,13] of the reaction

$$\mathrm{He}+\mathrm{H}_2^+(v)\rightarrow \mathrm{HeH}^++\mathrm{H} \tag{2}$$

for H_2^+ in its different vibrational states, we found that neglect of the leaky trajectories underestimated the reaction cross section, while their inclusion gave an overestimate (see Fig. 5 of Ref. 14). With increase in energy, the number of leaky trajectories decreased and the two approaches yield the same result (to within statistical error estimates). Since some of the different experimental results for the system are at variance with each other, particularly at low energies, it is difficult to ascertain the accuracy of one approach over the other based on experimental results alone. Subsequently[22–24] fully converged 3D quantum calculations have been carried out for the system and hence we have here the opportunity to test the different approximations within the quasiclassical framework.

In the present paper, we study some of the above mentioned techniques of alleviating the ZPL problem, in the $(\mathrm{He},\mathrm{H}_2^+)$ collisional system. In Sec. II, the notion of action billiards is elaborated upon, and a practical technique of reducing the zero-point leak is suggested. In application to a model system, this method is seen to interfere minimally with the intrinsic dynamics. Section III deals with the QCT results obtained through different approaches for collinear as well as 3D $(\mathrm{He},\mathrm{H}_2^+)$ collisions, and a detailed comparison is made with quantal results. Our conclusions follow in Sec. IV.

II. ACTION BILLIARDS

The notion of an action billiard was first introduced[10] by de Aguiar and Ozorio de Almeida (AO), in the following context.

Consider a classical dynamical system and the quantal system corresponding to it. The phase space of the classical system finds correspondence with the Hilbert space of the quantum system. In actual computations on quantum systems, however, it may happen that operators are expressed in a truncated basis, say for reasons of (computational) tractability. In this case, the question arises as to what the corresponding classical system actually is.

AO showed[10] that corresponding to the truncation of the Hilbert space is a truncation of the associated classical phase space, which is effected by introduction of a hypersurface boundary in the phase space, which orbits cannot traverse. Consider a classical Hamiltonian, $H(\mathbf{p},\mathbf{q})$, which can be written in action-angle form as $H(\mathbf{I},\phi)$. If the quantum-mechanics for this system is studied in a basis where the highest state is N, then the equivalent classical system, in some sense is actually given by

$$H_{\mathrm{equiv}}=H(\mathbf{I},\phi)(\Theta(I_N-I))^2, \tag{3}$$

where $\Theta(x)$ is the Heaviside step function, and I_N is the classical action corresponding to the quantum number N through the semiclassical correspondence principle.[1] (In many cases, especially for 1 degree of freedom systems, the usual correspondence is $I_N=(N+1/2)\hbar$.) Thus classically, the action will be constrained to be $\leqslant I_N$.

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If an orbit should collide with the action boundary as introduced above, it suffers specular reflection in action-angle coordinates. This gives the terminology[10] ''action billiards'' (AB).

Instead of the sharp action boundary introduced by the step function, AO also consider the smoothed step function,

$$H_\lambda = H(\mathbf{I},\phi)(\Theta_\lambda(I_N - I))^2 \tag{4}$$

with

$$\Theta_\lambda(I_N - I) = \frac{1-\tanh(\lambda^{-1}(I_N - I))}{2}. \tag{5}$$

Clearly, as $\lambda \to 0$, $\Theta_\lambda \to \Theta$ and $H_\lambda \to H_{\text{equiv}}$. These smooth AB's do not introduce sharp discontinuities in the dynamics, and for some cases may be preferable.

The above action billiards correspond to an outer boundary in the phase space, with trajectories unable to traverse it from the inside out. This is the classical equivalent of the truncation of the infinite-dimensional Hilbert space, as is done in any practical computation that employs a finite basis set. In simple applications, AO showed that the classical dynamics of certain trajectories—those that are in the neighborhood of the action boundary—can be quite significantly altered.

Here, we observe that in an exactly analogous manner, one can argue that the existence of a finite minimum energy—the zero-point energy—introduces a similar barrier in the phase space, but contrastingly, now trajectories are unable to traverse the barrier from the outside in. This is essentially the zero-point correction of Bowman, Gazdy, and Sun,[8] and one of the corrections suggested by Miller, Hase, and Darling,[9] and takes the form

$$H_{\text{equiv}} = H(\mathbf{I},\phi)(\Theta(I - I_G))^2, \tag{6}$$

where I_G is the action corresponding to the ground state.

The specular reflection of trajectories from this action boundary is exactly equivalent to the procedure suggested,[8,9] of following the energy in a given mode and reversing the corresponding momentum if it falls below the zero-point energy.

In the more general setting of an action-billiard, though, the rationale for such a technique of overcoming the ZPL becomes clearer. Indeed refinements suggest themselves, arising from the different choices for the action variable I to be used in Eq. (6).

In scattering problems, (an example is discussed below), where bound and unbound degrees of freedom are both present, the action billiard is introduced only for bound degrees of freedom. The simplest choice for the actions to be used in Eq. (6) is the zeroth-order action variable,[8,9] i.e., that which is appropriate asymptotically. We refer to this procedure of correcting the ZPL as the simple action billiard (AB).

However—and this is particularly important in scattering situations—the action variable itself is a function of the scattering coordinate, and what often occurs in practice is that while asymptotically, the final energy in a mode exceeds the zero-point energy, *during* the collision, the energy dips below the ZPE. The simple AB therefore corrects such trajectories, and since the dynamics is strongly affected by this procedure, this can be a significant *over*correction.

In order to reduce such overcorrection, another choice that has been suggested is the action variable corresponding to the instantaneous normal form of the classical Hamiltonian as a function of the scattering coordinate (Method B of Ref. 9). In this procedure, the classical Hamiltonian is transformed to normal form along the scattering coordinate, and the value of the normal-mode frequency is then used to determine the appropriate zero-point energy. Another possible choice, and one that is most appropriate for many systems of chemical interest is the ''adiabatic'' action, I_a, which gives the classical effective Hamiltonian

$$H_{\text{equiv}} = H(\mathbf{I_a},\phi_\mathbf{a})(\Theta(I_a - I_G))^2. \tag{7}$$

In subsequent discussion, we term this the adiabatic action billiard (AAB).

The efficacy of the AAB is demonstrated in a simple 1-dimensional nonreactive scattering example, where the adiabatic approximation holds well.

We study the model scattering system[25] with classical Hamiltonian

$$H(p,q,P,Q) = \frac{P^2}{2\mu} + \frac{e^{-Q}}{2} + \frac{p^2}{2} + \frac{\Omega^2 q^2}{2} \tag{8}$$

describing a collinear atom–diatom collision; p,q refer to the bound degree of freedom, while P and Q are the scattering momentum and coordinate, respectively. The frequency is given by

$$\Omega(Q) = \omega - C\ \text{sech}(\gamma Q), \tag{9}$$

ω, γ, and C being parameters. This system can be rewritten in the form

$$H(p,q,P,Q) = \frac{P^2}{2\mu} + V(q,Q) + \frac{p^2+\omega^2 q^2}{2}, \tag{10}$$

$$V(q,Q) = e^{-Q}/2 + C_q^2\ \text{sech}(\gamma Q)(\text{sech}(\gamma Q)/2 - \omega) \tag{11}$$

from which one sees that the zeroth order action is $I = (p^2+\omega^2 q^2)/2\omega$, while the adiabatic action[25] is

$$I_a(Q) = \frac{p^2+\Omega^2 q^2}{2\Omega}. \tag{12}$$

An important difference is that I is not a function of the scattering coordinate, while the adiabatic action, I_a is manifestly so. Asymptotically, though, $I_a(Q \to \infty) \to I$.

Consider a typical occurrence of the ZPL. Shown in Fig. 1 is an illustrative plot of the final action versus the initial phase (shown as circles) for the above system with parameters $\omega = 1$, $\gamma = 1/2$, $C = 1/2$. We take the initial action as $I = 1.5$ and the kinetic energy to be 0.5 in reduced units. It can be seen that for a range of initial phase, the final action is less than $I_G = 0.5$, which is the action of the ground state. Superimposed (crosses) is the final action versus initial angle plot obtained from using the AB, Eq. (6), with I, the zeroth-order action. While this procedure does not affect the majority of trajectories that have final action $\geqslant I_G$, it does correct some trajectories that have final action exceeding I_G. This is obviously due to the fact that at some point in time during

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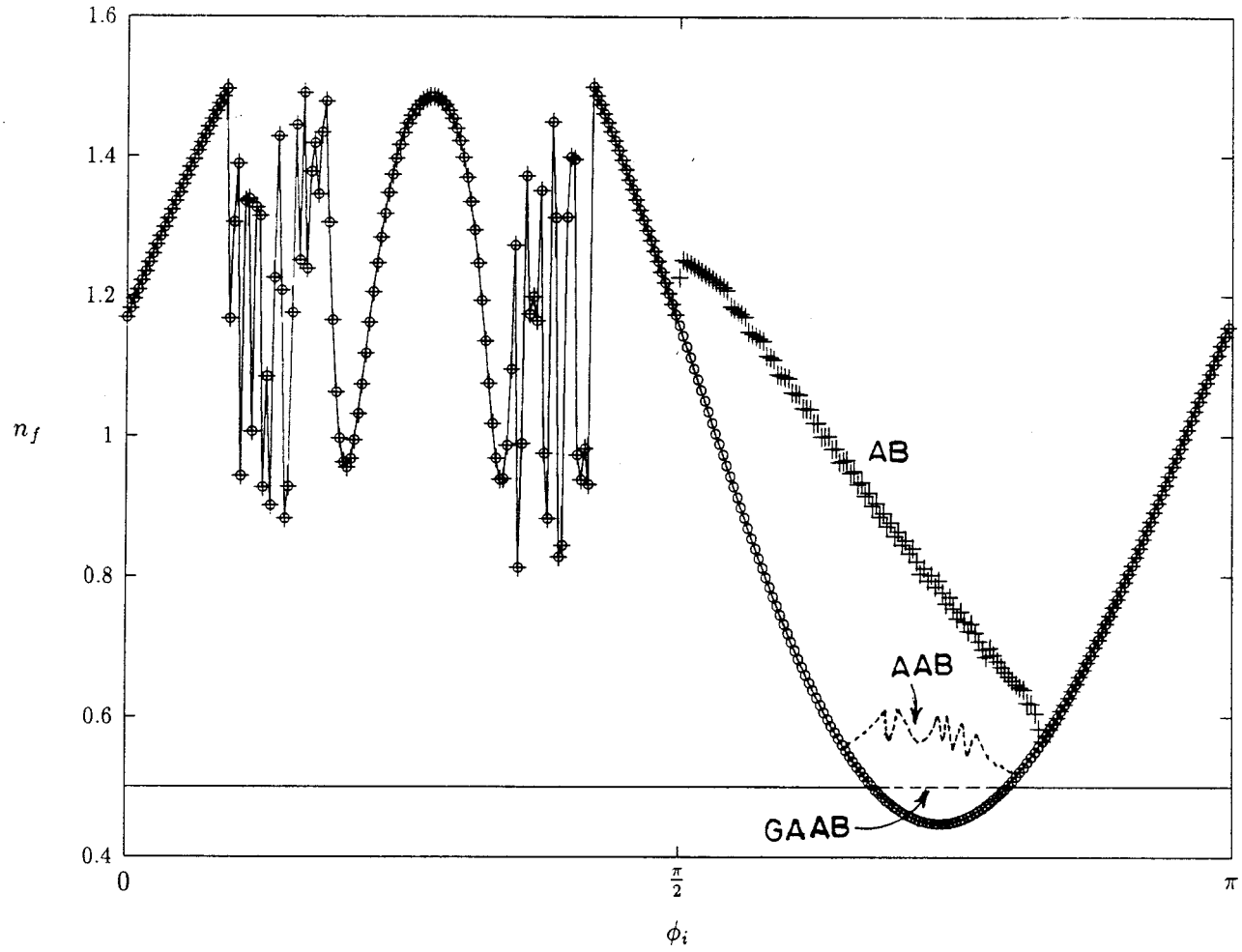

FIG. 1. Final quantum number, n_f vs the initial phase, ϕ_i for the model collinear atom–diatom system with initial $n_i=1$. Results are shown for the final action (a) when no correction is imposed (circles), (b) when the simple action billiard is introduced (crosses), (c) with the adiabatic action billiard (dotted line), and (d) the generalized adiabatic action billiard (dashed line).

the collision, the action falls below 0.5, leading to a modification of the dynamics by the Θ function boundary in the classical phase space.

Such overcorrection is reduced significantly if we use AABs—Eqs. (7) and (12), and the results are included in Fig. 1 (dotted line), where we see that essentially only those trajectories that show a ZPL are corrected. Furthermore, the correction introduced has the effect of bringing the final action to the minimum possible, i.e., to I_G.

It is possible to generalize the action billiard approach even further, as has been discussed by AO,[10] by replacing the Hamiltonian in Eq. (6) by

$$H_{\text{gen}}=(H(\mathbf{I_a},\phi_\mathbf{a})+A)(\Theta_\lambda(I_a-I_G))^2, \tag{13}$$

where A is a constant. With appropriate choice of A, it is possible to ensure that the effect on the dynamics is minimal—only leaky trajectories are affected: for a choice of $A=2$, this result is shown in Fig. 1 as dashed line (GAAB).

The choice of AABs in the model system, Eq. (8) above is particularly suitable,[25] since the system was essentially designed to be one where the adiabatic approximation would hold. We also feel that since nonlinear effects are incorporated already into the adiabatic action, this should be preferable to using normal-mode actions in the AB. In a variety of scattering cases, the adiabatic approximation is known to be a reasonable one, and hence the procedure suggested here is likely to have a wide applicability. In the next section we apply the above formalism to the case of (He,H_2^+) collisions.

III. He,H_2^+ DYNAMICS

A. Collinear collisions

Quantum mechanically computed reaction probabilities (P_v^R) for collinear collisions[26,27] of (He,H_2^+) are plotted as a function of E_{tot} in Fig. 2 for different vibrational states of H_2^+, and compared with the QCT results with and without neglecting the leaky trajectories. It is seen that for energies above the classical barrier (0.81 eV) but below the $E_{\text{th}}^{\text{QM}}$, $P_v^R\neq 0$. This is clearly unphysical and therefore it is fair[7] to ignore them and focus attention on the results for $E_{\text{tot}}\geqslant E_{\text{th}}^{\text{QM}}$. But for the undulations in the QM result, the QCT (ZPE uncorrected) results are, on an average, in agreement with the quantal results, particularly for $v=0,1$. For $v=2$ the QCT

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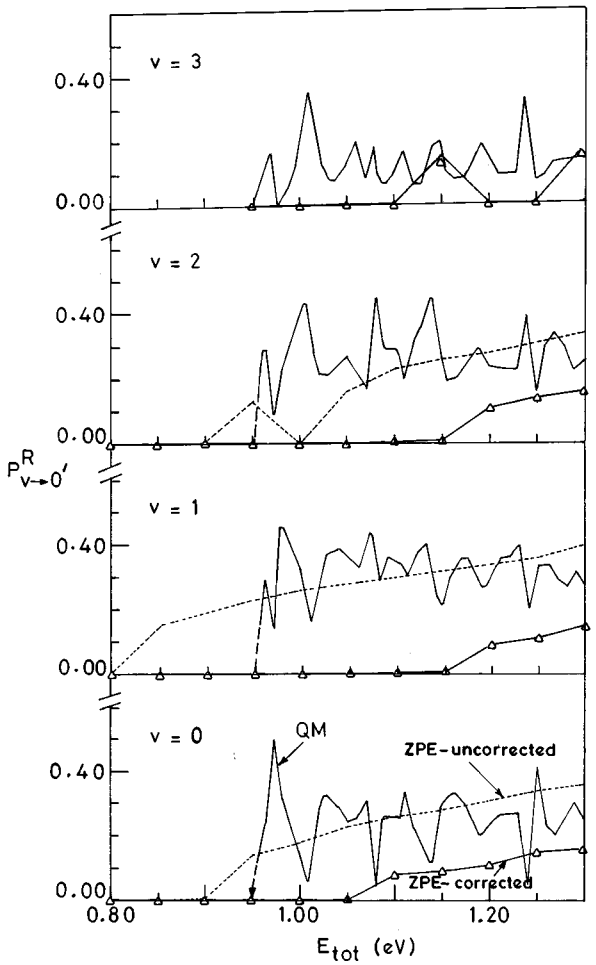

FIG. 2. Comparison of the standard (ZPE uncorrected) and the ZPE-corrected QCT results and the QM results for collinear $He+H_2^+$ ($v=0$–3) collisions. The arrow along the abscissa indicates the E_{th}^{QM}.

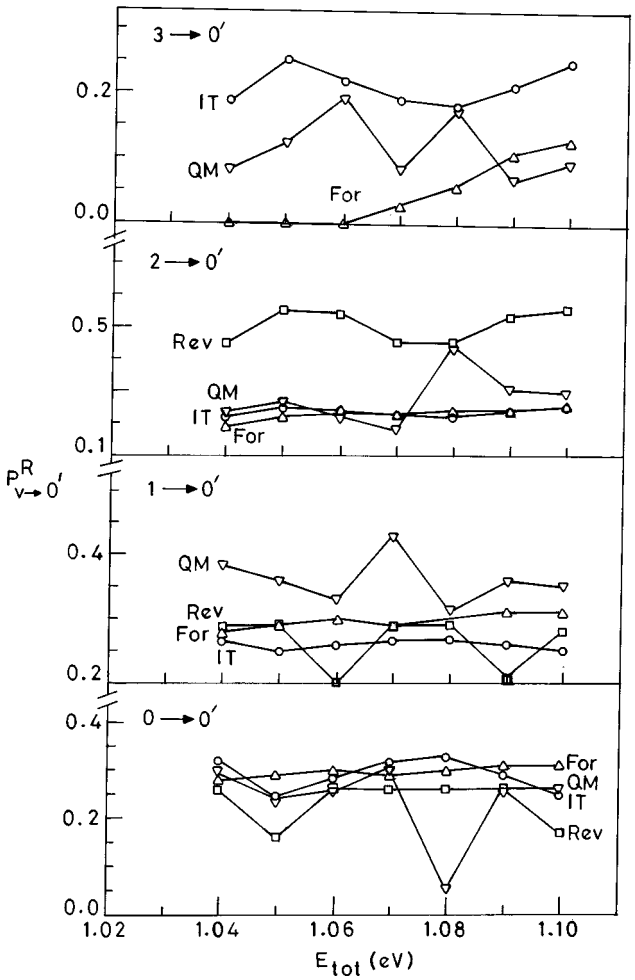

FIG. 3. Comparison of $P^R_{v\to 0}$ values obtained from the reverse QCT histogram (rev) and the moment methods (IT) with those obtained from the standard QCT method (for) and the QM approach.

results differ significantly from the QM results, near $E_{tot}=1.0$ eV, but again, at higher E_{tot}, the ZPE-uncorrected QCT results are, on an average, in accord with the QM results. For $v=3$, the reaction becomes classically forbidden for $E_{tot}<1.10$ eV. Neglecting the trajectories that show zero-point leak leads to a dramatic underestimate of P_v^R for the entire energy range shown in Fig. 2 for $v=0$, 1 and 2, while for $v=3$, it does not make any difference as there are hardly any reactive trajectories.

We have also examined the trajectories in the reverse direction, that is, for the reaction

$$HeH^+(v'=0)+H\rightarrow He+H_2^+(v) \tag{14}$$

in the neighborhood of $E_{tot}=1.05$ eV. For $E_{tot}\leqslant 1.30$ eV, only the $v'=0$ channel of HeH^+ is open. By the principle of microscopic reversibility, $P^R_{v\to 0}=P^R_{v\leftarrow 0}$. For the QCT calculations this equality is not expected to hold rigorously as histogramming is done for the final state only and not for the initial state in either direction. Results obtained by the reverse QCT histogram technique are comparable to those obtained from the forward trajectories for $v=0$ and 1 as illustrated in Fig. 3. For $v=2$ and 3 $(P_v^R)^{rev}$ values are significantly different from the $(P_v^R)^{for}$ and the $(P_v^R)^{QM}$.

All trajectories starting from $v'=0$ of HeH^+ are reactive and they end up in states $v=0$, 1, or 2 of H_2^+. Although the $v=3$ channel is open energetically, it is forbidden dynamically[28]—no trajectory starting from $v'=0$ ends up in $v=3$ in this energy range. We therefore computed the first moment of vibrational energy for the product (H_2^+) in the reverse direction and then, using the information theoretic approach, computed $(P_v^R)^{IT}$ values. The results, which are included in Fig. 3, are closer to $(P_v^R)^{for}$ than to $(P_v^R)^{rev}$ for $v=0$–2. For $v=3$, there are, of course, no $(P_v^R)^{rev}$ values and the $(P_v^R)^{for}$ values are lower than the $(P_v^R)^{QM}$ at lower E_{tot}. In contrast, $(P_v^R)^{IT}$ values are higher than $(P_v^R)^{QM}$. Therefore, we see that computing the reverse trajectories does not improve the QCT results vis-a-vis the QM values for this system.

In order to test the utility of some of the other approaches suggested in the literature, we examined the collinear [He,H_2^+ ($v=0$)] collisions at $E_{trans}=0.5$ eV, below the reaction threshold. Several trajectories led to H_2^+ with E_{vib} below its ZPE. Reversal of the sign of the momentum p_y along the H_2^+ vibrational coordinate, whenever E_{vib} decreased below the ZPE of H_2^+, prevented the leak for sure, but *all* trajectories, including the ones that did not show any

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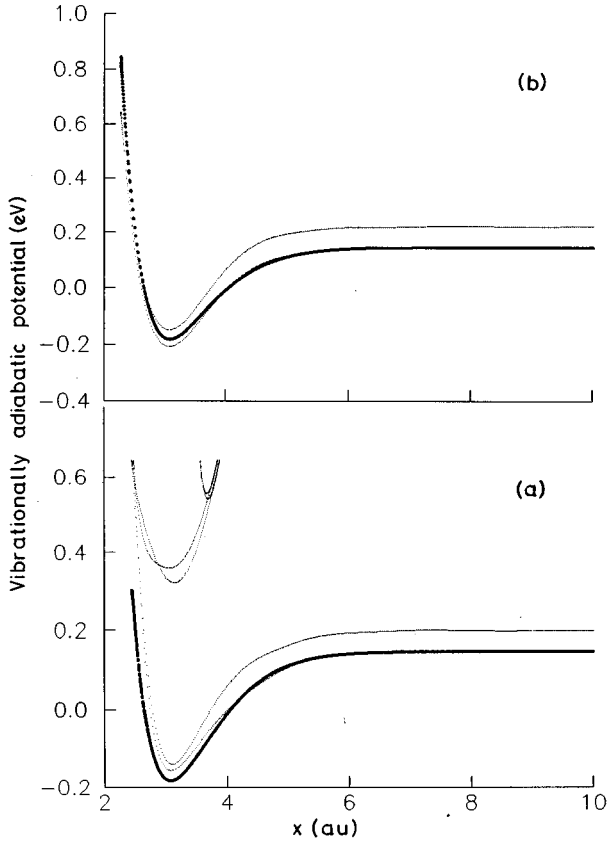

FIG. 4. Illustration of a trajectory (for $v=0$ of H_2^+, $E_{trans}=0.5$ eV) that (a) does not leak below $v'=0$ asymptotically and also has $E_{vib} \geqslant V_0$ throughout and (b) does not leak below $v'=0$ asymptotically but has $E_{vib}<V_0$ during the course of the collision. For reference, the vibrational adiabatic potential for $n=0$ of H_2^+ as a function of the approach coordinate (solid line) is included.

leak earlier were altered unnecessarily, leading to chaotic behavior in almost all of them.

In order to impose the AAB, we first need to examine the vibrationally adiabatic potential $V_0(x)$ for the state $n=0$ of H_2^+. This is shown as a function of the approach coordinate x (the center-of-mass separation between He and H_2^+) in Fig. 4(a). Clearly $\lim_{x\to\infty} V_0(x)=E_{v=0}$. Superimposed on $V_0(x)$ in Fig. 4(a) are the values of the vibrational energy for H_2^+ at each step during the course of a trajectory which leads to $E_{vib} \geqslant E_0$ (within ± 0.008 eV) and hence does not warrant any correction during its course. Clearly, if we use the asymptotic action as a criterion for testing the leak, we will unnecessarily alter the course of this trajectory. Such a system is ideal for using a vibrational AAB, from which we conclude that this trajectory does not, in actual fact, leak and hence does not warrant any intervention. Results from the AAB are plotted in Fig. 5 and show that the overcorrection has been avoided for a number of trajectories—a clear improvement over the simple AB approach. Unfortunately, there are still a number of trajectories which do not lead to E_{vib} below the ZPE at the end of the collision and yet have been corrected. An example is shown in Fig. 4(b). The trajectory which shows no leak asymptotically, actually, dips below $V_0(x)$ and hence contrives to get corrected unnecessarily. We have shown elsewhere[27] that the collinear (He,H_2^+) collisions are *not* strictly vibrationally adiabatic which is one reason why the AAB approach also does not lead to completely satisfactory results. One can therefore anticipate that the AAB approach will similarly meet with little success for the case of reactive collisions in this systems.

B. 3D collisions

In Fig. 6 we compare the 3D QCT results with the 3D quantal results for zero total angular momentum ($J=0$). For $v=0$ both the QCT and the QM calculations yield a P_v^R close to zero and hence they are not included in Fig. 6. For $v=1$–4, it is clear that the ZPE-uncorrected QCT results are closer to the quantal results than the corrected. Neglecting the ZPE leaky trajectories results in a substantial underestimate of P_v^R. In order to make sure that our conclusion is not dependent on the choice of J, we have compared cross section (σ^R) values computed by the 3D QCT method with the 3D quantal results for $v=1$–3 and found that neglecting the leaky trajectories results in a gross underestimate of σ^R for all three v states. The inclusion of the leaky trajectories, on the other hand, leads to an overestimate of σ^R near the threshold for $v=1$ and 2. With increase in energy, the uncorrected σ^R values converge to the QM result for $v=1$ and 2. For $v=3$, the uncorrected QCT results are in excellent agreement with the quantal results over the entire energy range. Therefore, it is fair to conclude that the neglect of the leaky trajectories in computing P_v^R and σ^R is unwarranted and that except near the threshold, the uncorrected 3D QCT results can be relied upon.

IV. SUMMARY AND CONCLUSION

In this paper we have introduced a set of new techniques for preventing the zero-point leak in classical trajectory simulations of molecular systems. These methods essentially construct impenetrable barriers (action billiards) in the classical phase space by appealing to an interpretation of the classical-quantum equivalence between a truncated Hilbert space, and the corresponding classical phase space. Through this procedure of altering the classical dynamics, the instantaneous action variable is always required to remain above the quantum mechanically allowed minimum, and this enforces the preservation of the zero-point energy. Since the action variables can be defined in a variety of ways depending on the coordinates used, a given system may dictate a particular choice of the ''most appropriate'' action variable. Thus, for example, this may be the asymptotic action, when this method becomes equivalent to that of Refs. 8 and 9, or the normal mode action, when this becomes one of the methods of Ref. 9. Since the adiabatic principle has such wide-ranging applicability in a variety of situations of chemical interest, in many cases, the action variable corresponding to the adiabatic coordinates may be appropriate. This leads to the adiabatic action billiard. Through application to a model problem, we demonstrate the efficacy of the procedure and its refinements, the generalized adiabatic action billiard.

An application of considerable practical as well as theoretical interest is that of (He,H_2^+) collisions which have been used as a test case to examine the various approaches that

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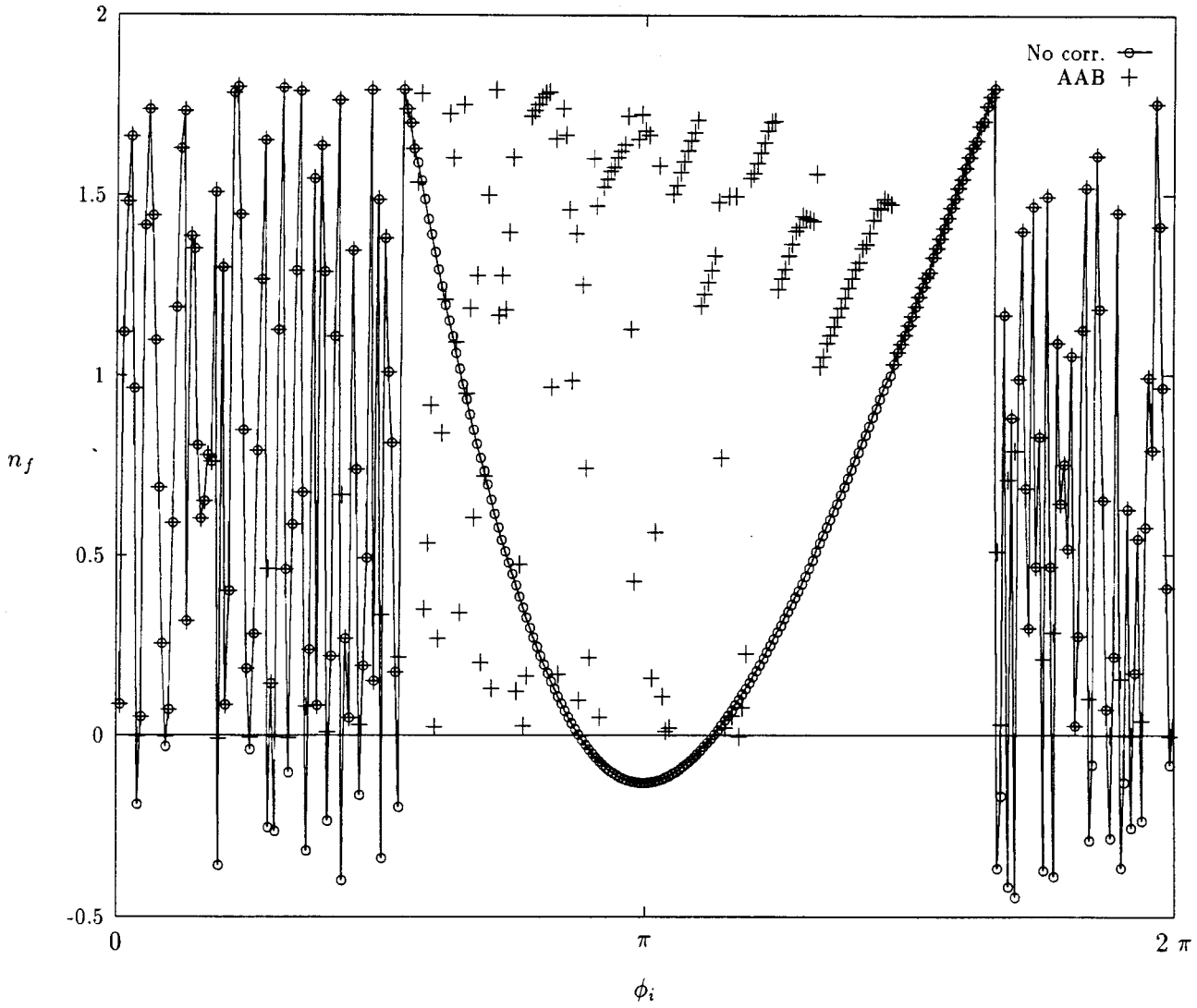

FIG. 5. Plot of the final quantum number, n_f vs initial vibrational phase (ϕ_i) obtained by correcting only trajectories that dip below the V_0, for $v=0$ of H_2^+ at $E_{\text{trans}}=0.5$ eV. The uncorrected results (○) are included for comparison.

have been tried over the years to circumvent the problem of adiabatic or zero-point leak. While it appears reasonable to neglect reactive trajectories for energies below the $E_{\text{th}}^{\text{QM}}$, neglect of the leaky trajectories leads to a gross underestimation of P_v^R for $E_{\text{tot}} \geqslant E_{\text{th}}^{\text{QM}}$. The QCT results are not expected to reproduce the quantal reactive scattering resonances in the system and they do not. But on an average, the uncorrected QCT results are in excellent agreement with the QM results for $v=0$ and 1. For $v=2$, the agreement is less and for $v=3$, the reaction becomes classically forbidden. The reverse QCT calculations also suffer from the problem of leaky trajectories and the uncorrected results from the reverse trajectories are very close to the uncorrected results from the forward trajectories. The reverse trajectories also confirm the classical forbiddenness of the $v=3 \rightarrow v'=0$ transition. This problem is circumvented to some extent by computing the first moment of energy transferred and using the information-theoretic synthesis.

Comparison of 3D QCT-computed reaction probabilities for zero total angular momentum and the reaction cross section values with the corresponding 3D QM results shows that neglecting the leaky trajectories leads to a dramatic underestimate of the reaction probability and the reaction cross section respectively. Oddly enough, despite the fact that the leaky trajectories seem unphysical, there does not seem to be any justification for arbitrarily neglecting them. The various corrections suggested in the literature, as well as the generalized action billiards introduced here have not been of much practical value.

Insofar as the (He,H_2^+) system is concerned, it is heartening that for energies well above the $E_{\text{th}}^{\text{QM}}$, there are very few leaky trajectories and the 3D QCT results do not seem to be influenced by them as any correction that results, falls within the statistical error estimates associated with the Monte Carlo sampling of initial conditions.

Investigations for collinear (nonreactive as well as reactive) collisions reveal that the simple AB approach leads to overcorrection in that leaky as well as nonleaky trajectories

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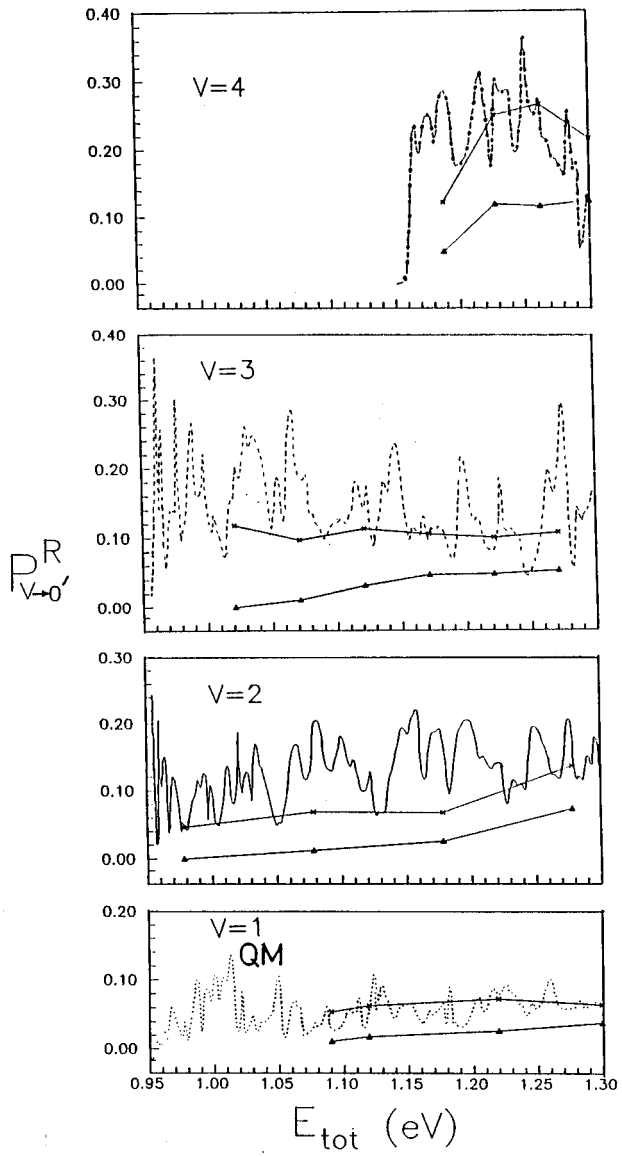

FIG. 6. Reaction probability $P^R_{v\to 0}$ (summed over final HeH^+ rotational states) for the reaction [Eq. (2)] as a function of E_{tot} for $v=1$–4 of H_2^+. The 3D time-independent QM results are reproduced from Ref. 22. 3D QCT results: (x) ZPE-uncorrected, ($\triangle$) ZPE-corrected.

get altered. The reversal of sign of the momentum along the H_2^+ vibrational coordinate at the point of the vibrational energy dipping below the asymptotic zero-point energy is tantamount to giving a ''kick'' to the vibrator. The soft action billiards approach works even better as it avoids the kicks by introducing a smoothened step function. Using the vibrationally adiabatic potential for zero action at intermediate configurations as the lower bound for H_2^+ vibrational energy is the procedure of choice. Fewer asymptotically nonleaky trajectories get altered, but the problem is not completely satisfactorily resolved since collinear He H_2^+ dynamics is fairly nonadiabatic. In systems that conform more fully to a vibrationally adiabatic description, the adiabatic action billiard based methods suggested in the present paper should have a strong advantage over other existing methods.

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