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Multitrajectory semiclassical method for the treatment of nonadiabatic atom-molecule collisions

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The problem of the choice of a trajectory in the time-dependent semiclassical treatment of nonadiabatic molecular collisions is reconsidered. The purpose of the work is to improve the semiclassical description of vibronic transitions in conditions where quantal calculations are hardly feasible. In order to bring out our proposal, the investigation is carried out in the framework of the infinite-order sudden approximation where quantal calculations are tractable and thereby provide a reliable testing ground. The way in which a classical trajectory emerges when deriving the time-dependent equations from the quantal ones is reexamined. Specific features are pinpointed which draw one's attention to the idea of a multitrajectory approach. A proposal is formulated and applied to vibronic charge transfer in the $H^+ + O_2$ collision. The proposed multitrajectory treatment is found to be superior to the other semiclassical treatments based on a simple common trajectory.

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I. INTRODUCTION

The past decade has witnessed the emergence of a new generation of experiments in the field of vibronically nonadiabatic atom-molecule collisions [1]. An important concern of these experiments has been the acquisition of state-specific dynamical information and angular distributions of the products. These experimental trends have been accompanied by an intense theoretical activity [2]. Though theory has achieved nice successes in explaining and reproducing many features of the experimental findings, detailed agreement is still not always met. Weaknesses of the theory lie either in the approximations made to obtain relevant potential-energy surfaces and related couplings or in the simplifying assumptions which make the dynamics tractable. The present contribution is concerned with a specific issue in the latter category of problems.

It is well known that a full quantum-mechanical treatment of the dynamics of nonadiabatic atom-molecule collision is prohibitively burdensome, especially at extrathermal energies. This situation owes particularly to the large number of open rotational states involved [2(a),3]. Invoking the shortness of typical collision times as compared to characteristic molecular rotation periods, two theoretical approaches have been proposed [2,3]. Both approaches are based on a sudden approximation *vis á vis* the molecule rotation: the molecule orientation enters the theory only as a fixed parameter. One theoretical approach makes use of the infinite-order sudden approximation (IOS) [2(a),2(c),3]. It assumes that *all* rotation motions are so slow that there is virtually no difference between the space-fixed reference frame and the body-fixed frame that accompanies the tumbling of the atom-molecule system as a whole. In this case, assuming that the molecule orientation remains fixed amounts to hold the relative angle $\gamma = (\mathbf{r}, \mathbf{R})$ fixed; $\mathbf{r}$ is the molecule bond vector, $\mathbf{R}$ the relative atom-molecule vector (r, R, γ form a set of internal Jacobi coordinates). The second theory makes use of the fixed-rotor approximation whereby the molecule orientation is held fixed in the space-fixed reference frame [2(a),2(b),3]. One advantage of the IOS approach is that it lends itself to a quantal treatment of the collision. However, inasmuch as it constrains the scattering to be governed by spherical potentials and couplings for each γ value [3], it forces the collision system to "see" the same interactions in the incoming and outgoing stages of the encounter. This constraint somewhat spoils the description of the actual anisotropy of the problem. The fixed-rotor approximation is more realistic in this respect. Yet, the corresponding quantal treatment is still prohibitively burdensome. This owes to the proliferation of the number of coupled equations one needs to treat in order to describe the coupling of relative angular momenta arising from the anisotropy of the potential [4]. This difficulty has been circumvented by using a semiclassical approach whereby the relative motion is treated classically and evolves along a trajectory $\mathbf{R}(t)$, whereas vibronic motions are treated quantally and obey a time-dependent Schrödinger equation [2(a),2(b),3]. We have recently shown in this context that the fixed-rotor picture provides a valid approximation at low extrathermal energies down to ≈ 1 eV/amu [5]. A problem that still remains open in the vibronic semiclassical treatment of nonadiabatic molecular collisions is the choice of the trajectory which is not precisely defined by the theory. Possible choices are the following.

(1) The trajectory deriving from the entrance [3,6] vibronic potential-energy surface.

(2) The trajectory associated with an arithmetic or geometric average of the involved potential surfaces [7].

(3) The trajectory obtained by weighting each potential by the instantaneous probability that the system be in the corresponding vibronic state [8].

(4) The SCECT (semiclassical self-consistent energy-

conserving trajectory) associated with the instantaneous expectation value of the quantal vibronic Hamiltonian [9].

The latter three choices attempt to force in the fact that in a nonadiabatic process the system evolves simultaneously on *several* potential-energy surfaces. Obviously, for potentials having similar shapes and lying close to one another [Figs. 1(a) and 1(b)] any of the above suggestions is acceptable. This is particularly the case for *pure vibrational* excitation problems:

$$A^{+}+BC(v)\rightarrow A^{+}+BC(v') ,$$

where the potential-energy surfaces correlating with each state v' of the BC vibrational manifold remain nearly parallel, except possibly near potential walls [3]. The success of semiclassical calculations, in the IOS framework, in reproducing quantal results for *pure vibrational excitation* in the $H^{+}+O_2$ collision provides a nice illustration of such a case (see Sec. III below). Yet, it is well acknowledged that for potentials having quite different shapes as those schematized in Fig. 1(c) the choice of the trajectory is an uncertain issue, especially at low energies [7(b),8]. This is actually the case for the $H^{+}+O_2$ charge-transfer collision. In a previous work [3] semiclassical calculations have been carried out for this process, in the IOS framework, using either the SCECT or the trajectory deriving from the entrance potential (see Sec. III C). Though often recommended in the literature, the SCECT calculation did not reproduce satisfactorily the quantal differential cross sections for charge transfer. The trajectory deriving from the entrance potential was more successful in this respect; still, inspection of the impact-parameter dependence of state-to-state transition probabilities revealed a clear dephasing of interference structures when compared to the corresponding quantal results. These shortcomings have led us to investigate, in the work reported below, whether better or optimum choices of the trajectory can be made. This quest has been undertaken in the IOS framework where quantal calculations are feasible and provide testing grounds for an eventual prescription. Our goal is of course not to build the *nec plus ultra* semiclassical treatment of the IOS approximation but to export the sought prescription to another context, namely, the fixed-rotor approximation. The objective is to increase the reliability of semiclassical calculations in a context where, as already mentioned above, quantum-mechanical calculations are not yet tractable.

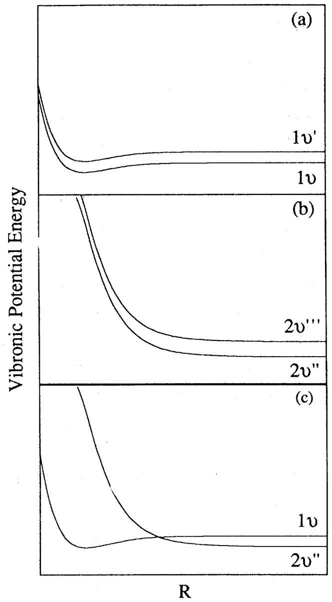

FIG. 1. Typical shapes of potential-energy curves involved in vibronically nonadiabatic transitions. (a) and (b) illustrate cases of vibronic potential-energy curves that correlate with a pair of vibrational levels belonging to a common electronic state [e.g., $A^{+}+BC(v)$ and $A+BC^{+}(v'')$, respectively]. The energy curves in (a) or (b) are nearly parallel and lie close to each other. For each case a common classical trajectory is valid and may be found easily. (c) illustrates the case of potential-energy curves having different shapes and correlating with vibrational levels that belong to different electronic states [say, one state of (a) and one state of (b)]. The present article addresses the problem of finding appropriate classical trajectories for the three cases (a), (b), and (c) simultaneously.

The outline of the paper is as follows. In Sec. II we briefly recall how the notion of a classical trajectory emerges when one proceeds to derive the semiclassical equations of motion from the quantal ones [7]. This enables us to pinpoint specific features, already noted by others [7(a)], that draw one's attention to the idea of a multitrajectory approach. A proposal is thereafter made to obtain scattering amplitudes for vibronically nonadiabatic processes. In Sec. III the method is applied to the case of vibrational excitation (VE) and vibronic charge transfer (VCT) in the $H^{+}+O_2$ collision at a center-of-mass energy, $E=23$ eV, where quantal IOS calculations are available. Our conclusions are presented in Sec. IV.

II. THE PROPOSAL OF A MULTITRAJECTORY APPROACH

A. The passage from a quantal to a semiclassical treatment

As is well known [2(c),3] the IOS approximation amounts to performing vibronic close-coupling calculations for *central* potentials and couplings parametrized by the relative angle γ. Except if stated otherwise, this parameter will be kept implicit in all the foregoing derivations and discussions. Without loss of generality we choose to expand the total wave function of the collision system in a vibronic basis describing the molecule's vibration and all electronic degrees of freedom. The quantal equations of relative (atom-molecule) motion thereafter become formally the same as those encountered in atom-atom collision problems. After effecting a partial-wave expansion [11] one arrives at a system of coupled second-order differential equations for each relative angular momentum l:

$$\left[\frac{1}{2\mu}\frac{d^2}{dR^2}+E-\varepsilon_i-H_{ii}(R)-\frac{l(l+1)}{2\mu R^2}\right]\mathcal{F}_{il}(R) = \sum_{j\ (\neq i)} H_{ij}(R)\mathcal{F}_{jl}(R) . \quad (1)$$

μ is the reduced atom-molecule mass, R the relative distance, and E the total energy; i is a vibronic state and ε_i the corresponding internal energy at infinite atom-molecule separation. At this point we only need to know that $H_{ii}(R)$ is a potential term and $H_{ij}(R)$ a coupling between two vibronic states; more explicit definitions will be given in Sec. III A. We elect throughout to work in a diabatic representation [10] and thereafter $H_{ij}(R)$ is a scalar operator. Both $H_{ii}(R)$ and $H_{ij}(R)$ tend sufficiently fast to zero as $R\rightarrow\infty$ [11].

Following the usual procedure [12], the $\mathcal{F}_{il}(R)$ functions are sought in the form

$$\mathcal{F}_{il}(R)=[k_{il}(R)]^{-1/2}\{a_{il}^{-}(R)\exp[-i\mathcal{S}_{il}(R)] -a_{il}^{+}(R)\exp[i\mathcal{S}_{il}(R)]\} , \quad (2a)$$

$$k_{il}(R)=\left\{2\mu\left[E-\varepsilon_i-H_{ii}(R)-\frac{(l+\frac{1}{2})^2}{R^2}\right]\right\}^{1/2} , \quad (2b)$$

$$\mathcal{S}_{il}(R)=\int_{(\ )}^{R}k_{il}(R')dR'+\frac{\pi}{4} . \quad (2c)$$

$k_{il}(R)$ is seen to take into account Langer's substitution of $l(l+1)$ by $(l+\frac{1}{2})^2$ [11(b)]. The lower bound of the action integral [Eq. (2c)] is usually taken, according to the JWKB approximation [11(b),13], to be the turning point R_i^{Tl} defined by

$$k_{il}(R_i^{Tl})=0 . \quad (3)$$

The $\pi/4$ term then arises from the connection of the elastic solutions in the classical and nonclassical regions of motion. Here, we do not specify the lower bound of this integral to provide some freedom in the foregoing discussions; the $\pi/4$ term is retained for convenience. It is worth mentioning that, unlike some earlier works [11(b),12(c),12(e),12(f)], we do not impose from the outset a common wave number in the above expressions as this procedure does not specify the way in which the common wave number is to be chosen. The form of wave functions in Eq. (2) conveys the idea that "one may attempt to describe inelastic scattering of heavy particles using a superposition of elastic-type JWKB wavelets in each channel i weighted by proper probability amplitudes" $a_{il}^{\pm}(R)$ [2(a)].

The replacement of each $\mathcal{F}_{il}(R)$ function by two unknowns $a_{il}^{\pm}(R)$ gives the freedom to impose an arbitrary condition between the latter two; for convenience one chooses [7(b)]

$$\exp[i\mathcal{S}_{il}(R)]\frac{da_{il}^{+}}{dR}=\exp[-i\mathcal{S}_{il}(R)]\frac{da_{il}^{-}}{dR} . \quad (4)$$

One then plugs these relations in Eq. (1) and makes use of the following approximations.

(1) The JWKB approximation [11(b),13,14]

$$k_{il}(R)\gg 1 , \quad (5a)$$

$$[k_{il}(R)]^{-3/2}\frac{d^2[k_{il}(R)]^{-1/2}}{dR^2}\ll 1 . \quad (5b)$$

(2) The high-frequency approximation: owing to the importance of $k_{il}(R)$ ($\gg 1$), terms involving $\exp\{\pm i[\mathcal{S}_{il}(R)+\mathcal{S}_{jl}(R)]\}$ ($\forall i,j$) phase factors oscillate much faster than those involving $\exp\{\pm i|\mathcal{S}_{il}(R)-\mathcal{S}_{jl}(R)|\}$ factors and have comparatively negligible contributions. This leads to

$$i\frac{da_{il}^{\pm}(R)}{dR}=\sum_{j\ (\neq i)}\mu\frac{H_{ij}(R)}{[k_{il}(R)k_{jl}(R)]^{1/2}}a_{jl}^{\pm}(R) \times\exp\{\pm i[\mathcal{S}_{jl}(R)-\mathcal{S}_{il}(R)]\} . \quad (6)$$

It is usually at this point that a common classical trajectory is introduced in order to arrive at the corresponding semiclassical time-dependent equations [2(a),2(b),3,6–9,11,12]

$$\frac{idc_{il}(t)}{dt}=\sum_{j\ (\neq i)}H_{ij}(R)c_{jl}(t) \times\exp\left\{-i\int^{t}[\varepsilon_j+H_{jj}(R) -\varepsilon_i-H_{ii}(R)]dt'\right\} . \quad (7)$$

In that treatment the coefficients $c_{jl}(t)$ represent, for each partial wave l, the probability amplitude to find the system in state j [2(a),2(b),3,6–9,11,12]. The new variable t arises from a prescription for a classical trajectory establishing a relation between R and t. Once this is done, the remainder of the procedure consists of identifying $c_{jl}(t<0)$ and $c_{jl}(t>0)$ with $a_{jl}^{-}(R)$ and $a_{jl}^{+}(R)$, respectively.

For each i, j pair of states, it is immediately seen that two definitions of a classical trajectory suggest themselves:

$$\mathring{R}_{ij}^{(G)l}=\frac{[k_{il}(R)k_{jl}(R)]^{1/2}}{\mu} , \quad (8)$$

$$\mathring{R}_{ij}^{(A)l}=\frac{k_{il}(R)+k_{jl}(R)}{2\mu} . \quad (9)$$

The way in which the geometric mean velocity (G) comes about is obvious from the comparison of Eqs. (6) and (7). The appearance of the arithmetic average (A) velocity is somewhat more subtle [7(a)]. If some common trajectory exists it assumes a common lower bound R_{ij}^{Tl} for the integrals defining $\mathcal{S}_{jl}(R)$ and $\mathcal{S}_{il}(R)$; this yields

$$\mathcal{S}_{jl}(R)-\mathcal{S}_{il}(R)\simeq\int_{R_{ij}^{Tl}}^{R}\frac{k_{jl}^2(R')-k_{il}^2(R')}{k_{il}(R')+k_{jl}(R')}dR' \simeq-\int_{R_{ij}^{Tl}}^{R}[\varepsilon_j+H_{jj}(R')-\varepsilon_i -H_{ii}(R')]\frac{dR'}{\mathring{R}_{ij}^{(A)l}} . \quad (10)$$

A choice of $\mathring{R}$ different from $\mathring{R}_{ij}^{(A)l}$ in Eq. (9) is thereby likely to produce an incorrect dephasing of interference structures in the impact-parameter dependence of the nonadiabatic transition probabilities. As recalled in Sec. I this is precisely the shortcoming of the common trajectory deriving from the entrance potential. These remarks suggest that the appropriate trajectory would be the one associated with the average potential $V_{ij}^{(A)}(R) = [H_{ii}(R)+H_{jj}(R)]/2$ which yields, when taking the centrifugal term $(l+\frac{1}{2})^2/R^2$ into account, the classical radial velocity $\mathring{R}_{ij}^{(A)l}$.

Inasmuch as there is one trajectory of this sort for each pair of states i,j this prescription implies, for a total number of states N, the use of $N(N-1)/2$ trajectories. The proposed semiclassical multitrajectory description thus descends from the quantal one following a well-established procedure. Its newness lies in the use, for reasons just stated, of $\mathring{R}_{ij}^{(A)l}$ instead of a common $\mathring{R}$ in Eq. (10).

B. The scattering matrix

The asymptotic behavior of Eq. (2a) when $R \to \infty$ can be set in the form

$$\mathcal{F}_{jl}(R) \sim \frac{1}{k_j^{1/2}} \left[a_{jl}^{-}(R) e^{-i(\eta_{jl}+k_jR-l\pi/2)} - a_{jl}^{+}(R) e^{i(\eta_{jl}+k_jR-l\pi/2)} \right], \tag{11a}$$

$$k_j = k_{jl}(R \to \infty),$$

$$\eta_{jl} = \lim_{R\to\infty} [\mathcal{S}_{jl}(R) - k_jR + l\pi/2]$$

$$= \int_{(\ )}^{R} k_{jl}(R')dR' - \int_{b_j}^{R} \kappa_{jl}(R')dR' \quad (R \to \infty)a, \tag{11b}$$

$$b_j = (l+\tfrac{1}{2})/k_j,$$

$$\kappa_{jl}(R) = \left[2\mu \left[E - \varepsilon_j - \frac{(l+\frac{1}{2})^2}{R^2} \right] \right]^{1/2}.$$

The comparison of Eq. (11) with the required asymptotic behavior,

$$\mathcal{F}_{jl}(R) \sim \frac{1}{k_j^{1/2}} \left[\delta_{0j} e^{-i(k_0R-l\pi/2)} - S_{0j,l} e^{i(k_jR-l\pi/2)} \right], \tag{12}$$

yields the $0 \to j$ scattering matrix element:

$$S_{0j,l} = \frac{a_{jl}^{+}(R\to\infty)}{a_{0l}^{-}(R\to\infty)} e^{i(\eta_{jl}+\eta_{0l})}$$

$$= \frac{c_{jl}(t\to+\infty)}{c_{0l}(t\to-\infty)} e^{i(\eta_{jl}+\eta_{0l})}. \tag{13}$$

The phase difference defining η_{jl} [Eq. (11b)] may be handled in the same way as done in Eq. (10). With the approximation that the lower bound of the integral defining $\mathcal{S}_{jl}(R)$ and the impact parameter b_j lie close to each other one readily gets

$$\eta_{jl} \simeq \int_{\mathcal{R}_{jl}^T}^{R} \frac{k_{jl}^2(R') - \kappa_{jl}^2(R')}{k_{jl}(R') + \kappa_{jl}(R')} dR' \quad (R \to \infty)$$

$$= -\int_{\mathcal{R}_{jl}^T}^{R} H_{jj}(R') \frac{dR'}{\mathring{\mathcal{R}}_{jl}^{(A)}} \quad (R \to \infty), \tag{14}$$

$$\mathring{\mathcal{R}}_{jl}^{(A)}(R) = \frac{k_{jl}(R) + \kappa_{jl}(R)}{2\mu}. \tag{15}$$

The outcome of the above treatment is that in order to set the JWKB-type phase shift η_{jl} in the well-known time-dependent form $-\int_0^\infty H_{jj}(R)dt$ one should use the classical trajectory $\mathcal{R}_{jl}^{(A)}(t)$ which according to Eqs. (14) and (15) is associated with the potential $\mathcal{V}_j^{(A)} = H_{jj}(R)/2$ and not $H_{jj}(R)$ as one could have expected intuitively.

It is thus seen that in addition to the $N(N-1)/2$ trajectories required to determine the probability amplitudes $a_{jl}^{\mp}(R\to\infty)$, or equivalently $c_{jl}(t\to\pm\infty)$ (Sec. II A), one needs to introduce N trajectories obeying Eq. (15) to obtain the JWKB-type phase shifts in Eq. (14). Then Eq. (13) reads

$$S_{0j,l} = \frac{c_{jl}(t\to+\infty)}{c_{0l}(t\to-\infty)} \exp\left\{ -i\int_0^\infty H_{jj}(\mathcal{R}_{jl}^{(A)}(t')) + H_{00}(\mathcal{R}_{0l}^{(A)}(t'))dt' \right\}$$

$$= C_j(t\to\infty;b) \exp\left\{ -i\int_{-\infty}^{+\infty} H_{jj}(\mathcal{R}_{jl}^{(A)}(t'))dt' \right\} \tag{16}$$

with

$$C_j(t;b) = c_{jl}(t) \exp\left\{ +i\int_{-\infty}^{0} H_{jj}(\mathcal{R}_{jl}^{(A)}(t'))dt' \right\}, \tag{17}$$

$$C_0(t\to-\infty;b) = 1, \tag{18a}$$

$$b \approx b_j \approx b_0. \tag{18b}$$

C. Recapitulation

The described multitrajectory procedure follows the same general lines as those enabling one to derive the time-dependent semiclassical close-coupling equations from the quantal ones. Likewise, it is primarily based on the conditions of validity of the JWKB approximation. The derivation thus requires that the local wave number in each channel be large and that the difference between two channel wave numbers be small compared to some common average wave number. Because interference patterns are sensitive to the actual path followed by the system, we have come to the conclusion that the relevant choice of trajectory should be made when passing from phase factors of the form $\exp\{i(\mathcal{S}_{jl}(R) - \mathcal{S}_{il}(R))\}$ to the form

$$\exp\left\{-i\int^{t}[H_{jj}(R)+\varepsilon_j-H_{ii}(R)-\varepsilon_i]dt'\right\} .$$

In doing so, we admitted, as also done in the usual derivations [7(b),11(b)], that the actual turning points lie close enough to a common turning point. This gives rise to a set of pairwise trajectories $R_{ij,l}^{(A)}(t)$ along which the coupling terms $H_{ij}(R)$ and energy differences $H_{ii}(R)+\varepsilon_i-H_{jj}(R)-\varepsilon_j$ are calculated when solving the set of time-dependent coupled equations [Eq. (7)]. The elastic JWKB phase shifts needed to derive elements of the scattering matrix from the probability amplitudes have also been inspected in the same spirit. In order to set those phase shifts in the familiar time-dependent form a new trajectory $\mathcal{R}_{jl}^{(A)}(t)$ has to be used for each channel.

III. APPLICATION TO THE SEMICLASSICAL TIME-DEPENDENT TREATMENT OF THE $H^+ + O_2$ COLLISION

A. Reduction of the number of trajectories

When addressing the problem of vibrational state-to-state excitation and charge transfer in an ion plus molecule collision it is convenient to characterize each channel by a pair of indices (nv) instead of the single index i of Sec. II: n labels a reactant or product electronic state of the system and v designates a corresponding vibrational state of the molecule. We may thereafter rewrite the system of equations (7) using Eqs. (18) in the form

$$\begin{aligned} i\mathring{C}_{nv}= & \sum_{v'\,(\neq v)} H_{nn}^{vv'}C_{nv'}\exp\left[-i\int_{-\infty}^{t}[H_{nn}^{v'v'}+\varepsilon_{nv'}-H_{nn}^{vv}-\varepsilon_{nv}]dt'\right] \\ & +\sum_{n''\,(\neq n),v''} H_{nn''}^{vv''}C_{n''v''}\exp\left[-i\int_{-\infty}^{t}[H_{n''n''}^{v''v''}+\varepsilon_{n''v''}-H_{nn}^{vv}-\varepsilon_{nv}]dt'\right] \end{aligned} \tag{19}$$

with [2(b),3]

$$H_{nm}^{v_n v_m}=\langle g_{v_n}|H_{nm}(R,r,\gamma)-\delta_{nm}U_n(r)|g_{v_m}\rangle\ , \tag{20a}$$

$$\left[-\frac{1}{2m}\frac{d^2}{dr^2}+U_n(r)\right]|g_{v_n}\rangle=\varepsilon_{nv_n}|g_{v_n}\rangle\ , \tag{20b}$$

$$U_n(r)=\lim_{R\to\infty}H_{nn}(R,r,\gamma)\ , \tag{20c}$$

$$H_{nm}(R,r,\gamma)=\langle n|H_{\text{el}}|m\rangle\ . \tag{20d}$$

H_{el} is the electronic Hamiltonian for a fixed geometry of the nuclei, r is the molecule bond distance, and m its reduced mass. Once again, the electronic states are assumed to be diabatic [10] and thus

$$\left\langle n\left|\frac{\partial}{\partial q}\right|m\right\rangle\simeq 0\ ,\quad q=r,R,\gamma\ . \tag{21}$$

Two types of terms are distinguished in the right-hand side of Eq. (19). One term corresponds to *intramanifold* transitions $v\to v'$, i.e, transitions between different vibrational states associated with the same electronic state $(n\equiv n')$. The other term corresponds to *intermanifold* transitions $n\to n''$, $v\to v''$ which change both the electronic and vibrational states of the system. This distinction enables us to exploit the property of vibrational states belonging to a common manifold to have closely lying and nearly parallel energy curves [Figs. 1(a) and 1(b)] in order to reduce the number of trajectories that appear when using the multitrajectory treatment of Sec. II. Indeed for *intramanifold transitions* at collision energies $E\geq 1$ eV/amu Eq. (9) becomes, according to this property,

$$\mathring{R}_{nn,l}^{(A)vv'}=\frac{k_{nl}^{v}(R)+k_{nl}^{v'}(R)}{2\mu}\simeq\frac{K_{nn,l}(R)}{\mu}\ ,\quad \forall v,v'\ , \tag{22}$$

where $K_{nn,l}(R)$ is a common local wave number characteristic of the vibrational manifold n. Likewise, we have for the *JWKB phases* [Eq. (15)]

$$\mathring{\mathcal{R}}_{nl}^{(A)v}=\frac{k_{nl}^{v}(R)+\kappa_{nl}^{v}(R)}{2\mu}\simeq\frac{\mathcal{K}_{nl}(R)}{\mu}\ ,\quad \forall v\ . \tag{23}$$

Similarly, for *intermanifold* transitions we may introduce another common wave number characteristic of the pair of electronic indices:

$$\mathring{R}_{nn'',l}^{(A)vv''}=\frac{k_{nl}^{v}(R)+k_{n''l}^{v''}(R)}{2\mu}\simeq\frac{K_{nn'',l}(R)}{\mu}\ ,\quad \forall v,v''\ . \tag{24}$$

For the following processes:

$$H^+ + O_2\ (X\,^3\Sigma_g^-, v=0)\to H^+ + O_2(X\,^3\Sigma_g^-, v'\leq 14)\ \ [\text{vibrational excitation (VE)}] \tag{25}$$

$$\to H + O_2^+\ (X\,^2\Pi_g, v''\leq 14)\ \ [\text{vibronic charge transfer (VCT)}]\ , \tag{26}$$

the above properties reduce the total number of trajectories needed in the multitrajectory method to five (instead of 465): two trajectories of type Eq. (22), two of type Eq. (23), and one of type Eq. (24). In the calculations reported below these trajectories were chosen to correspond to Eqs. (22)–(24) with $v=v'=0$ and $v''=2$. In the foregoing discussions $n=1$ and 2 will be used, wherever needed, as electronic labels for the direct and charge-transfer channels [Eqs. (25) and (26)], respectively.

B. Technicalities

The $H_{nn'}^{vv'}$ matrix elements in Eqs. (19) and (20) are the same as those used in Ref. 3. According to the above, the classical trajectories are determined by solving Hamilton's equations with the respective spherical potentials: $H_{11}^{00}(R;\gamma)$, $H_{22}^{22}(R;\gamma)$, $H_{11}^{00}(R;\gamma)/2$, $H_{22}^{22}(R;\gamma)/2$, and $[H_{11}^{00}(R;\gamma)+H_{22}^{22}(R;\gamma)]/2$ for each fixed angle γ and impact parameter b [Eq. 18(b)]. These equations are actually solved in the conserved plane of the trajectory in fixed space. Aside from the calculation of five trajectories instead of one, the differences between the earlier computation algorithm [3] and the present one just lie in the interpolation of the $H_{nn'}^{vv'}$ matrix elements between tabulated points. At each integration step, instead of interpolating all matrix elements at a common point $R(t)$, five sets of matrix elements have to be interpolated at the point reached along the corresponding trajectory. With the calculated scattering matrix [Eq. (16)] one easily obtains the sought differential and total cross sections [see Eqs. (20) and (21) in Ref. 3].

C. Results

Figure 2 recalls a result obtained in Ref. 3 for $\gamma=15°$ when the $H_{12}^{v'v''}$ couplings are switched off, thereby preventing charge transfer to occur; in this case only vibrational excitation can occur [15]. The semiclassical $(n=1,v=0)\rightarrow(n=1,v'=1)$ vibrational excitation probability $P_{10,11}$ in this figure was obtained using the common trajectory associated with the $H_{11}^{00}(R;15°)$ potential. The nice agreement between the semiclassical and quantal results supports a claim made in the Introduction as to the validity of the common trajectory for closely lying and nearly parallel energy levels; it also demonstrates the cogency of Eq. (22).

Figure 3 shows a comparison of quantal and multitrajectory semiclassical (MTSC) results for sample vibrational excitation: $(n=1,v=0)\rightarrow(n=1,v'=0,1)$ and vibronic charge transfer: $(n=1,v=0)\rightarrow(n=2,v''=2)$ transition probabilities versus impact parameter for $\gamma=45°$. For this orientation the couplings between direct and charge-transfer channels are close to maximum [16]. Generally, impact parameters $b\geq 2a_0$ show close agreement between quantal and MTSC results. Smaller impact parameters show some discrepancy in the amplitudes of the weakest transition probabilities. The origin of this feature has not yet been elucidated.

Figure 4 illustrates the degree of improvement of the present multitrajectory semiclassical calculation upon that based on the common trajectory associated with the entrance $H_{11}^{00}(R;45°)$ potential.

Figure 5 compares VE and VCT differential cross sections summed over all final vibrational states and averaged over the parameter γ. For the vibrational excitation process [Fig. 5(a)] the cross section is not very sensitive to

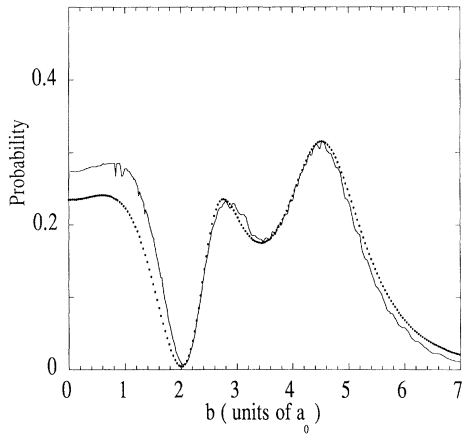

FIG. 2. Impact-parameter dependence of quantal (full lines) and semiclassical (dotted lines) IOS transition probabilities $P_{10,11}$ for $\gamma=15°$ obtained by switching off the $H_{12}^{v'v''}$ couplings (pure vibrational excitation). The shapes of the vibronic potential-energy curves are those schematized in Fig. 1(a). This result was obtained in Ref. 3 using the common trajectory associated with the $H_{11}^{00}(R;15°)$ potential.

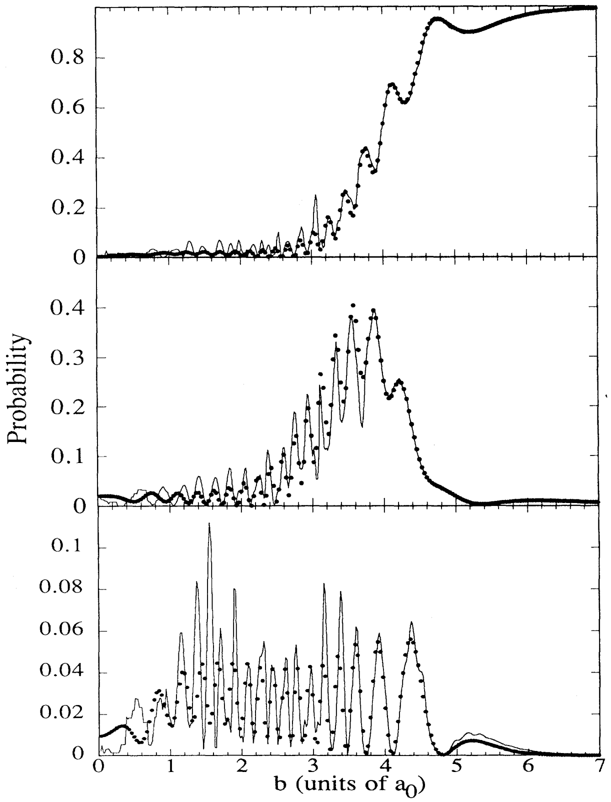

FIG. 3. Comparison of MTSC and quantal results for the impact-parameter dependence of IOS transition probabilities $P_{10,nv}(\gamma=45°)$. Full lines: quantal calculations of Ref. 3; dots: present MTSC results. The $P_{10,10}$ (elastic, $v'=0$), $P_{10,11}$ (VE $v'=1$), $P_{10,22}$ (VCT $v''=2$) probabilities appear successively from top to bottom.

various treatments of the trajectory problem. Yet it is noticeable that among all the reported semiclassical calculations the multitrajectory result is the closest to the quantal one. The superiority of the multitrajectory calculations upon those based on a common trajectory, the SCECT one or that deriving from the entrance potential, is clearly seen for the vibronic charge-transfer process [Fig. 5(b)]. As mentioned in Ref. 3 and recalled in Sec. I, the SCECT treatment yields the poorest agreement with the quantal calculation. Though much more successful, the other common trajectory treatment attenuates the rainbow structure in the vibronic charge-transfer cross section [3] as a result of an imperfect shape at large scattering angles $13° \leq \Theta \leq 20°$. These results definitely lend support to the present multitrajectory proposal.

IV. CONCLUSION

The multitrajectory method (MTSC) constitutes an effective means to solve the problem of choosing a trajectory in the time-dependent semiclassical treatment of nonadiabatic collisions. The method depends on the same conditions of validity as the well-known common trajectory method. Yet, it introduces a new trajectory each time a difference of two action integrals appears. Basically, both the multitrajectory and common trajectory approaches require the closeness of the relevant local wave numbers to an assumed mean. Still, the MTSC tries to be more accurate in the evaluation of accumulated

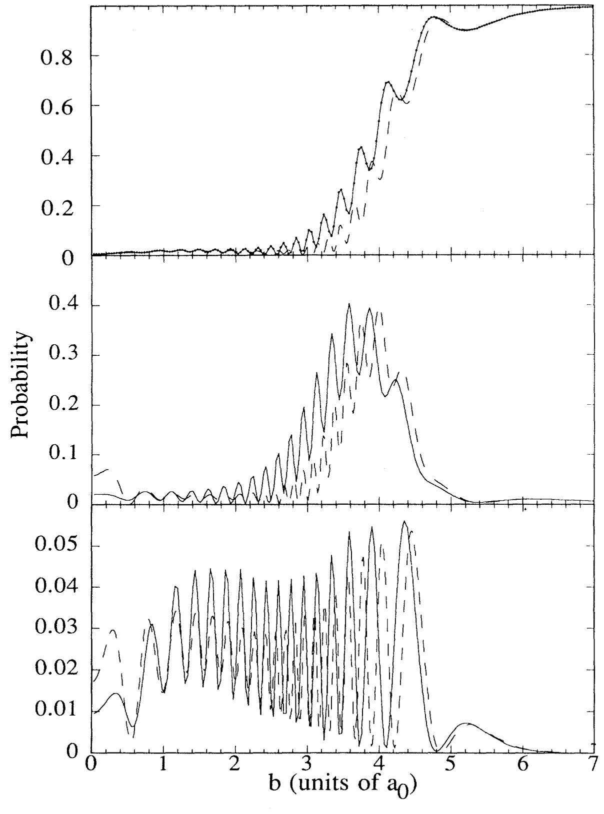

FIG. 4. Comparison of MTSC and common trajectory results for the impact-parameter dependence of IOS transition probabilities $P_{10,nv}$ ($\gamma=45°$). Full lines: present MTSC results; dashed lines: common trajectory calculations of Ref. 3. The $P_{10,10}$ (elastic, $v'=0$), $P_{10,11}$ (VE $v'=1$), $P_{10,22}$ (VCT $v''=2$) probabilities appear successively from top to bottom.

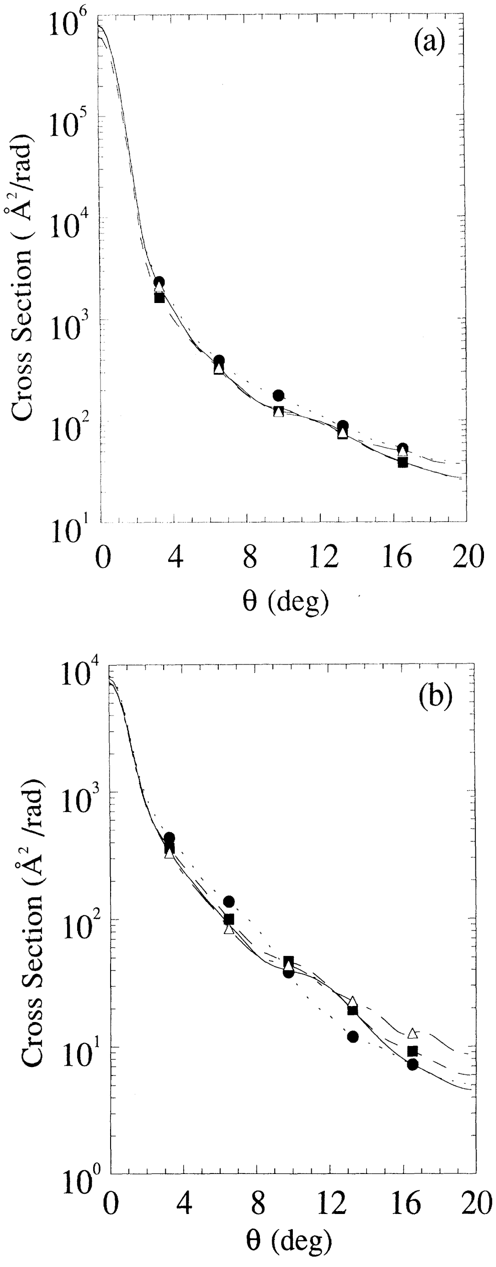

FIG. 5. Differential IOS cross sections, summed over all final vibrational states, for the $H^+ + O_2$ ($X\,^3\Sigma_g^-$, $v=0$) collision at $E=23$ eV. Full lines: present MTSC results; closed squares and short-dashed lines: quantal results of Ref. 3; open triangles and long-dashed lines: common trajectory results of Ref. 3; closed circles and dotted line: SCECT results. (a) VE cross sections and (b) VCT cross sections.

phase differences during the collision. It is also worth pointing out that, as formulated in Sec. II, the MTSC approach obeys microreversibility; this is a feature that some common trajectory prescriptions fail to account for. In conclusion, the success of the MTSC approach in reproducing quantal results in the IOS context constitutes a strong incitement to further its use in a context where quantal calculations are still not feasible, namely the fixed-rotor approximation. Work in this direction is progressing.

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