Mean-trajectory approximation for charge- and energy-transfer processes at surfaces

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We discuss electronic energy and charge-transfer processes at surfaces in terms of curve-crossing models. We suggest that at low kinetic energies the trajectory approximation should be replaced by a mean-trajectory approximation (MTA), in which the nuclear motion gets feedback from and adjusts to the curve-crossing dynamics. We discuss two derivations of MTA by using an eikonal approximation and a path-integral method. The effects of phonon or electron-hole pair excitations on the charge-transfer process are also incorporated.

I. INTRODUCTION

The dynamics of atomic and molecular processes at solid surfaces is often dominated by nonadiabatic transitions between quantum states of the atomic or molecular system or between states of the substrate. Frequently discussed examples are those involving charge exchange between the external atom or molecule and the surface. The simplest process of this kind is the ionization (neutralization) of an atom (ion) incident on a metal surface.[1-7] More complicated examples are charge transfer during sputtering,[8] chemiluminescence,[9,10] electron- or photon-stimulated desorption,[11] and energy transfer via an intermediate charge-transfer process.[12] Auger neutralization of an incident ion[13] is a still more involved example. Other important processes that may be described by curve crossing model are the surface-induced de-excitation of electronically or vibrationally excited molecule and, in some cases, molecular dissociation during molecule-surface collision.

The theoretical treatment of these processes usually involves the classical trajectory approximation[3-6,8-14] (reviewed in Sec. II), which is valid only when the kinetic energy of the incident atom or molecule is very large. For incident energies of the order of the energy differences between relevant quantum levels of the incident species or of the surface, this approximation fails. While much ion scattering work is carried out at high kinetic energy, the low kinetic-energy regime is very important in electron-stimulated desorption and in the thermal desorption and the sticking of alkali atoms. Since a fully quantum-mechanical treatment of these processes is difficult (especially in three dimensions) and since one expects that the motion of the incident atom is essentially classical and quantum effects mostly control the transition between the electronic states, one would like to seek an improved trajectory approximation. While such a theory may yield a time-dependent Hamiltonian for the electronic problem (as does the trajectory approximation), it should obtain the nuclear trajectory by a procedure that will recognize the continuous occurrence of the electronic transition and use this information to guide the evolution of the otherwise classical trajectory.

In this paper we examine the implications of the mean-trajectory approximation for charge-transfer processes at metal surfaces. In this approximation the "classical" degrees of freedom (denoted collectively by R) evolve under the potential $\sum_{i,j} X_i^* X_j H_{ij}(R)$, where X_i is the instantaneous amplitude of the electronic state i (characterizing the quantum degrees of freedom) and $H_{ij}(R)$ is the matrix element of the Hamiltonian for the quantum system (which depends parametrically on R) between the i and j quantum states.

This approximation has been applied by several workers in the past[15-21] to problems in molecular dynamics. Here we are concerned with its justification from first principles as well as with its extension to situations specific to surface science. Thus we derive the approximation by two methods: The first is based on the use of wave packets (the eikonal approximation) while the second is obtained by taking the extremum of the action functional in a path-integral expression for the quantum propagator. We then proceed to apply this procedure to charge-exchange processes at metal surfaces, taking as a prototype the ionization-neutralization processes involving an alkali atom colliding with a metal surface. We derive the equations of motion which govern the dynamics of the alkali atom motion towards and away from the surface, the transition between the neutral and the ionic state, and the energy exchange with electron-hole pairs and phonons.

The mean-potential approximation is superior to the classical trajectory approximation in that it responds (in an average way) to the quantum process. As a result the time evolution in the effective trajectory approximation conserves the average energy, in contrast to classical trajectory approximation which does not. At the same time the equations of motion in the effective potential approximation are as easy to integrate as those of the classical trajectory approximation. We hope to present in future work numerical results for both dynamics[22] and for electronic structure calculations[23] of the diabatic[24] curves as well as some experimental results.[25-26]

The paper is organized as follows. In Sec. II we describe the charge-transfer process as a curve crossing. The effective trajectory approximation is derived by using the eikonal approximations (Sec. III) and by using a stationary phase approximation in a path-integral representation (Sec. IV). In Secs. V and VI we show how to imple-

ment the resulting equations of motion for a charge-transfer problem typical of surface science, which involves continuous manifolds of crossing electronic states, and phonon or electron-hole pair excitations. In Sec. VII we summarize our results and discuss the advantages and the shortcomings of the present treatment.

II. ALKALI ADSORPTION AS A CHARGE-TRANSFER PROCESS

We present here in detail the physical arguments used to construct a curve-crossing model for the alkali adsorption as a charge-transfer process described by the "chemical reaction"

$$M(\psi_\alpha^0) + A(\psi^1) \rightarrow (M^-)^*(\psi_\alpha^1) + A^+(\psi^0) . \tag{2.1}$$
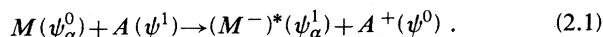
Here, M, A, and A^+ denote the ground-state metal, the neutral alkali atom, and the alkali ion, respectively. $(M^-)^*$ denotes the metal surface with an extra electron; the asterisk indicates that the "negative ion" M^- is excited (the transferred electron is placed above the Fermi level). In the parentheses accompanying these symbols we indicate the orbitals involved in the charge-transfer process. The superscripts specify the number of electrons occupying each orbital. The electron to be transferred is initially located in the atomic orbital ψ and ends up in the empty metal orbital ψ_α, whose orbital energy (with respect to the Fermi level) is ϵ_α. There is an infinite number of final states [i.e., an infinite number of excited, negative ions $(M^-)^*$], one for each ψ_α.

To construct the energy curves corresponding to the initial and final states specified by Eq. (2.1) we use the Fermi energy of the surface as a convenient point of reference. Since in all the relevant experiments the sample is grounded, the Fermi level is not changed when the surface gains an electron or when it is disturbed by the approaching ion. The potential surfaces discussed below correspond to electronic energy levels of the combined metal-atom system and not to single electronic orbitals. The energy difference $\Delta V_\alpha(R)$ between the final and the initial states specified by Eq. (2.1), at a fixed atom-surface distance R and for fixed ϵ_α, is the energy $I(R)$ required to ionize the atom, minus the energy $\phi_\infty - \epsilon_\alpha$ recovered by placing the electron in the orbital ψ_α. The ionization potential $I(R)$ is given by $I_\infty + V_i(R) - V_n(R)$, where I_∞ is the ionization potential of the isolated atom, and $V_i(R)$ and $V_n(R)$ are the ion-metal and the atom-metal interaction energies, respectively. If the ion binds more strongly to the surface than the neutral we have $I(R) < I_\infty$. In what follows we assume this to be the case. Note that the work function ϕ_∞ appears, rather than a local work function.[27] This is because we define the ionization potential $I(R)$ as the work required to remove the electron to infinity; therefore we need the work recovered by taking the electron from infinity to ϵ_α.

The energy curves corresponding to the initial and the final states of Equation (2.1) are shown in Fig. 1. We have assumed that the energy curve corresponding to the initial (neutral) state has a small attractive well and a rapidly rising repulsive part. The ionic curve can then be
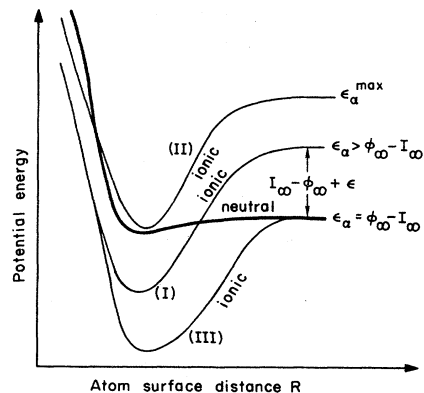

FIG. 1. Energies of the neutral and the ionic states involved in the description of the ionization process. Various ionic curves differ through the final energy ϵ_α of the transferred electron, with respect to the Fermi level. I_∞ is the ionization potential of the neutral in the absence of the surface. ϕ_∞ is the work required to remove an electron from the metal to infinity.

qualitatively drawn by using the expression

$$\Delta V_\alpha(R) = I(R) - \phi_\infty + \epsilon_\alpha$$

$$= I_\infty + [V_i(R) - V_n(R)] - \phi_\infty + \epsilon_\alpha , \tag{2.2}$$

which gives the energy difference between the ionic and the neutral curve. At large particle-surface distances the separation between these curves is

$$\Delta V_\alpha(\infty) = I_\infty - \phi_\infty + \epsilon_\alpha . \tag{2.3}$$

In what follows we call $\Delta V_\alpha(\infty)$ the asymptotic mismatch of curve α. Using this expression we can rewrite Eq. (2.2) as

$$\Delta V_\alpha(R) = \Delta V_\alpha(\infty) + [I(R) - I_\infty] . \tag{2.4}$$

The energy difference $\Delta V_\alpha(R)$ becomes zero at the distance R_α given by

$$\Delta V_\alpha(R_\alpha) = 0 = \Delta V_\alpha(\infty) + I(R_\alpha) - I_\infty . \tag{2.5}$$

If this equation has a solution the neutral and the ionic curves cross [curve (I), Fig. 1] at R_α and, at that distance, the initial and the final states of Eq. (2.1) are degenerate. The charge-transfer process resulting in the creation of $(M)^*(\psi_\alpha^1)$ is most likely to occur at R_α.

The crossing occurs only if the "image effects"[28] contained in the term $I(R_\alpha) - I_\infty$ are able to compensate the asymptotic mismatch $\Delta V_\alpha(\infty)$. If the asymptotic mismatch is zero, then Eq. (2.4) gives $I(R_\alpha) = I_\infty$ and the crossing occurs at very large values of R_α. As the mismatch is increased, the crossing point moves to smaller values of R_α, provided that $\Delta V_\alpha(\infty) > 0$. Obviously if $\Delta V_\alpha(\infty) < 0$ the curves cannot cross at any distance. Also if $\Delta V_\alpha(\infty)$ becomes too large the image field cannot compensate for it and the curves do not cross. We denote by $\Delta V_\alpha^m(\infty)$ the maximum value of $\Delta V_\alpha(\infty)$ that can be compensated.

The ionic curves can thus be characterized by any of the following parameters: the asymptotic mismatch

$\Delta V_\alpha(\infty)$, the crossing distance R_α, the orbital energy ϵ_α, or the index α. When $\Delta V_\alpha(\infty)$ increases, R_α gets smaller and ϵ_α increases.

In discussing the dynamic processes possible in this system of curves we assume that we have a procedure for generating a classical trajectory $R(t)$ describing the motion of the incident neutral. This incident particle can undergo transitions to any of the ionic curves as long as they cross the neutral one. A transition to an ionic state $\Delta V_\alpha(\infty)$ tends to take place near the crossing point R_α. At any other point R there is an energy mismatch $\Delta V_\alpha(R)$, which means that after the transition to the curve α the nucleus must change suddenly its velocity. Since the electron transfer cannot provide a large momentum transfer such an event is unlikely unless $\Delta V_\alpha(R)$ is very small, that is, unless R is very close to R_α.

Let us assume that a transition to the ionic state α has occurred at R_α, while the neutral was on its incoming trajectory. This places the transferred electron in the empty surface orbital ϵ_α. The ion hits the wall, turns around, and approaches again the point R_α, where it could be neutralized by the electron initially placed in ϵ_α if that electron has not already moved into the bulk. In what follows we assume that surface residence time τ_r of the transferred electron is much smaller than the collision time τ_c (which is the time interval in which the atom or the ion are close enough to the surface to undergo charge transfer). Since, strictly speaking, the electron is not transferred into a one-electron state ψ_α but into a localized wave packet centered around ϵ_α, the electron moves towards the bulk with the group velocity of the packet. The surface residence time of interest here can be defined by $\tau_r = L/v$, where L is the displacement required to cancel the overlap between the wave packet and the hole state in the atom, and v is the group velocity. An equivalent statement is that τ_r^{-1} is roughly given by $(2\pi/\hbar)|H_{12}(R_\alpha)|^2\rho(\epsilon_\alpha)$, where $H_{12}(R_\alpha)$ is the coupling between the ionic and the neutral states at their crossing distance R_α and $\rho(\epsilon_\alpha)$ is the density of the ionic states. The condition $\tau_r \ll \tau_c$ precludes the neutralization of the ion by a recrossing of the incident neutral curve on the outgoing trajectory. The dynamics occurs as if the *incident neutral curve disappears* as soon as a transition to an ionic curve is completed.

While the ion cannot be reneutralized by the electron which was previously transferred to the surface, neutralization can occur by tunneling of thermally excited electrons. The condition $\phi_\infty - I_\infty > 0$ precludes the electrons at or below the Fermi level from participating in the neutralization of the ion; furthermore, if $\phi_\infty - I_\infty \gg k_B T$, only very few thermal electrons have enough energy to neutralize the ion resonantly and the neutralization rate is extremely small. The behavior of the ion in the extreme case in which $\tau_r \ll \tau_c$ and $\phi_\infty - I_\infty \gg k_B T$, depends on the value of $\Delta_\alpha \equiv K - \Delta V_\alpha(\infty)$, where K is the kinetic energy of the incident atom. If the ionization occurred by a transition for which $\Delta_\alpha < 0$, the ion is trapped; if $\Delta_\alpha > 0$, trapping occurs only if the ion loses (to phonons or electron-hole pairs) an amount of energy larger than Δ_α. Otherwise the ion escapes into the vacuum.

If $\phi_\infty - I_\infty > 0$ but is not much larger than $k_B T$, the ion

can be neutralized by tunneling of thermally excited electrons. This process can be described by the chemical reaction

$$M(\psi_\beta^1) + A^+(\psi^0) \rightarrow M^+(\psi_\beta^0) + A(\psi^1) . \quad (2.6)$$
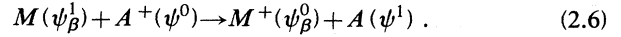
Here $M(\psi_\beta^1)$ represents the metal having a thermally excited electron in the orbital ψ_β whose energy η_β is above the Fermi level (η_β is the energy of the transition from the Fermi level to ψ_β). $M^+(\psi_\beta^0)$ is the metal after electron removal from ψ_β.

The energy required for the process described by Eq. (2.6) is

$$\Delta \mathscr{E}_\beta(R) = \phi_\infty - \eta_\beta - I(R) . \quad (2.7)$$

In Fig. 2 we plot the ionic curve $\mathscr{E}_i(R)$ and the set of neutral curves given by

$$\mathscr{E}_{n,\beta}(R) = \mathscr{E}_i(R) + \phi_\infty - \eta_\beta - I(R) . \quad (2.8)$$

(We assume, for simplicity that the neutral curve is independent of R.)

If $\eta_\beta = 0$ (i.e., we consider an electron at the Fermi level) then $\mathscr{E}_{n,\beta}(\infty) - \mathscr{E}_i(\infty) = \phi_\infty - I_\infty$ and the neutral curve is above the ionic one (we consider the case $\phi_\infty > I_\infty$). The neutral curve $\mathscr{E}_{n,\beta}$ and the ionic curve $\mathscr{E}_i$ do not cross. If $\phi_\infty - I_\infty = \eta_\beta$, the two curves coincide for $R \rightarrow \infty$. If $\eta_\beta > \phi_\infty - I_\infty$ the neutral curve crosses the ionic one for all η_β smaller than η_β^m given by $\phi_\infty - \eta_\beta^m - I_\infty = \min \mathscr{E}_i(R)$.

A newly formed ion starts interacting with the thermally excited electrons as soon as it is produced. The rate of neutralization is the quantum-mechanical transition rate to the neutral curve labeled η_β, multiplied by the probability that η_β is thermally occupied.

We can now summarize the overall dynamic picture for the case $\tau_r \ll \tau_c$ and $\phi_\infty - I_\infty > 0$. There is a finite probability that the incident neutral is not ionized, in which case it will scatter back into the vacuum. The ionization brings about some complexity. If it takes place by a transition to the ionic curve labeled α, the electron is placed in the empty metal orbital ϵ_α from where it promptly moves into the bulk and disappears. If the ionizing transition
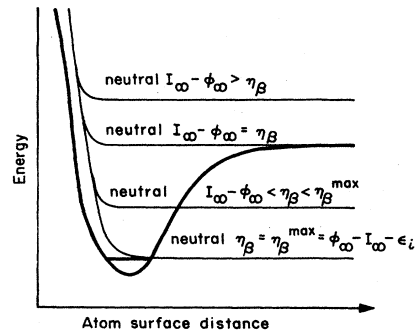

FIG. 2. Energies of the neutral and the ionic curves invoked in discussing the neutralization of the ion. The neutral curves all differ through the initial energy η_ρ of the thermally excited electron used for neutralizing the ion. $\mathscr{E}_i$ is the binding energy of the ion to the surface.

occurs to a curve α for which $\Delta_\alpha = K - \Delta V_\alpha < 0$ (i.e., the kinetic energy of the neutral is below the ionic curve α), the ion can escape from the surface only by subsequent neutralization, caused by tunneling of thermally excited electrons (since the ion crosses the neutral curves shown in Fig. 2). The chance of neutralization depends on the kinetic energy of the ion. A low kinetic energy ion is deep in the ionic well and can only undergo transitions on the neutral curves located below it, which correspond to larger values of η_β, therefore to smaller probabilities that η_β is thermally occupied by an electron. Ionizing transitions that take place at small R_α [i.e., large ϵ_α means large asymptotic mismatch $\Delta V_\alpha(\infty)$] end up deeper in the ionic well than those occurring at large R_α and have a smaller chance of neutralization, therefore they have a larger trapping probability. Furthermore, the probability of trapping goes up with $\phi_\infty - I_\infty$ since this forces the ionization to occur at smaller values of R_α.

This qualitative picture can also be used to understand coverage effects. As alkali atoms coverage is increased, ϕ_∞ is lowered dramatically[25] and $\phi_\infty - I_\infty$ becomes negative. The alkali atom cannot be fully ionized and adsorption must occur by usual chemisorption. The desorption process must occur exclusively through neutral desorption until the coverage is lowered so much (by desorption) that $\phi_\infty - I_\infty$ becomes positive and both ion and neutral desorption become possible. Such behavior is observed, for example for K desorption from Ni(111).[26]

Interesting situations appear when the surface residence time of the transferred electron is comparable to or larger than the collision time. This might happen either when the electron is transferred into an empty surface state with a lifetime $\tau \geq \tau_c$, or when the kinetic energy of the incident particle is very high, or when the conductivity of the material is low. The surface state can be included in the model presented here as a discrete state with a finite width Γ (Γ^{-1} is the lifetime of the electron in the state). The presence of an electron with an infinitely long surface residence time can be included by allowing the ion to recapture the lost electron on its outgoing trajectory. A finite surface residence time can be simulated by adding a rate of disappearance of the electron from the surface region.

III. THE MEAN-TRAJECTORY APPROXIMATION DERIVED BY USING THE EIKONAL APPROXIMATION

A. Introduction

In order to specify in the simplest manner the reasons for the present work, we first consider a model in which only two curves are important. The dynamics of such a system is considerably simplified by making the so-called trajectory approximation,[3,4,6,8,9-13,24] which is briefly described below. Consider a system with two kinds of degrees of freedom denoted x and R. In our case x denotes collectively the coordinates of all the electrons, and R is the surface-atom distance.

The full Hamiltonian for this system can be written as

$$H(x,\hat{R}) = -(\hbar^2/2m)\nabla^2 + H_e(x,\hat{R}) . \tag{3.1}$$

This is the sum of the kinetic energy of the nuclei and the electronic Hamiltonian $H_e(x,\hat{R})$, which contains the kinetic energy of the electrons and the interaction energy between electrons and nuclei. The trajectory approximation uses the Hamiltonian

$$H(x,R(t)) = H_e(x,R(t)) , \tag{3.2}$$

where $R(t)$ is the position of the atom, whose time dependence is given by classical mechanics. Note that while $\hat{R}$ appearing in Eq. (3.1) is an operator, the quantity $R(t)$ is a classical field. In what follows we also use $\hat{R}$ to denote the nuclear position appearing as an argument in the wave function.

The state $\psi(x,\hat{R})$ associated with the Hamiltonian $H(x,\hat{R})$ depends on both x and $\hat{R}$. If two electronic states $\phi_1(x,\hat{R})$ and $\phi_2(x,\hat{R})$ (2 for the neutral and 1 for the ionic state) are sufficient to describe the system, then

$$\psi(x,\hat{R}) = X_1(\hat{R})\phi_1(x,\hat{R}) + X_2(\hat{R})\phi_2(x,\hat{R}) , \tag{3.3}$$

where $X_1(\hat{R})$ and $X_2(\hat{R})$ are nuclear wave functions. In the trajectory approximation the total wave function is obtained by replacing $\hat{R}$ in $H_e(x,R)$ and $\psi(x,R)$ with the trajectory $R(t)$ and the nuclear wave functions $X_i(R)$ with the amplitudes $c_i(t)$:

$$\psi(x,t) = c_1(t)\phi_1(x,R(t)) + c_2(t)\phi_2(x,R(t)) . \tag{3.4}$$

Inserting Eq. (3.4) in the time-dependent Schrödinger equation, and assuming, for simplicity, that

$$\int \phi_i^*(x,R(t))\phi_j(x,R(t))dx = \delta_{ij} \tag{3.5}$$

leads to

$$i\hbar\dot{c}_i = H_{ii}(R(t))c_i(t) + H_{ij}(R(t))c_j(t) ,$$
$$j,i = 1,2 \ (i \neq j) \tag{3.6}$$

with

$$H_{ij}(t) = H_{ij}(R(t))$$
$$= \int dx \, \phi_i^*(x,R(t))H_e(x,R(t))\phi_j(x,R(t)) . \tag{3.7}$$

H_{11} and H_{22} are the ionic and the neutral energy curves, respectively, and H_{12} is the coupling between them. The matrix element H_{12} given by Eq. (3.7) is nonzero because the states ϕ_i, $i = 1,2$ are diabatic. We have neglected here, as is customary when using diabatic states,[24] terms containing the time derivatives of the wave functions ϕ_i. We assume throughout this paper that the dependence of $H_{ij}(R)$, $i,j = 1,2$, on R is known. Furthermore, we note that the removal of the assumption (3.5) is straightforward.

In order to solve Eq. (3.6) we must propose a method for computing the dependence of R on t. If the incident kinetic energy is much higher than the variation of $H_{ii}(R)$ with R and the difference $H_{22} - H_{11}$, we can use a straight-line trajectory and a hard wall reflection from the surface. At low kinetic energy, such as that involved in the processes considered here, the choice of trajectory is rather difficult. If the particle stays neutral throughout the collision process, then $R(t)$ is given by

$$m\ddot{R}(t) = -\frac{\partial H_{22}(R(t))}{\partial R(t)} \ . \qquad (3.8)$$

If the particle is ionic throughout, then $R(t)$ should be given by

$$m\ddot{R}(t) = -\frac{\partial H_{11}(R(t))}{\partial R(t)} \ . \qquad (3.9)$$

If the incident kinetic energy is small these two trajectories are rather different. Equation (3.8) gives small changes in velocity, while Eq. (3.9) strongly accelerates the particle as it approaches the surface.

The fact that in most practical cases the amplitudes $c_1(t)$ and $c_2(t)$ are both nonzero and the motion of the nucleus takes place simultaneously on both surfaces gives rise to interesting complications. A more realistic description of the nuclear motion requires the use of a new kind of force $F(c_1, c_2)$, which depends on the amplitudes $c_i(t)$. A dependence on $|c_i|^2$, $i = 1, 2$, alone would be unsatisfactory since it eliminates quantum interference effects. Neither Eq. (3.8) nor Eq. (3.9), nor any simple average of the two, would be satisfactory.

This deficiency of the trajectory approximation is not confined to the charge-transfer problem discussed here; it is a general problem to be faced whenever a degree of freedom that we wish to treat classically is strongly coupled to a quantum degree of freedom x.[29] A reasonable method of producing an improved trajectory approximation is to take the classical limit in R while treating x fully quantum mechanically. There are several ways of doing this and they can lead to different classical mechanics for the variable R. We present here a "mean-trajectory" approximation, obtained by using an eikonal approximation (Sec. III) and a path-integral method (Sec. IV). A more elaborate method using multiple Gaussian wave packets is planned to be presented elsewhere.[22]

B. The use of the eikonal method for generating classical trajectories in the one-state problem

We review here the manner in which the eikonal method generates a classical trajectory in a simple one-dimensional, one-electronic-state problem. We use for the wave function the form

$$\psi(\hat{R}, t) = C_t A(\hat{R}, t)\exp[iS(\hat{R}, t)/\hbar]$$
$$\equiv \exp\{[S_0(\hat{R}, t) + iS(\hat{R}, t)]/\hbar\} \ , \qquad (3.10)$$

where the amplitude A, the eikonal S, the normalization constant C_t, and the function S_0 are real. We use the notation $\hat{R}$ when the position of the particle is a quantum variable, to distinguish it from the classical trajectory $R(t)$. Inserting $\psi(\hat{R}, t)$ in the time-dependent Schrödinger equation leads to

$$\left[i\frac{\partial S_0}{\partial t} + \frac{\partial S}{\partial t}\right]A = H\left[\hat{R}, \hat{P} + \frac{\partial S}{\partial \hat{R}}\right]A \ , \qquad (3.11)$$

where $\hat{P}$ is the momentum operator and $\partial S/\partial \hat{R}$ is an un-

known operator (which is diagonal in the coordinate representation).

If we assume that

$$\left[\hat{P} + \frac{\partial S}{\partial \hat{R}}\right]^2 \simeq \left[\frac{\partial S}{\partial \hat{R}}\right]^2 \qquad (3.12)$$

and

$$\frac{\partial S_0}{\partial t} \ll \frac{\partial S}{\partial t} \ , \qquad (3.13)$$

Eq. (3.11) reduces to the Hamilton-Jacobi equation[30]

$$\frac{\partial S}{\partial t} = H\left[\hat{R}, \frac{\partial S}{\partial \hat{R}}\right] \ . \qquad (3.14)$$

Its solution $S_c(\hat{R}, t)$, obtained after specifying classical initial conditions, is the classical Hamilton's principal function, or the classical action.

To establish the meaning of the conditions (3.12) and (3.13) we take matrix elements with respect to the amplitude A to turn the operator equations into numerical ones. Since we expect R to behave nearly classically, we use for the wave function Eq. (3.10) a Gaussian form[31] defined by

$$S_0(\hat{R}, t) = -\alpha_t(\hat{R} - R_t)^2 + \hbar \ln C_t \ , \qquad (3.15)$$

and

$$S(\hat{R}, t) = P_t(\hat{R} - R_t) + \gamma_t \ , \qquad (3.16)$$

where

$$C_t = (2\alpha_t/\pi\hbar)^{1/4} \ . \qquad (3.17)$$

Here α_t, P_t, R_t, and γ_t are real functions of time and C_t is the normalization constant appearing in Eq. (3.10). The meaning of these functions can be understood by computing the following matrix elements:

$$\int \psi^*(\hat{R}, t)\hat{R}\psi(\hat{R}, t)d\hat{R} \equiv \langle \hat{R} \rangle = R_t \ , \qquad (3.18)$$

$$\langle \hat{P} \rangle = P_t \ , \qquad (3.19)$$

$$\langle (\hat{R} - R_t)^2 \rangle = \hbar/4\alpha_t \ , \qquad (3.20)$$

$$\langle (\hat{P} - P_t)^2 \rangle = \hbar\alpha_t \ . \qquad (3.21)$$

We see that R_t and P_t are the expectation values of the position and momentum, γ_t is a phase, and α_t is proportional to the quantum fluctuation of the momentum around its expectation values and inversely proportional to the fluctuations in the position.

Taking the matrix element of the condition (12) with respect to A leads to

$$\int A(\hat{R}, t)\left[\hat{P} + \frac{\partial S}{\partial \hat{R}}\right]^2 A(\hat{R}, t)d\hat{R} \simeq \int A\left[\frac{\partial S}{\partial \hat{R}}\right]^2 A \, d\hat{R} \ . \qquad (3.22)$$

If we use, as an approximation to S the classical action S_c, and the classical equation $P(t) = \partial S_c/\partial R(t)$, we can easily perform the integrals in Eq. (22), to obtain

$$\hbar\alpha_t \ll P_t^2 \ . \qquad (3.23)$$

We have identified $P(t) = \partial S_c / \partial R(t)$ with the expectation value of the momentum P_t, and this will be justified later. The condition (3.12) is thus equivalent to the requirement of Eq. (3.23) that the quantum fluctuations of the momentum are much smaller than its expectation value.

Treating the condition (3.13) in a similar manner requires the evaluation of

$$\int A \frac{\partial S_0}{\partial t} A \, d\hat{R} \ll \int A \frac{\partial S}{\partial t} A \, d\hat{R} \ . \tag{3.24}$$

Performing the integrals leads to

$$\int A \frac{\partial S_0}{\partial t} A \, d\hat{R} = 0 \tag{3.25a}$$

and

$$\int A \frac{\partial S}{\partial t} A \, d\hat{R} = H_c(R(t), P(t)) \ . \tag{3.25b}$$

We have replaced $\partial S / \partial t$ with $\partial S_c / \partial t$, which in turn is equal[30] to the classical Hamiltonian H_c. Furthermore, we used Eq. (3.10) for S_0. Clearly condition (3.24) is always satisfied since the classical Hamiltonian is positive.

The conditions discussed above establish under what circumstances we can replace the eikonal $S(\hat{R}, t)$ with the classical action $S_c(R(t), P(t))$. So far the classical mechanics appears as a device to compute the eikonal: There is no guarantee that the classical trajectory has any relationship with the motion of the particle as given by the time-dependent Schrödinger equation. For example, if $\alpha_t = 0$ the Gaussian wave packet becomes a planar wave, and the condition (3.23) is fulfilled. However, it is impossible to describe the behavior of a particle in a planar wave state by any kind of classical trajectory.

The condition under which the trajectory generated by the Hamilton-Jacobi equation approximates the behavior of the quantum system can be obtained by using the wave packet defined by Eqs. (3.15), (3.16), and (3.10), and the Ehrenfest theorem[32]

$$\frac{d}{dt} \int \psi^*(\hat{R}, t) \hat{R} \psi(\hat{R}, t) d\hat{R} = -\int \psi^*(\hat{R}, t) \frac{\partial V}{\partial \hat{R}} \psi(\hat{R}, t) d\hat{R} \ . \tag{3.26}$$

According to the equation (3.18) the left-hand side of the above equation is dR_t / dt. Since the wave function appearing on the right-hand side is localized over a spatial range given by $(2\hbar / \alpha_t)^{1/2}$, we can expand $V(R)$ in Eq. (3.26) in powers of $\hat{R} - R_t$, and this leads to

$$\frac{dR_t}{dt} = -\frac{\partial V(R_t)}{\partial R_t} - \frac{1}{2} \frac{\partial^3 V(R_t)}{\partial R_t^3} \langle (\hat{R} - R_t)^2 \rangle \ . \tag{3.27}$$

The expectation value R_t of $\hat{R}$ satisfies the classical equation of motion if the second term in Eq. (3.27) is much smaller than the first. Using Eq. (3.20) we can write this condition as

$$\frac{\hbar}{8\alpha_t} \frac{\partial^3 V(R_t)}{\partial R_t^3} \ll \frac{\partial V(R_t)}{\partial R_t} \ . \tag{3.28}$$

If conditions (3.23) and (3.28) are satisfied, the eikonal is given by the classical action, and the trajectories generated by classical mechanics are a reasonable description of the mean quantum motion of the system.

In what follows we postulate that the above procedure can be used to generate a "classical mechanics" for cases in which the variable R to be treated classically is strongly coupled to a quantum companion x, and we apply this idea to the case of a two-state system.

C. The application of the eikonal method to the two-state problem

To apply the method outlined in Sec. III B we assume a wave function of the form

$$\begin{aligned}
\psi(x, \hat{R}; t) &= A(x, \hat{R}; t) \exp[iS(\hat{R}, t) / \hbar] \\
&= [\chi_1(\hat{R}, t) \phi_1(x, \hat{R}) + \chi_2(\hat{R}, t) \phi_2(x, \hat{R})] \\
&\quad \times \exp(iS / \hbar) \ .
\end{aligned} \tag{3.29}$$

Here $S(\hat{R}, t)$ is an unknown real function (the eikonal) of the nuclear coordinate $\hat{R}$ and the time t, and $\chi_i(\hat{R}, t)$, $i = 1, 2$ are the nuclear wave functions when the system is in the electronic state $\phi_i(x, \hat{R}; t)$, $i = 1, 2$. To derive the appropriate classical limit for the nuclear motion we eliminate first the electronic degrees of freedom from the problem by introducing the wave function $\psi(x, \hat{R}; t)$ given by Eq. (3.29) in the time-dependent Schrödinger equation, and by operating on the resulting equation, from the left, with $\int dx \, \phi_i^*(x, \hat{R})$, $i = 1, 2$. We obtain

$$\begin{aligned}
&\left[-\frac{\partial S}{\partial t} + i\hbar \frac{\partial}{\partial t} \right] \chi_1(\hat{R}, t) \\
&= \left[\frac{1}{2m} \left[\hat{P} + \frac{\partial S}{\partial \hat{R}} \right]^2 + H_{11}(\hat{R}) \right] \chi_1 + H_{12}(\hat{R}) \chi_2
\end{aligned} \tag{3.30a}$$

and

$$\begin{aligned}
&\left[-\frac{\partial S}{\partial t} + i\hbar \frac{\partial}{\partial t} \right] \chi_2(\hat{R}; t) \\
&= \left[\frac{1}{2m} \left[\hat{P} + \frac{\partial S}{\partial \hat{R}} \right]^2 + H_{22}(\hat{R}) \right] \chi_2 + H_{21}(\hat{R}) \chi_1 \ .
\end{aligned} \tag{3.30b}$$

We have neglected the matrix elements containing $\partial \phi_i / \partial R$ or $\partial^2 \phi_i / \partial R^2$ since we work with a diabatic representation and assume that the term H_{12} is the largest coupling between the electronic states. The matrix elements $H_{ij}(\hat{R})$ are defined by Eq. (3.7) and the orthonormality condition (3.5) has been assumed.

The classical limit is taken by assuming that

$$i\hbar \frac{\partial \chi_i}{\partial t} + \frac{\partial S}{\partial t} \chi_i \simeq \frac{\partial S}{\partial t} \chi_i$$

and

$$\left[\hat{P}+\frac{\partial S}{\partial \hat{R}}\right]^2 \simeq \left[\frac{\partial S}{\partial \hat{R}}\right]^2 ,$$

and the Eqs. (3.30a) and (3.30b) become

$$-\frac{\partial S}{\partial t}\chi_1 = \left[\frac{1}{2m}\left[\frac{\partial S}{\partial \hat{R}}\right]^2 + H_{11}\right]\chi_1 + H_{12}\chi_2 \quad (3.31a)$$

and

$$-\frac{\partial S}{\partial t}\chi_2 = \left[\frac{1}{2m}\left[\frac{\partial S}{\partial \hat{R}}\right]^2 + H_{22}\right]\chi_2 + H_{21}\chi_1 . \quad (3.31b)$$

Multiplying Eq. (3.31a) with χ_1 and (3.31b) with χ_2 and adding the results leads to

$$-\frac{\partial S}{\partial t} = \frac{1}{2m}\left[\frac{\partial S}{\partial \hat{R}}\right]^2 + V(\hat{R},t) \quad (3.32)$$

with

$$V(\hat{R},t) = \left[\sum_{i=1}^2 \sum_{j=1}^2 \chi_i^* H_{ij}(\hat{R})\chi_j\right]\left[\sum_{i=1}^2 \chi_i^*\chi_i\right]^{-1} . \quad (3.33)$$

Equation (3.32) is a Hamilton-Jacobi equation with an effective potential $V(\hat{R},t)$ which depends on the potential energies $H_{ii}(R)$ of the two states, on the coupling $H_{12}(R)$ between them, on the probability $\chi_i^*\chi_i(\sum \chi_i^*\chi_i)^{-1}$ that the particle is in the state i ($i=1,2$) and on the "coherent term" $\chi_i^*\chi_j$ which introduces the effect of quantum interference between the two nuclear states. As in Sec. III B classical mechanics appears only as a device to compute the eikonal.

Using Eq. (3.32) we can rewrite Eqs. (3.30) as

$$i\hbar\frac{\partial \chi_1}{\partial t} = \frac{1}{2m}\left[\hat{P}^2 + 2\frac{\partial S}{\partial \hat{R}}\hat{P} + \frac{\hbar}{i}\frac{\partial^2 S}{\partial \hat{R}^2} - V(\hat{R},t)\right]\chi_1$$

$$+ H_{11}(R)\chi_1 + H_{22}(R)\chi_2 \quad (3.34a)$$

and

$$i\hbar\frac{\partial \chi_2}{\partial t} = \left[\frac{1}{2m}\left[\hat{P}^2 + 2\frac{\partial S}{\partial \hat{R}}\hat{P} + \frac{\hbar}{i}\frac{\partial^2 S}{\partial \hat{R}^2}\right] - V(\hat{R};t)\right]\chi_2$$

$$+ H_{22}(R)\chi_2 + H_{21}(\hat{R})\chi_1 . \quad (3.34b)$$

If the wave function is such that the momentum fluctuations are small compared to the classical momentum given by Eq. (3.32), and the functions of coordinate $S(\hat{R},t)$, $H_{ij}(\hat{R})$, and $V(\hat{R},t)$ vary smoothly with $\hat{R}$ over the spatial scale set by the quantum fluctuations in coordinate, we can replace $\hat{P}$ and $\hat{R}$ in Eqs. (3.34) with their classical values $P(t)$ and $R(t)$. Furthermore, the diagonal matrix element common to both equations can be eliminated by introducing in the wave function $\psi(x,R;t)$ defined by Eq. (3.29) the appropriate phase factor. With these changes the (3.33) become

$$i\hbar\dot{\chi}_i(t) = H_{ii}(R(t))\chi_i(t) + H_{ij}(R(t))\chi_j(t)$$

$$j,i = 1,2 \ (i\neq j) \quad (3.35)$$

and the effective potential is

$$V(R(t),t) = \frac{\displaystyle\sum_{i=1}^2 \sum_{j=1}^2 \chi_i^*(t)\chi_j(t)H_{ij}(R(t))}{\displaystyle\sum_i \chi_i^*(t)\chi_i(t)} . \quad (3.36)$$

Here the nuclear wave function depends on time only.

We can now summarize the result obtained by using the eikonal method for the two-state problem. The quantum amplitudes $\chi_i(t)$ are given by the same equations as those of the customary trajectory method (Sec. III A). The classical equation of motion is however deeply modified since the potential energy given by Eq. (3.36) is neither H_{11} nor H_{22}, nor a simple classical average $\sum \chi_i^*\chi_i H_{ii}(R)$.

IV. PATH-INTEGRAL FORMULATION

As we have mentioned our strategy in generating improved trajectory approximations is to formulate the problem quantum mechanically and then to take the classical limit in the degrees of freedom whose motion is to be described by a trajectory, while maintaining a quantum theory for the other variables. The classical limit can be taken by a variety of methods. When applied to all the degrees of freedom of a one-state problem, all these methods lead to Newton's equation. However, the same methods applied to a many-state problem in which some degrees of freedom are treated quantum mechanically lead to different trajectory equations. The acceptance of such approximations and the choice of the best among them is based on our prior intuitive expectations of what such a mechanics should be, on their agreement with the experiments (where reliable comparisons can be made) and on their computational advantages. Given this situation it seems to us worthwhile to explore under what circumstances various methods of taking the classical limit lead to the same results. Here we show that within a path-integral formulation the theory derived in Sec. III is recovered if we use a coherent-state representation to describe the electronic states and then treat *all* degrees of freedom classically (by taking the stationary phase approximation).

We consider the Hamiltonian

$$H = \sum_{n=1}^N H_{nn}(R)|n\rangle\langle n| + \sum_{n,m=1}^N H_{nm}(R)|n\rangle\langle m|$$

$$+ \frac{P^2}{2M}\sum_{n=1}^N |n\rangle\langle n| , \quad (4.1)$$

where $|n\rangle$ are the electronic states, and R, P, and M denote nuclear position momentum and mass, respectively. This Hamiltonian corresponds to a diabatic representation in which the different electronic states are coupled by H_{nm} and the coupling due to the nuclear kinetic energy operator is disregarded. We wish to derive a path-integral representation for the propagator

$$K(R\psi, R_0\psi_0 \mid t) = \langle R\psi \mid e^{-(i/\hbar)Ht} \mid R_0\psi_0 \rangle \ , \qquad (4.2)$$

where $\mid R\psi \rangle$ denotes a state of the system in which the electronic state is $\psi = \sum \chi_n \mid n \rangle$ and the nuclear state is given by the eigenfunction $\mid R \rangle$ of the nuclear position operator. To this end we use the resolutions of the identity operator in nuclear space

$$\int dR \mid R \rangle \langle R \mid = 1 \qquad (4.3)$$

and in the electronic space

$$\int d\psi \mid \psi \rangle \langle \psi \mid = 1 \ . \qquad (4.4)$$

Here

$$\int d\psi \equiv (N+1)! \int' \left[\prod_{n=1}^{N} \frac{d(\mathrm{Re}\chi_n) d(\mathrm{Im}\chi_n)}{\pi i} \right] \ , \qquad (4.5)$$

where the prime denotes integration under the restriction $\sum \mid \chi_n \mid^2 = 1$.

The identity (4.4) and (4.5) may be easily proven by showing that

$$\left\langle n \left| \int d\psi \left| \psi \right\rangle \langle \psi \mid m \right\rangle = (N+1)! \int' (dx_1 dy_1 / \pi)(x_n - iy_n) \right.$$
$$\times (x_m + iy_m) = \delta_{nm} \ .$$

The path integral can be constructed in the usual way

$$K(R\psi, R_0\psi_0 \mid t) = \left\langle R_L\psi_L \left| \prod_{j=1}^{L} e^{-(i/\hbar)H\Delta t} \right| R_0\psi_0 \right\rangle$$

$$= \left[\prod_{j=1}^{L-1} \int dR_j \int d\psi_j \right] \prod_{j=1}^{L} \langle R_j\psi_j \mid e^{-iH\Delta t/\hbar} \mid R_{j-1}\psi_{j-1} \rangle \ , \qquad (4.6)$$

where $\Delta t = t/L$, $\psi_j = \psi(t_j)$, $t_j = t_0 + j\Delta t$, and where R_L and ψ_L represent R and ψ at time t. Focusing now on the matrix element $\langle R_j\psi_j \mid e^{-H\Delta t/\hbar} \mid R_{j-1}\psi_{j-1} \rangle$, we evaluate its electronic part first, keeping R and P in the Hamiltonian (4.1) as parameters. For completeness we outline the procedure in the Appendix. The result is

$$\langle R_j\psi_j \mid \exp(-iH\Delta t/\hbar) \mid R_{j-1}\psi_{j-1} \rangle = \exp(-\langle \psi_j \mid \dot{\psi}_j \rangle) \left\langle R_j \left| \exp\left[-\frac{i}{h} \left[\frac{P^2}{2M} + V_j(R) \right] \Delta t \right] \right| R_{j-1} \right\rangle \ . \qquad (4.7)$$

Here P and R are operators in the space spanned by the nuclear wave functions, and $\langle \psi_j \mid \dot{\psi}_j \rangle$ is given in terms of the coefficients χ by

$$\langle \psi_j \mid \dot{\psi}_j \rangle = \sum_n \chi_n^*(t_j) \dot{\chi}_n(t_j) \ . \qquad (4.8)$$

$V_j(R)$ is

$$V_j(R) = \sum_n \mid \chi_n(t_j) \mid^2 H_{nn}(R)$$

$$+ \sum_n \sum_{\substack{m \\ n \neq m}} \chi_n^*(t_j) \chi_m(t_j) H_{nm}(R) \ . \qquad (4.9)$$

The nuclear matrix element in (4.7) is now seen to take a form which is normally obtained for a quantum particle moving under the influence of a potential $V(R)$. Evaluating the R matrix element in the standard way and inserting it into (4.6), then taking the $L \rightarrow \infty$ limit, yields

$$K(R\psi, R_0\psi_0 \mid t) = \int_{R_0\psi_0}^{R\psi^*} D\psi \, DR \, e^{iS(R\psi, R_0\psi_0 \mid t)} \qquad (4.10)$$

with

$$S(R\psi, R_0\psi_0 \mid t) = \int_{t_0}^{t} dt' L(R(t'), \dot{R}(t'), \chi(t), \dot{\chi}(t'), t')$$

$$\qquad (4.11)$$

and the "Lagrangian" L given by

$$L = i \sum_n \chi_n^* \dot{\chi}_n + \frac{1}{\hbar} \left[\frac{1}{2} M\dot{R}^2 - \sum_n \mid \chi_n \mid^2 H_{nn}(R) \right.$$

$$\left. - \sum_n \sum_{\substack{m \\ n \neq m}} \chi_n^* \chi_m H_{nm}(R) \right] \ . \qquad (4.12)$$

The symbols $D\psi$ and DR are

$$D\psi \equiv \lim_{L \rightarrow \infty} \prod_{j=1}^{L-1} \left[(N+1)! \prod_{l=1}^{N} \frac{d[\mathrm{Re}\chi_l(t_j)] d[\mathrm{Im}\chi_l(t_j)]}{\pi i} \right]$$

$$\qquad (4.13)$$

and

$$DR \equiv \lim_{L \rightarrow \infty} \left[\left[\frac{M}{2\pi i\hbar(t/L)} \right]^{L/2} \prod_{j=1}^{L-1} dR(t_j) \right] \ . \qquad (4.14)$$

Equation (4.10) is an exact representation of the propagator in terms of a path integral over all the paths which lead from the state R_0, $\psi_0 = \sum \chi_n(t_0) \mid n \rangle$ at time t_0 to the final state R and $\psi = \sum \chi_n(t) \mid n \rangle$, at time t. Having found this form it is of interest to look for the optimal path, the analog of the classical limit, as an approximation to the path integral. For this purpose define $X_n = \mathrm{Re}\chi_n$, $Y_n = \mathrm{Im}\chi_n$ and replace in Eq. (4.12) $\chi_n = X_n + iY_n$ and $\chi_n^* = X_n - iY_n$ everywhere. To satisfy the restriction $\sum \mid \chi_n \mid^2 = 1$ we may add to L a term $\lambda \sum (X_n^2 + Y_n^2)$, where λ is a Lagrange multiplier, but it

turns out that this does not change the result. The optimal path is the solution of the Euler-Lagrange equations of motion generated by minimizing the action given by Eqs. (4.11) and (4.12):

$$\frac{\partial L}{\partial R} - \frac{d}{dt}\frac{\partial L}{\partial \dot{R}} = 0 \; ,$$

$$\frac{\partial L}{\partial X_n} - \frac{d}{dt}\frac{\partial L}{\partial \dot{X}_n} = 0 \; , \quad \frac{\partial L}{\partial Y_n} - \frac{d}{dt}\frac{\partial L}{\partial \dot{Y}_n} = 0 \; \text{(all } n\text{)} \; . \tag{4.15}$$

These yield the following equations of motion (EOM's):

$$\ddot{R} = -\frac{1}{M}\frac{\partial V(R,\{\mathcal{X}_n\})}{\partial R} \; , \tag{4.16}$$

$$\dot{\mathcal{X}}_n = -\frac{i}{\hbar}\left[H_{nn}(R)\mathcal{X}_n + \sum_{\substack{k \\ k \neq n}} H_{nk}(R)\mathcal{X}_k \right]$$
$$(n = 1, \ldots, N) \tag{4.17}$$

with the effective potential

$$V(R,\{\mathcal{X}_n\}) = \sum_n H_{nn}(R)|\mathcal{X}_n|^2 + \sum_n \sum_{\substack{m \\ n \neq m}} H_{nm}(R)\mathcal{X}_n^*\mathcal{X}_m \; . \tag{4.18}$$

To obtain Eq. (4.17) we have recombined the equations obtained for $\dot{X}_n$ and $\dot{Y}_n$. Equations (4.16)—(4.18) are identical to the equations of motion derived in Sec. III.

The following comments should be made with respect to this derivation. (a) The same results are obtained if instead of replacing $\mathcal{X}_n$ by $X_n + iY_n$ we regard $\mathcal{X}_n$ and $\mathcal{X}_n^*$ as independent variables and use the Euler-Lagrange equations in the form $\partial L/\partial \mathcal{X}_n - (d/dt)(\partial L/\partial \dot{\mathcal{X}}_n) = 0$. (b) In the absence of coupling the nuclear motion (i.e., if we were evaluating the time evolution of an N-level system) the resulting EOM (4.17) is just the Schrödinger equation for this system. Obviously the optimal path is overdetermined by the requirements that $\psi(t_0) = \psi_0$ and $\psi(t) = \psi$ are given, and generally we will not find a path that will satisfy both these requirements and Eq. (4.17). The result may be still interpreted in the following way. The probability amplitude to be in a final state ψ_t starting from an initial state ψ_0 may be written in the form $\int d\psi \langle \psi_t | \psi \rangle K(\psi,\psi_0 | t)$. The optimization procedure replaces this integral by the maximum value of the integrand which is obtained if $\psi = \sum \mathcal{X}_n | n \rangle$ is the solution of Eq. (4.17).

The procedure described above may be used to obtain equations of motion for more general situations involving coupled quantum-classical systems. For example, the Hamiltonian (4.1) can be supplemented with coupling terms arising from the effect of the nuclear kinetic energy operator on the electronic states, leading to

$$H = \sum_{n,m=1}^{N} \bar{H}_{nm}(R)|n\rangle\langle m| + \frac{P}{M}\sum_{n,m=1}^{N} W_{nm}(R)|n\rangle\langle m|$$
$$+ \frac{P^2}{2M}\sum_n |n\rangle\langle n| \tag{4.19}$$

with

$$\bar{H}_{nm}(R) = E_n(R)\delta_{nm} + V_{nm}(R)$$
$$+ \frac{\hbar^2}{2M}\int d^2r\, \phi_n^*(r,R)\frac{\partial^2}{\partial R^2}\phi_m(r,R) \tag{4.20}$$

and

$$W_{nm}(R) = -i\hbar \int d^3r\, \phi_n^*(r,R)\frac{\partial}{\partial R}\phi_m(r,R) \; . \tag{4.21}$$

Here $\phi_n(r,R) \equiv |n\rangle$ is used to denote the explicit dependence of the electronic wave function on the electronic (r) and nuclear (R) coordinates. The procedure described above may be used to obtain the propagator in the form

$$K(R\psi,R_0\psi_0 | t) = \lim_{L\to\infty} \int \frac{dP_L}{2\pi}\left[\prod_{j=1}^{L-1}\int \frac{dR_j dP_j}{2\pi}\right]$$
$$\times \left[\prod_{j=1}^{L-1}\int d\psi_j\right]e^{iS} \; , \tag{4.22}$$

with

$$S = \int_0^t dt' \left[i\langle \psi | \dot{\psi}\rangle + \frac{i}{\hbar}\left[P\dot{R} - \frac{P^2}{2M} - \frac{P}{M}W(R,\psi) \right. \right.$$
$$\left.\left. -U(R,\psi) \right] \right] \; , \tag{4.23}$$

where

$$W(R,\psi) = \sum_n \sum_m \mathcal{X}_n^*\mathcal{X}_m W_{nm}(R) \; ,$$
$$U(R,\psi) = \sum_n \sum_m \mathcal{X}_n^*\mathcal{X}_m \bar{H}_{nm}(R) \; . \tag{4.24}$$

Here we have used the phase space (R,P) representation of the nuclear part of the path integral. The EOM's for the optimal path, obtained from the extremum of the action S given by Eq. (22), are

$$\dot{P} = -\frac{P}{M}\frac{\partial W(R,\psi)}{\partial R} - \frac{\partial U(R,\psi)}{\partial R} \; ,$$

$$\dot{R} = \frac{1}{M}[P + W(R,\psi)] \; ,$$

$$\dot{\mathcal{X}}_n = -\frac{i}{\hbar}\sum_n \left[\bar{H}_{nm}(R) - \frac{P}{M}W_{nm}(R) \right]\mathcal{X}_m \; .$$

The implications of these equations will be explored elsewhere.

V. CROSSING OF A DISCRETE STATE BY A CONTINUUM

As we discussed in Sec. II if a neutral atom approaches the surface it can be ionized by crossing to an infinite number of states differing from each other through the final state of the transferred electron, the position of the crossing point, and the amount of asymptotic energy mismatch to be compensated. To treat this case of a neutral curve crossing a continuum of ionic curves we use for the amplitude of the total wave function Eq. (3.10) the form

$$A(x,\hat{R};t) = \chi_1(\hat{R})\phi_1(x,\hat{R}) + \int d\epsilon\,\rho(\epsilon)\chi_\epsilon(\hat{R},t)\phi_\epsilon(x,\hat{R})$$

$$(5.1)$$

leading to

$$i\hbar\dot{\chi}_1(t) = H_{11}(R(t))\chi_1(t) + \int d\epsilon\,\rho(\epsilon)H_{1\epsilon}(R(t))\chi_\epsilon(t) \quad (5.2)$$

and

$$i\hbar\dot{\chi}_\epsilon(t) = H_{\epsilon\epsilon}(R(t))\chi_\epsilon(t) + H_{\epsilon 1}(R(t))\chi_1 \ . \quad (5.3)$$

We neglect the matrix elements $H_{\epsilon\epsilon'}$ ($\epsilon \neq \epsilon'$), since the continuum states do not interact with each other. In the present context this means that the motion of the ion does not induce transitions of the transferred electron from ϵ to ϵ', so the electron-hole pair excitations of the metal by the ionic motion is disregarded. The effective classical interaction is

$$V(R(t)) = H_{11}(R(t))|\chi_1(t)|^2$$

$$+ \int d\epsilon\,\rho(\epsilon)[H_{1\epsilon}(R(t))\chi_1^*(t)\chi_\epsilon(t)$$

$$+ H_{\epsilon 1}(R(t))\chi_\epsilon^*(t)\chi_1(t)]$$

$$+ \int d\epsilon\,\rho(\epsilon)H_{\epsilon\epsilon}(R(t))|\chi_\epsilon(t)|^2 \ . \quad (5.4)$$

The "classical" trajectory can be computed by using Hamilton equations with the Hamiltonian $P(t)^2/2m + V(R(t))$.

We can simplify these equations by following a standard procedure used in situations when a discrete state interacts with a continuum. We start by integrating exactly

Eq. (5.3) to express χ_ϵ as a function of χ_1; we introduce this equation for χ_ϵ in Eq. (5.2) and obtain a closed equation for χ_1:

$$i\hbar\dot{c}_1(t) = \int_{-\infty}^{t} dt'\,G(t,t')c_1(t') \quad (5.5)$$

with

$$G(t,t') \equiv (-i/\hbar)\int dE\,\rho(E)H_{1E}(t)H_{1E}(t')$$

$$\times \exp\{-(i/\hbar)[\mu(t)-\mu(t')]\}$$

$$\times \exp[-(i/\hbar)E(t-t')] \ ,$$

$$\mu(t) \equiv \int_{-\infty}^{t} [H_{11}(\tau)-H_{00}(\tau)]d\tau \ . \quad (5.6)$$

and

$$\chi_1(t) = c_1(t)\exp\left[-(i/\hbar)\int_{-\infty}^{t} H_{11}(\tau)d\tau\right] \ . \quad (5.7)$$

Here we use the fact that the ionic curves are parallel to each other. We pick one of them as a reference state and denote it by $H_{00}(R(\tau)) \equiv H_{00}(\tau)$, and write the others as $H_{00}(R(\tau)) + E$, where E is a time-independent energy giving the difference between the parallel curves H_{EE} and H_{00}. If we assume that the "amplitude" $H_{1E}(t')c_1(t')$ varies with t' on a time scale much slower that the phase $\mu(t)-\mu(t')+E(t-t')$, then we can replace $H_{1E}(t')c_1(t')$ with $H_{1E}(t)c_1(t)$ and remove it from the integral over t'. After that we can perform the integral over t' by inserting a factor $\exp(+\eta t)$, $\eta > 0$, to ensure that the integral converges. We get

$$\int_{-\infty}^{t} dt'\exp\left[-(i/\hbar)\int_{-\infty}^{t'}[f(\tau)-\epsilon+i\eta]d\tau\right] \cong -(\hbar/i)[f(t)-\epsilon+i\eta]^{-1}\exp\left[-(i/\hbar)\int_{-\infty}^{t}[f(\tau)-\epsilon+i\eta]d\tau\right] \ . \quad (5.8)$$

In deriving this we assume that $f(\tau)$ [which in our case is $H_{11}(\tau)-H_{00}(\tau)+E$] can be replaced by $f(t)$ and be treated as a nearly constant quantity. After performing these calculations we obtain

$$i\hbar\dot{c}_1(t) = [\Delta(t)-i\Gamma(t)]c_1(t) \quad (5.9)$$

with

$$\left.\begin{matrix}\Delta(t)\\\Gamma(t)\end{matrix}\right\} = \lim_{\eta\to 0}\left\{\begin{matrix}\text{Re}\\\text{Im}\end{matrix}\right\}\int dE\,\rho(E)|H_{1E}(t)|^2[E+H_{00}(t)-H_{11}(t)+i\eta]^{-1} \ . \quad (5.10)$$

If the integration interval is practically infinite, the last equation leads to

$$\Delta(t) = P\int_{-\infty}^{+\infty}\frac{dE\,\rho(E)|H_{1E}|^2}{E+H_{00}(t)-H_{11}} \quad (5.11)$$

where P denotes the principal part, and

$$\Gamma(t) = \pi\int_{-\infty}^{+\infty} dE\,\rho(E)|H_{1E}|^2\delta(E+H_{00}(t)-H_{11}(t)) \ . \quad (5.12)$$

If the continuum states form a narrow band [which means that $\rho(\epsilon)$ is zero outside a narrow energy range], these equations will be modified by "edge effects." A very nar-

row ionic band influences the neutral state just like a single ionic state.

The calculations carried out above permit us to rewrite the effective potential given by Eq. (5.4) in terms of $|c_1(t)|^2$, $\Delta(t)$, and $\Gamma(t)$ alone. The last term in Eq. (5.4) can be written as

$$\int dE\,\rho(E)H_{EE}(t)|c_E(t)|^2 = [1-|c_1(t)|^2]H_{00}(t) \ . \quad (5.13)$$

We obtain this by observing that $H_{EE}(t) = H_{00}(R(t)) + E$ and that we need only the gradient of H_{EE} (to compute the force) so we can take $H_{EE}(t) = H_{00}(R(t))$. Also we use the normalization condition

$$\int dE\,\rho(E)\,|c_E(t)|^2 + |c_1(t)|^2 = 1 \ . \tag{5.14}$$

The middle two terms in Eq. (5.4) can be rewritten by expressing χ_ϵ in terms of χ_1 and using the approximations presented under Eq. (5.7); the result is that the two terms are equal to $-2\Delta(t)\,|c_1(t)|^2$.

The above calculations allow us to write the effective potential as

$$V(R(t),t) = |c_1(t)|^2[H_{11}(R(t)) - 2\Delta(t)]$$
$$+ H_{00}(R(t))[1 - |c_1(t)|^2] \tag{5.15}$$

with

$$c_1(t) = c_1(0)\exp\left[-(i/\hbar)\int_0^t \Delta(\tau)d\tau\right]$$
$$\times \exp\left[-\int_0^t \Gamma(\tau)d\tau\right] . \tag{5.16}$$

The results (5.11) and (5.12) may be improved by recognizing from the beginning that $c_1(t)$ has a (yet unknown) phase $-1/\hbar \int \Delta(\tau)d\tau$ and by determining this phase self-consistently. The result is

$$\Delta(t) = P\int_{-\infty}^{+\infty} \frac{dE\,\rho(E)\,|H_{1E}|^2}{E + H_{00}(t) - H_{11}(t) - \Delta(t)} \tag{5.17}$$

and

$$\Gamma(t) = \pi\int_{-\infty}^{+\infty} dE\,\rho(E)\,|H_{1E}|^2$$
$$\times \delta(E + H_{00}(t) - H_{11}(t) - \Delta(t)) . \tag{5.18}$$

Since Δ and Γ are the real and imaginary parts of the self-energy of the state 1, these equations are reminiscent of random phase approximation (RPA) results. This is not surprising since the corrections in Eqs. (5.17) and (5.18) are of the type appearing in the time-dependent Hartree approximation.

Before concluding this section we briefly discuss the case where a local surface state with a long lifetime exists above the Fermi level. It is easy to treat this case along lines similar to those described above where we now have two discrete states 1 (neutral) and 2 (surface state) coupled to the continuum of ionic states. The neutral state coupling to the surface state leads to the ionization of the neutral. The electron transferred into the surface state can be recaptured by the ion (the coupling is $H_{2\epsilon}$) leading to neutralization. The mean potential for this case is

$$V(R(t)) = \sum_{i=1}^{2}\sum_{j=1}^{2} H_{ij}(R(t))\chi_i^*\chi_2 + \sum_{j=1}^{2}\int d\epsilon\,\rho(\epsilon)[H_{j\epsilon}(R(t))\chi_i^*\chi_\epsilon + H_{\epsilon j}(R(t))\chi_\epsilon^*\chi_j] + \int d\epsilon\,\rho(\epsilon)H_{\epsilon\epsilon}(R(t))\,|\chi_\epsilon|^2 \ . \tag{5.19}$$

The classical equation for $R(t)$ is, as before,

$$M\ddot{R} = -\frac{\partial V(R)}{\partial R} \ , \tag{5.20}$$

while the equations for the amplitudes χ are

$$\dot{\chi}_1 = -\frac{i}{\hbar}\left[H_{11}(R(t))\chi_1 + H_{12}(R(t))\chi_2 + \int d\epsilon\,\rho(\epsilon)H_{1\epsilon}(R(t))\chi_\epsilon\right] ,$$

$$\dot{\chi}_2 = -\frac{i}{\hbar}\left[H_{22}(R(t))\chi_2 + H_{21}(R(t))\chi_1 + \int d\epsilon\,\rho(\epsilon)H_{2\epsilon}(R(t))\chi_\epsilon\right] , \tag{5.21}$$

$$\dot{\chi}_\epsilon = -\frac{i}{\hbar}[H_{\epsilon\epsilon}(R(t))\chi_\epsilon + H_{\epsilon 1}(R(t))\chi_1 + H_{\epsilon 2}(R(t))\chi_2] \ .$$

Proceedings along lines similar to those described below Eq. (5.4) leads to the set of equations

$$\dot{c}_1 = -\frac{i}{\hbar}[H_{12}(R) - \Sigma_{12}(R)]\exp\left[-\frac{i}{\hbar}\int_{-\infty}^{t} d\tau\,\epsilon_{21}(\tau)\right]c_2 + \frac{i}{\hbar}\Sigma_{11}(R)c_1 \ , \tag{5.22a}$$

$$\dot{c}_2 = -\frac{i}{\hbar}[H_{21}(R) - \Sigma_{21}(R)]\exp\left[-\frac{i}{\hbar}\int_{-\infty}^{t} d\tau\,\epsilon_{12}(\tau)\right]c_1 + \frac{i}{\hbar}\Sigma_{22}(R)c_2 \ , \tag{5.22b}$$

and

$$m\ddot{R} = -\left\{[H'_{11}(R) - H'_{00}(R)]\,|c_1|^2 + [H'_{22}(R) - H'_{00}(R)]\,|c_2|^2\right.$$
$$\left. - H'_{00}(R) + 2\,\mathrm{Re}\left[\Sigma'_2(R)\,|c_2|^2 - [H'_{12}(R) - \Sigma'_{12}(R) - \Sigma'^*_{21}(R)]\exp\left[-\frac{i}{\hbar}\int_{-\infty}^{t} d\tau\,\epsilon_{21}(\tau)\right]c_1^*c_2\right]\right\} , \tag{5.23}$$

where

$$\epsilon_{21} = H_{22} - H_{11} \, , \tag{5.24}$$

$$\Sigma_{kl} = D_{kl} - i \Gamma_{kl} \quad (k, l = 1, 2) \, , \tag{5.25}$$

$$D_{kl}(R) = P \int dE \, \rho(E) \frac{H_{kE}(R) H_{El}(R)}{H_{00}(R) + E - H_{11}(R)} \, , \tag{5.26}$$

$$\Gamma_{kl}(R) = \pi \int dE \, \rho(E) H_{kE}(R) H_{El}(R)$$
$$\times \delta(H_{00}(R) + E - H_{11}(R)) \, , \tag{5.27}$$

and where the prime denotes derivative with respect to R. [In Σ'_{kl} this derivative is obtained by replacing $H_{kE}(R) H_{El}(R)$ by its R derivative with $H_{11}(R)$ kept fixed.] The set of equations (5.22) and (5.23) may be now integrated numerically if a model for the coupling matrix elements is constructed.

VI. THE INCLUSION OF PHONON AND ELECTRON-HOLE EXCITATION AS ENERGY-LOSS CHANNELS

As we have discussed in Sec. II, if the kinetic energy K of the incident neutral is higher than the asymptotic energy mismatch $\Delta_\alpha V(\infty)$ [i.e., $\Delta_\alpha = K - \Delta V_\alpha(\infty) > 0$] the ion formed by charge transfer sticks to the surface only if it loses (to phonons or electron-hole pairs) an amount of energy larger than Δ_α. In what follows we outline a curve-crossing theory which includes such energy-loss processes. Both consist of deriving Langevin equations in which the action of phonons or electron-hole pairs generates friction and random forces in the mean trajectory equation.

A. The inclusion of phonons

We consider here the two-state problem discussed in Sec. III C, and in both the wave function and the electronic Hamiltonian we include the coordinates of all the lattice atoms. For simplicity we denote all these coordinates by X and consider the one-dimensional case only. The extension to three dimensions and more than two electronic states is straightforward.

By repeating the derivations presented in Sec. III C we obtain equations identical to (3.35) and (3.36) in which the matrix elements H_{ij} depend on $R(t)$ and $X(t)$. We must now specify a procedure that gives the equation of motion for $R(t)$ and $X(t)$ under the influence of the effective potential

$$V(R, X; t) = \sum_{i=1}^{2} \sum_{j=1}^{2} \chi_i^*(t) \chi_j(t) H_{ij}(R, X) \, . \tag{6.1}$$

We assume here that the neutral curve, which we denote H_{22}, is independent of X. In other words, the energy lost by the neutral to phonons is disregarded since in this context it does not have marked effects on sticking. It can however be easily included, if necessary.

In order to derive a Langevin equation for the present situation we follow Adelman and Doll[33] and divide the lattice atoms into a primary zone which suffers the bulk of the collision with ion, and a secondary zone which interacts with the primary atoms only. For simplicity we

take only one primary atom and denote its coordinate by $Y(t)$; the other lattice atoms form the secondary zone and their coordinates are denoted either by X_μ, $\mu = 1, \ldots, N$, when we need to specify all of them, or by $\overline{X}$, when they are denoted collectively. The equation of motion for the ion is

$$m \frac{d^2 R}{dt^2} = - \sum_{i,j=1}^{2} \chi_i^* \chi_j \frac{\partial H_{ij}(R(t), Y(t), \overline{X}_0)}{\partial R} \, . \tag{6.2}$$

The equation of motion for the primary zone atom is

$$M \frac{d^2 Y}{dt^2} = - |\chi_1|^2 \frac{\partial H_{11}(R, Y, \overline{X}_0)}{\partial Y}$$
$$- 2 \operatorname{Re} \chi_1^* \chi_2 \frac{\partial H_{12}(R, Y, \overline{X}_0)}{\partial Y} + \sum_{\mu=1}^{N} K_\mu X_\mu \, . \tag{6.3}$$

Here K_μ is the force constant coupling X_μ to Y. The equation of motion for the secondary atoms is that of the harmonic lattice in the absence of the ion. $\overline{X}_0$ represents the coordinates of the secondary atoms in their equilibrium positions.

Following the Adelman-Doll procedure we can eliminate the secondary lattice atoms to obtain a Langevin equation for the primary atom:

$$M \frac{d^2 Y}{dt^2} = - |\chi_1|^2 \frac{\partial H_{11}}{\partial Y} - 2 \operatorname{Re} \chi_1^* \chi_2 \frac{\partial H_{12}}{\partial Y}$$
$$+ \int_{-\infty}^{t} \gamma(t - t') Y(t') dt' + F(t) \, . \tag{6.4}$$

The friction kernel is proportional to the linear-response function of the lattice in the absence of the primary atom. The random force $F(t)$ is Gaussian and its correlation function is the Green's function of the secondary lattice in the absence of the primary atom. The Green's function and the linear-response function are related by the fluctuation-dissipation theorem. The Langevin equation can be solved efficiently by modeling the friction and generating $F(t)$ on the computer as shown by Sugard et al.[34]

The coupling to the lattice affects not only the nuclear motion but also the transition amplitudes $c_i(t)$ since $H_{ij}(R, Y, \overline{X}_0)$ are now function of the stochastic variable Y. Both the crossing point and the coupling strength are random variables. The observable quantities of the theory must be computed by running many stochastic trajectories and averaging the quantity of interest over them.

B. Energy loss due to electron-hole pair excitations

Recently there has been a lively interest in the manner in which the excitation of electron-hole pairs in the surface influences the dynamics of adsorbates.[3,4,9,10,12,21,35-55] Two types of mechanisms are possible in the problem of interest here. In the first, the electron jumping from the atom into the metal interacts with the electrons already there and it is inelastically scattered. If the interaction partner is below the Fermi level the interaction can excite an electron-hole pair. This is similar

to a shakeup process and it could be represented by giving each ionic state a width which corresponds to the rate of energy loss from the transferred electron to the electrons below the Fermi level. The transferred electron can also interact with the electrons thermally excited above the Fermi level and this leads to either energy loss or gain. This can also be represented by giving the ionic state a width. The second mechanism consists in direct energy transfer from the moving ion to the electrons in the metal, and it is discussed here in detail. This also has two distinct aspects. One corresponds to electron-hole pair excitations caused by the sudden creation of the ion through electron transfer and it was discussed previously in a different physical context by Gadzuk and Metiu[43] and Schönhammer and Gunnarson.[46] The other corresponds to electron-hole pair excitations by the ionic motion and was considered, for example, by d'Agliano et al.,[37] Sugard et al., and Korzeniewski et al.[54]

In this section we consider the effect of the energy transfer, the excitation of electron-hole pairs, on the motion of the ion. In the spirit of the Langevin approach to many-body dynamics we would like to produce an equation which does not make explicit reference to the detailed electron-hole pair dynamics. Since the motion of the ion drives the excitation of the electrons, it must provide the excitation energy; therefore, the desired equation must contain a friction term. Furthermore, the interaction of the ion with the polarization fields caused by the thermal fluctuations of the electron in the metal must be taken into account through the presence of a random force in the equation of motion of the ion. Since the metal screens the ion field we can assume that the screened interaction causes a small perturbation in the motion of the electrons in the metal. Therefore we expect the random force and the friction kernel, appearing in the equation of motion of the ion, to be related through a "fluctuation-dissipation" relationship.

To include in the curve-crossing problem of interest here the effects of electron-hole pair excitation we use a formulation developed by Leung et al.,[55] who showed that within the random phase approximation (RPA) the electron gas can be "bosonized" so that its Hamiltonian, in the presence of an ion located at $\mathbf{R}(t)$, is

$$H_{e\text{-}h} = \sum_1 \hbar\omega_q \eta_q^\dagger \eta_q + \sum_q [V_q(R(t))\eta_q^\dagger + V_q^*(R(t))\eta_q]$$
$$\times |c_1(t)|^2 . \tag{6.5}$$

Here $\eta_q^\dagger$ and η_q are boson creation and annihilation operators and ω_q is their frequency (corresponding to the electron-hole pair excitation frequency). The quantity $|c_1(t)|^2$ appears in Eq. (6.5) because the electrons of the metal interact with the ion only. The frequencies ω_q and the screened interaction $V_q(\mathbf{R})$ are expressed in terms of the generalized eigenvalues and eigenvectors of the frequency-dependent, nonlocal, longitudinal, dielectric constant $\epsilon(\mathbf{r},\mathbf{r}';\omega)$ of the metal (with surface) given by RPA.[55] The solutions ω_q of the equation

$$\det\epsilon(\mathbf{r},\mathbf{r};\omega_q) = 0 \tag{6.6}$$

provide the boson frequencies. The generalized eigenvectors $\xi_q(\mathbf{r})$, given by

$$\int \epsilon(\mathbf{r},\mathbf{r};\omega_q)\xi_q(\mathbf{r}')d\mathbf{r}' = 0 , \tag{6.7}$$

are used to obtain $V_q(R(t))$ from the equation

$$V_q(R(t)) = e^2 Z \int |\mathbf{r}-\mathbf{R}(t)|^{-1}\xi_q(\mathbf{r})d\mathbf{r} . \tag{6.8}$$

$V_q(R)$ is the screened ion-electron coupling. Here e and Ze are electron and ion charges.

We now wish to obtain the equations of motion in which the coordinate $R(t)$, its conjugate momentum $P(t)$ and η_q and $\eta_q^\dagger$ are classical variables moving in a mean potential analogous to the one obtained in the previous sections. The procedure used in the previous sections leads to the following classical Hamiltonian:

$$H_c(R,P,\eta,\eta^*;\chi_1,\chi_2) = \frac{P^2}{2m} + \sum_q \hbar\omega_q \eta_q^* \eta_q + |\chi_1|^2 H_{11}(R) + |\chi_2|^2 H_{22}(R) + \chi_1^* \chi_2 H_{12}(R) + \chi_1 \chi_2^* H_{21}(R)$$

$$+ |\chi_1|^2 \sum_q [V_q(R)\eta_q^* + V_q^*(R)\eta_q] . \tag{6.9}$$

Note that η_q^*, the complex conjugate of η_q, appears in place of the operator $\eta_q^\dagger$, in accord with the classical equivalent of the boson creation operator.

From this Hamiltonian the equations of motion in the mean-trajectory approximation are obtained using Hamilton's equations:

$$\dot{R} = \frac{\partial H_c}{\partial P} = \frac{P}{m} , \tag{6.10}$$

$$\dot{P} = -\frac{\partial H_c}{\partial R} = -|\chi_1|^2 \left\{ \frac{\partial H_{11}}{\partial R} + \sum_q \left[\left[\frac{\partial V_q}{\partial R}\right]\eta_q^* + \left[\frac{\partial V_q^*}{\partial R}\right]\eta_q \right] \right\} - |\chi_2|^2 \frac{\partial H_{22}}{\partial R} - 2\,\mathrm{Re}\left[\chi_1^*\chi_2 \frac{\partial H_{12}}{\partial R}\right] , \tag{6.11}$$

$$\dot{\eta}_q = \frac{i}{\hbar} \frac{\partial H_c}{\partial \eta_q^*} = -i\omega_q \eta_q - \frac{i}{\hbar} V_q(R) |X_1|^2 , \qquad (6.12)$$

$$\dot{\eta}_q^* = \frac{i}{\hbar} \frac{\partial H_c}{\partial \eta_q} = i\omega_q \eta_q^* + \frac{i}{\hbar} V_q^*(R) |X_1|^2 . \qquad (6.13)$$

In addition, the quantum equations of motion for the amplitudes X_1 and X_2 are obtained in the form

$$i\hbar\dot{X}_1 = \left[H_{11}(R) + \sum_q [V_q(R)\eta_q^* + V_q^*(R)\eta_q] \right] X_1$$
$$+ H_{12}(R)X_2 , \qquad (6.14)$$

$$i\hbar\dot{X}_2 = H_{22}(R)X_2 + H_{21}(R)X_1 . \qquad (6.15)$$

The equations (6.12) and (6.13) can be formally integrated to give

$$\eta_q(t) = \eta_q^0(t) + \int_0^t (i/\hbar) V_q(R(t'))$$
$$\times |X_1(t')|^2 e^{i\omega_q(t'-t)} dt' , \qquad (6.16)$$

where $\eta_q^0(t) = \eta_q^0(0) e^{-i\omega_q t}$ is the value of $\eta_q(t)$ in the absence of the ion. The initial value $\eta_q^0(0)$ may be regarded as a stochastic variable given by the (classical) thermal distribution

$$P(\eta_q^0, \eta_q^{0*}) = \left[\frac{\hbar\omega_q}{\pi^2 k_B T} \right]^{-1} \exp[-(4\hbar\omega_q/k_B T)|\eta_q^0|^2]. \qquad (6.17)$$

Note that Planck's constant appears in this classical distribution because it is used to construct the dimensionless quantities η_q and η_q^* from the momentum and the coordinate of the oscillator.

We summarize these results by outlining how they should be used in a calculation in which all practical concerns (i.e., computer cost) are disregarded. Let us assume that we want to calculate the thermal average of a quantity $A(t) \equiv A(X_1(t), X_2(t), R(t))$. This is the expectation value of the dynamic quantity A [i.e., $A(X_1(t), X_2(t), R(t)) \equiv \langle \psi(t) | \hat{A} | \psi(t) \rangle$] and can, in general, depend on X_1, X_2, and R. To start the calculation we generate by Monte Carlo the values of $\eta_q(0)$ and $\eta_q^*(0)$ for all the bosons (i.e., $q = 1, 2, \ldots, N$) required for a realistic description of the electron excitations of the gas system. We denote the set $\{\eta_q(0), \eta_q^*(0)\}_{q=1,\ldots,N}$ by p. We can now solve simultaneously Eq. (6.16) for $\eta_q(t)$ and $\eta_q^*(t)$, Eqs. (6.14) and (6.15) for $X_1(t)$ and $X_2(t)$, and Eqs. (6.10) and (6.11) for $R(t)$. This provides the quantities $R(t)$, $X_1(t)$, and $X_2(t)$, for any desired time. We can therefore compute $A_p(t)$, corresponding to the set p initial condition. Using important sampling Monte Carlo we can generate more initial conditions and repeat the calculation outlined above. The thermal average $\langle A \rangle$ of $\hat{A}$ is given by

$$\langle A \rangle = \sum_p A_p(X_1(t), X_2(t), R(t)) . \qquad (6.18)$$

While this calculation illustrates the structure of the theory, it is rather expensive. A simpler procedure is to write [by using Eq. (6.16)]

$$\sum_q [V_q(R)\eta_q^*(t) + V_q(R)^* \eta_q]$$
$$\equiv \xi(t) + \int_0^t \gamma(t-\tau)|X_1(\tau)|^2 d\tau \qquad (6.19)$$

with

$$\xi(t) = 2 \, \mathrm{Re} \sum_q V_q^*(t)\eta_q^0(t)$$

and

$$\gamma(t-\tau) = \mathrm{Re}(2/i\hbar) \sum_q V_q(t)V_q^*(\tau) \exp[i\omega_q(t-\tau)] .$$
$$(6.20)$$

We can now treat $\xi(t)$ as a Gaussian variable at each time t with the correlation function

$$\langle \xi(t)\xi(\tau) \rangle = \mathrm{Re} \sum_q V_q(t)V_q^*(\tau)(kT/\hbar\omega_q) \exp[i\omega_q(t-\tau)] .$$
$$(6.21)$$

We can model the sum above by using a simple, but appropriate, function of t and τ; this can save substantial computer time, since we need to generate one Gaussian variable, i.e., $\xi(t)$, for each time point. In making such models we must assure that the exact relationship between $\gamma(t-\tau)$ and $\langle \xi(t)\xi(\tau) \rangle$ is preserved; otherwise fluctuation-dissipation theorem is violated.

VII. DISCUSSION

The main thrust of this paper is that the theory of low-energy collision phenomena which can be described as two- or many-state problems, may have to discard the trajectory approximation. The reason for this is rather general and the problem is present whenever we deal with two sets of degrees of freedom x and R and we must treat x quantum mechanically, but intend to treat R classically.[29] If we replace R in the Hamiltonian with a trajectory $R(t)$, obtained by following some classical prescription, we generate a time-dependent Hamiltonian for the quantum variables x; this forces the quantum subsystem to undergo transitions from the initial state $|i\rangle$ to some set of final states $|f\rangle$, $f = 1, 2 \ldots$. The system conserves energy only if the energy loss (or gain) along the trajectory $R(t)$ equals $E_f - E_i$. Since the latter is different for each final state, energy conservation requires a different trajectory $R_{i,f}(t)$ for each transition $i \rightarrow f$. Therefore the force

$F_{i,f}(R_{i,f}(t))$ appearing in the "Newton" equation for $R_{i,f}(t)$,

$$M\ddot{R}_{i,f}(t) = F_{i,f}(R_{i,f}(t)) \qquad (7.1)$$

must be such that it will guarantee that

$$M\dot{R}_{i,f}(t_2)^2/2 + E_f = M\dot{R}_{i,f}(t_1)^2/2 + E_i \;. \qquad (7.2)$$

Here t_2 and t_1 are times post and prior the collision (for simplicity we assume that the interaction between R and x is nonzero only during the collision; this is true for the charge- and energy-transfer problems considered here). Since energy conservation fixes the final state of the classical degrees of freedom we expect $F_{i,f}(R_{i,f}(t))$ to be a functional of the trajectory and the Eq. (7.1) to be an integrodifferential equation.[29,55,56] Furthermore, due to the nature of quantum mechanics, each transition $i \rightarrow f_\alpha$ for the quantum subsystem has a probability $W_{i-f}(R_{i,f}(t))$ which is a functional of the appropriate trajectory $R_{i,f}(t)$. Thus a complete description of all the events possible in such a system consists of a catalog of all the transitions $i \rightarrow f$ that do not violate conservation laws, a set of integrodifferential Newton's equations of the form (7.1) which give a trajectory for each transition, and a set consisting of one transition probability per transition.

These general considerations do not, however, tell us how to derive these equations. The obvious strategy is to formulate the problem fully quantum mechanically and then to take the classical limit for R. We have explored three such methods: One using the stationary phase approximation in the path-integral expression for the transition amplitude;[56,57] a second, using wave packets to generate classical-like equations for the position of the center of the packet and its group velocity;[31] and a third, which uses the eikonal method. The classical approximation for $R(t)$ can be carried out within each method at various levels, generating different classical theories for $R(t)$. The mean-trajectory approximation (MTA) presented here is the simplest of them.

Within a path-integral representation the MTA is obtained by using a coherent state representation for the electronic degrees of freedom and by obtaining equations of motion for all the variables by using the stationary phase approximation.[56] Thus the electronic amplitudes are treated as classical fields. Despite this we get for them a time-dependent Schrödinger equation driven by an effective, mean potential. If we were to take a classical limit for the nuclear coordinates only, then we would have obtained[57] one integrodifferential equation for the trajec-

tory $R_{i,f}(t)$, depending on the initial and final electronic state.

Within the wave-packet formalism, MTA is obtained by taking one Gaussian packet for both electronic states. A refined version[58] takes two packets, one for each electronic state, and generates two "classical" equations, for two trajectories which jointly drive the electronic degrees of freedom.

Finally the eikonal method used here can be refined by defining two eikonals, one for each electronic state.[58]

This brief survey of various possibilities serves to pinpoint the limitations of the mean-trajectory approximation. Since it generates only one trajectory it satisfies energy conservation only in average. More specifically the two-trajectories theory[58] generated by propagating two Gaussians, one for each electronic state, gives an ionic trajectory and a neutral one. If the incident trajectory is neutral then the kinetic energy of the outgoing neutral trajectory is the same as the kinetic energy of the incoming one. However, the kinetic energy of the outgoing ionic trajectory is less than the incident kinetic energy of the neutral by an amount equal to the ionization energy. The mean-trajectory method gives the same kinetic energy for the ion and neutral. Furthermore, the two-trajectory method can generate an ionic trajectory that is trapped in the ionic well and a neutral one which leaves the surface. The mean trajectory cannot split in this way. It is therefore not useful in dealing with trapping. Finally, the two-trajectory method gives ion and neutral trajectories having turning points on the ionic and the neutral curves, respectively; the mean trajectory has a turning point at a mean position between the two turning points mentioned above. This comparison between the two methods shows that one should not use the MTA at very low energy when sticking (i.e., trajectory splitting) is important, or when one intends to analyze detailed kinetic energy measurements. However, it is difficult to believe that the ionization probabilities at moderate and low energies are very sensitive to the details of the nuclear motion. For such situations the mean-trajectory method should be an adequate tool for calculating the ionization yield.

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APPENDIX

The derivation of Eq. (4.7) is similar to the procedure used to obtain the coherent state representation of the path integral:

$$\left\langle \psi_j \left| \exp\left[\frac{i}{\hbar}H(t_j)\Delta t\right] \right| \psi_{j-1} \right\rangle \simeq \langle \psi_j | \psi_{j-1} \rangle \left[1 - \frac{i}{\hbar}\Delta t \frac{\langle \psi_j | H(t_j) | \psi_{j-1} \rangle}{\langle \psi_j | \psi_{j-1} \rangle}\right] \simeq \langle \psi_j | \psi_{j-1} \rangle \exp\left[\frac{i}{\hbar}\langle \psi_j | H(t_j) | \psi_j \rangle \Delta t\right] ,$$

$$(A1)$$

where $\psi_j = \psi(t_j)$. Here we allowed for an explicit time dependence of H and have made the substitution

$$\langle \psi_j | H(t_j) | \psi_{j-1} \rangle / \langle \psi_j | \psi_{j-1} \rangle \simeq \langle \psi_j | H | \psi_j \rangle$$

because this quantity already multiplies the small Δt. Also

$$\langle \psi_j | \psi_{j-1} \rangle = \langle \psi_j | \psi_j - \dot{\psi}_j \Delta t \rangle = 1 - \langle \psi_j | \dot{\psi}_j \rangle \Delta t$$

$$\simeq e^{-\langle \psi_j | \dot{\psi}_j \rangle \Delta t} . \tag{A2}$$

Combining Eqs. (A1) and (A2) and using

$$\langle \psi_j | H | \psi_j \rangle = \left\langle \left[\sum_n X_n(t_j) | n \rangle \right] | H | \left[\sum_n X_n(t_j) | n \rangle \right] \right\rangle$$

with H of Eq. (4.1) yields Eqs. (4.7)–(4.9).

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