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Neutralization of ions at surfaces

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A theory has been developed to describe neutralization of ions colliding with solid surfaces. The theory encompasses adiabatic (resonance and Auger neutralization) and nonadiabatic processes, and incorporates effects due to energy, symmetry, localization, and lifetime of surface electronic states. The formalism is also applicable to ionization, excitation, and de-excitation processes. Application to 300–2500-eV He^+ scattering from Cd, Ga, Pb, In, Sn, and Sb reproduces the recently observed oscillatory intensity spectra, and demonstrates conclusively that this behavior arises from a near-resonant charge-exchange mechanism. The theory helps to clarify the roles of various neutralization processes occurring at surfaces, it suggests some potentially interesting new experiments, and there is hope that in conjunction with experiment it may provide important information about the properties of solid surfaces.

I. INTRODUCTION

The neutralization of ions scattered by surfaces provides the basis for several important experimental tools for investigating properties of solid surfaces. *Ion surface scattering*[1] (ISS) measures the intensity, kinetic energy, and angular distribution of surviving backscattered ions—those that are not neutralized—as a function of incident energy and direction. These data contain information about the composition and structure of the surface, identity and location of absorbed species, and possibly the electronic structure of the surface.[2,3] *Ion-neutralization spectroscopy*[4,5] (INS) employs the kinetic-energy distribution of electrons emitted by Auger neutralization to obtain an effective surface electronic density of states. Surface electronic properties can also be probed by detecting light emitted from particles which have been neutralized into excited states.[6]

Extraction of desired information about the surface from these experiments requires a sound understanding of the operative neutralization processes. Direct resonance and Auger mechanisms of neutralization have been described by Hagstrum.[7,8] The two-electron Auger process, which is thought to dominate in most low-energy situations,[7] has been analyzed extensively and employed to obtain surface densities of states from INS spectra.[4,5] Theoretical calculations of Auger neutralization at surfaces have been reported recently by Appelbaum and Hamann.[9]

Both Auger and direct resonance neutralization can be described as nearly adiabatic processes; they do not require exchange of energy between electronic and nuclear motion. However, there is dramatic recent evidence that nonadiabatic processes can also be very important. The first indication of this was reported by Erickson and Smith,[10] who observed striking oscillatory behavior in the intensity of He^+ scattered from Pb, Ge, Bi, and In surfaces as a function of incident ion velocity. Related behavior has now been observed by several laboratories.[11-17] In all cases, oscillatory behavior has been observed only in systems for which the ionization energy of the incident atom is within 5 eV or so of the binding energy of a d-electron level in the solid. This suggests that a near-resonant charge-exchange mechanism similar to that documented in gas-phase ion-atom experiments[18,19] might be responsible for this effect. Analysis by Tolk *et al.*[11,17] of the angular dependence of backscattered oscillatory intensities provides strong additional support for this near-resonant charge-exchange picture; i.e., for nonadiabatic behavior. It is evident that ion-surface scattering intensity measurements contain considerable information about surface composition and electronic properties, and that to fully utilize this information requires development of a unified theory of ion neutralization that can incorporate both adiabatic (Auger and resonance) and nonadiabatic neutralization processes.

We present such a theory in this paper. The theory encompasses incident ion velocities ranging from very slow to order of 10^8 cm/sec. We consider only ions that are reflected at or near the surface region, not those which penetrate deeply into the solid. The theory invokes a classical mechanical description of atomic motion, and regards neutralization as one possible consequence of the time-dependent response of the electrons to this atomic motion. Effects due to the energy, symmetry, localization, and lifetime of surface electronic states are shown to be important and are incorporated directly in the theory.

Application of the theory to He^+ scattering from Cd, Ga, Pb, In, Sn, and Sb surfaces and comparison with experiment demonstrate conclusively that the observed irregular and oscillatory backscatter intensities do indeed result from a nonadiabatic neutralization mechanism; i.e., near-resonant charge exchange.

II. THEORY

A. Classical path equations

We will assume in this treatment that nuclear motion evolves according to classical mechanics over some appropriate effective potential energy hypersurface; i.e., for any prescribed set of initial conditions, we can define a classical trajectory

$$\vec{R} = \vec{R}(t). \tag{1}$$

As the ion approaches the surface, collides, and then recedes along this trajectory, the electrons respond quantum mechanically until finally, after the collision is over, a variety of possible final electronic states may be populated, some corresponding to neutralization of the ion. In the following discussion we derive expressions for the probabilities of formation of final electronic states for some as yet unspecified trajectory $\vec{R}(t)$. We defer until later questions concerning the validity of the classical path assumption, the actual prescription of trajectories, and possible averaging of results over a Monte Carlo sampling of initial ion directions and speeds, thermal motion of solid atoms, etc.

The development that follows is an outgrowth of the commonly used classical path method for gas-phase collisions, apparently first suggested by Mott.[20] The method has since evolved in a variety of directions.[21] We further extend the approach here to the present problem of describing adiabatic and nonadiabatic ion-surface collisions.

We denote electronic coordinates by $\vec{r}$, and nuclear coordinates by $\vec{R}$. The total Hamiltonian describing both electronic and nuclear motion can be written

$$\mathcal{H}(\vec{r},\vec{R}) = \mathcal{T}_R + \mathcal{H}_{\text{el}}(\vec{r},\vec{R}), \tag{2}$$

where $\mathcal{H}_{\text{el}}$ is the electronic Hamiltonian for fixed positions $\vec{R}$ of all the nuclei, and $\mathcal{T}_R$ is the nuclear kinetic energy operator. Under the assumption that the nuclei follow a classical trajectory, Eq. (1), $\mathcal{H}_{\text{el}}$ becomes a time dependent operator, depending on time through $\vec{R}(t)$. We can define a wave function $\Phi(\vec{r}, t)$ describing electronic motion and satisfying the time-dependent Schrödinger equation,

$$\mathcal{H}_{\text{el}}(\vec{r},\vec{R})\Phi(\vec{r}, t) = i\hbar \frac{\partial \Phi(\vec{r}, t)}{\partial t}. \tag{3}$$

We now define a set of discrete, φ_d, and continuum, φ_c, electronic basis functions which depend parametrically on the nuclear coordinates $\vec{R}$. The φ's are assumed to vary continuously with $\vec{R}$, and for any fixed value of $\vec{R}$ they are complete and orthonormal; i.e.,

$$\begin{aligned} \langle \varphi_d(r,R) | \varphi_{d'}(r,R) \rangle &= \delta_{dd'}, \\ \langle \varphi_d(\vec{r},\vec{R}) | \varphi_c(\vec{r},\vec{R}) \rangle &= 0, \\ \langle \varphi_c(\vec{r},\vec{R}) | \varphi_{c'}(\vec{r},\vec{R}) \rangle &= \delta(c-c')/n(c). \end{aligned} \tag{4}$$

Brackets denote integration over electronic coordinates only, $n(c)$ is some real positive normalization function, and Eqs. (4) apply for any value of $\vec{R}$. Aside from satisfying Eqs. (4), the basis functions are, for now, left unspecified. Note that they must be considered to be many-electron basis functions, or at least two-electron, if Auger processes are to be incorporated in the theory.

We expand the total electronic wave function Φ in terms of the basis functions φ,

$$\begin{aligned} \Phi(\vec{r}, t) = &\sum_d a_d(t)\varphi_d(\vec{r},\vec{R}) \exp\left(-\frac{i}{\hbar}\int_0^t W_{dd}(\vec{R})\,dt'\right) \\ &+ \int d\mathcal{E}\,\rho(\mathcal{E}) a_{\mathcal{E}}(t)\varphi_c(\vec{r},\vec{R}) \exp\left(-\frac{i}{\hbar}\mathcal{E}t\right). \end{aligned} \tag{5}$$

The density of continuum states at energy $\mathcal{E}$ is defined by

$$\rho(\mathcal{E})d\mathcal{E} = n(c)dc \tag{6}$$

and

$$\begin{aligned} W_{dd'} &= \langle \varphi_d \mathcal{H}_{\text{el}} \varphi_{d'} \rangle, \\ W_{dc} &= \langle \varphi_d \mathcal{H}_{\text{el}} \varphi_c \rangle, \\ W_{cc'} &= \langle \varphi_c \mathcal{H}_{\text{el}} \varphi_{c'} \rangle = \delta(c-c')\mathcal{E}/n(c). \end{aligned} \tag{7}$$

In Eq. (5) the expansion coefficients have been written as the product of a function $a_d(t)$ or $a_c(t)$ and an exponential factor (i.e., in the interaction representation) simply for convenience. Substitution of Eq. (5) into Eq. (3), and operating from the left by $\langle \varphi_d |$ and $\langle \varphi_c |$, we obtain

$$\begin{aligned} i\hbar \dot{a}_d = &\sum_{d' \neq d} a_{d'} W_{dd'} \exp\left(-\frac{i}{\hbar}\int_0^t (W_{d'd'} - W_{dd})dt'\right) \\ &+ \int d\mathcal{E}\,\rho(\mathcal{E}) a_{\mathcal{E}} W_{dc} \exp\left(-\frac{i}{\hbar}\int_0^t (\mathcal{E} - W_{dd})dt'\right) \end{aligned} \tag{8}$$

and

$$i\hbar \dot{a}_{\mathcal{E}} = \sum_d a_d W^*_{dc} \exp\left(-\frac{i}{\hbar}\int_0^t (W_{dd} - \mathcal{E})dt'\right) \tag{9}$$

We will refer to Eqs. (8) and (9) as the *classical path equations*. In deriving these equations we have neglected velocity-dependent coupling; i.e., terms involving $\langle \varphi_d | \vec{\nabla}_R \varphi_{d'} \rangle$, $\langle \varphi_c | \vec{\nabla}_R \varphi_d \rangle$, etc., have been dropped. This assumption is not necessary, but it greatly simplifies the ensuing treatment. It is justified if the basis functions φ_d and φ_c have been defined such that they are independent or very weakly dependent on the nuclear coordinates $\vec{R}$. In the language of gas-phase collision theory, we must employ *diabatic* basic functions.[21-24]

B. Treatment of continuum states

In gas-phase applications, the infinite system of classical path equations, Eqs. (8) and (9), are usually simplified by omitting the continuum states and truncating the discrete states to a manageably small number. Transition probabilities $|a_d(t\rightarrow\infty)|^2$ are then obtained by direct numerical integration of the remaining coupled equations along some assumed trajectory $\vec{R}(t)$. For ion-surface collisions this procedure is not useful. The wave function describing a ground state ion in the neighborhood of the surface can be represented by a discrete state φ_0. We can denote this by $c_0\Psi_r$, where Ψ_r is a reference wave function describing a neutral ground state atom in the vicinity of the surface, and c_0 is the destruction operator that removes a discrete electron from Ψ_r. However, a neutral atom resulting from capture of an electron from the surface must be represented by continuum states, since the electron is removed from a band in the solid; i.e., the hole created in the solid has a continuum of possible energies ϵ, with corresponding wave function $c_s(\epsilon)\Psi$, where the operator $c_s(\epsilon)$ removes an electron of energy ϵ from the surface. Similarly, Auger neutralization generates two continuum holes plus a free electron, $c_s(\epsilon)c_s(\epsilon')c_f^\dagger(\epsilon'')\Psi_r$, where $c_f^\dagger(\epsilon'')$ creates a free electron of energy ϵ''. Therefore, all channels corresponding to neutralization of the ion lie in a continuum, and continuum states, Eq. (9), cannot be neglected.

We can make progress by formally solving Eq. (9) for the continuum amplitudes:

$$a_{\mathcal{E}}(t) = -\frac{i}{\hbar}\sum_d \int_0^t dt'\, a_d(t')W^*_{dc}(t') \times \exp\left(-\frac{i}{\hbar}\int_0^{t'} [W_{dd}(t'') - \mathcal{E}]dt''\right). \tag{10}$$

Substitution into Eq. (8) results in a finite system of coupled equations involving only discrete states;

$$\begin{aligned} i\hbar\dot{a}_d(t) = {} & \sum_{d'\neq d} a_{d'}(t)W_{dd'}(t)\exp\left(-\frac{i}{\hbar}\int_0^t [W_{d'd'}(t) - W_{dd}(t)]dt'\right) \\ & -\frac{i}{\hbar}\sum_{d'}\int_0^t dt'\, a_{d'}(t')\int d\mathcal{E}\,\rho(\mathcal{E})W_{dc}(t)W^*_{d'c}(t') \\ & \times\exp\left[-\frac{i}{\hbar}\left(\int_0^{t'} W_{d'd'}(t'')dt'' - \int_0^t W_{dd}(t'')dt''\right)\right]\exp\left(-\frac{i}{\hbar}\mathcal{E}(t-t')\right). \end{aligned} \tag{11}$$

This finite system of equations is, of course, as intractable as the equivalent infinite set, Eqs. (8) and (9). We now note that if the quantities $\rho(\mathcal{E})$ and $W_{dc}(t)$ vary slowly with energy, then because of the final exponential factor in Eq. (11), integration over $\mathcal{E}$ will produce a sharply peaked function approaching the δ function $\delta(t-t')$. Therefore, it is reasonable to replace $a_{d'}(t')$ and $W^*_{d'c}(t')$ by $a_{d'}(t)$ and $W^*_{d'c}(t)$, respectively. The validity of this approximation will be discussed below in Sec. II D.

Invoking this approximation in Eq. (10), and carrying out the integration over time, we obtain

$$a_{\mathcal{E}}(t) \simeq \lim_{\eta\rightarrow 0^+}\sum_d a_d(t)W^*_{dc}(t)[W_{dd}(t) - \mathcal{E} + i\eta]^{-1} \times\exp\left(-\frac{i}{\hbar}\int_0^t [W_{dd}(t') - \mathcal{E}]dt'\right), \tag{12}$$

where η is a small real positive number inserted as a convergence factor. Substitutation of Eq. (12) into Eq. (8) and separation into real and imaginary parts gives finally,

$$\begin{aligned} i\hbar\dot{a}_d(t) = {} & [\Delta_{dd}(t) - \tfrac{1}{2}i\Gamma_{dd}(t)]a_d(t) \\ & + \sum_{d'\neq d} a_{d'}(t)[W_{dd'}(t) + \Delta_{dd'}(t) - \tfrac{1}{2}i\Gamma_{dd'}(t)] \\ & \times\exp\left(-\frac{i}{\hbar}\int_0^t (W_{d'd'} - W_{dd})dt'\right), \end{aligned} \tag{13}$$

where

$$\begin{aligned} \Delta_{dd'}(t) = \lim_{\eta\rightarrow 0^+} & \int d\mathcal{E}\rho(\mathcal{E})W_{dc}(t)W^*_{d'c}(t) \\ & \times[W_{d'd'}(t) - \mathcal{E}] \\ & \times\{[W_{d'd'}(t) - \mathcal{E}]^2 + \eta^2\}^{-1}, \end{aligned} \tag{14}$$

$$\begin{aligned} \Gamma_{dd'}(t) = \lim_{\eta\rightarrow 0^+} 2 & \int d\mathcal{E}\,\rho(\mathcal{E})W_{dc}(t)W^*_{d'c}(t) \\ & \times\eta\{[W_{d'd'}(t) - \mathcal{E}]^2 + \eta^2\}^{-1}. \end{aligned} \tag{15}$$

Equations (13)–(15) represent a considerable simplification over the infinite system, Eqs. (8) and (9). Equation (13) involves discrete states only. The effects of continuum states are incorporated via the addition of local (velocity-dependent and complex) interaction potentials, $\Delta_{dd'} - \frac{1}{2}i\Gamma_{dd'}$ given by Eqs. (14) and (15).

C. Adiabatic limit

Neutralization of ions at surfaces has been treated in the past almost exclusively as an adiabatic process; i.e., neutralization processes are considered electronically resonant, in that no exchange of energy occurs between electrons and translational motion of the ion or phonons of the solid. In the present development, the adiabatic approximation can be implemented in two stages. In the first stage we require that all electronic matrix elements $W_{dd'}(\vec{R})$, $\Gamma_{dd'}(\vec{R})$, etc., vary relatively slowly with nuclear coordinate $\vec{R}$. Then at some sufficiently low ion velocity, these quantities will change insignificantly over several oscillation periods of the exponential in Eq. (13), and integration of Eq. (13) over the trajectory will produce a δ function $\delta(W_{d'd'} - W_{dd})$. Therefore, except in the case of accidental degeneracies which must be handled by the methods of Sec. II D, the discrete states are uncoupled, and we are left with a simple equation for the amplitude of the initial ground-state ion channel

$$i\hbar \dot{a}_0(t) = [\Delta_{00}(t) - \tfrac{1}{2}i\Gamma_{00}(t)]a_0(t)\,, \tag{16}$$

where $\Delta_{00}(t)$ and $\Gamma_{00}(t)$ are given by Eqs. (14) and (15). Thus the ion moves in a local complex potential. Complex effective potentials of similar form have been derived in a variety of ways for several related problems involving bound states imbedded in a continuum.[25-27] The real part of the effective potential is given by W_{00} plus a (usually negligible) shift Δ_{00}. The imaginary part is given by Γ_{00} and results in leaking away of the amplitude a_0 due to coupling with the continuum; i.e., Γ_{00} describes neutralization.

The effective potentials Δ_{00} and Γ_{00} given by Eqs. (14) and (15) are velocity dependent, and contain contributions from nonadiabatic coupling to continuum states. The second stage in achieving the adiabatic limit is to assume that $\rho(\mathcal{E})$ and W_{0c} vary sufficiently slowly that they can be taken outside the integrals in Eqs. (14) and (15). Then

$$\Delta_{00}(r) = 0\,, \tag{17}$$

$$\Gamma_{00}(t) = 2\pi\rho[W_{00}(t)]\,|W_{0c}(t)|^2\,, \tag{18}$$

and Eq. (16) becomes

$$\dot{a}_0(t) = \tfrac{1}{2}\hbar^{-1}\Gamma_{00}(t)a(t)\,. \tag{19}$$

Γ_{00} is seen to be directly related to the phenomenological neutralization rate $R_t(s)$ defined by Hagstrum,[7]

$$\Gamma_{00}(s(t)) = \hbar R_t(s(t))\,, \tag{20}$$

where $s(t)$ is the distance between the ion and the surface.

This rate could be obtained by a variety of methods with a range of sophistication. We will not go into this here, but refer, for example, to the recent calculation of Appelbaum and Hamann,[9] who employ self-consistent-field (SCF) wave functions in the "golden-rule" expression, Eq. (18), to compute the Auger neutralization rate of He^+ near Si(111) surfaces. These workers invoke a Lorentzian broadening function to account for nonadiabatic effects, following a suggestion by Hagstrum *et al.*[28] The Lorentzian form and a quantitative estimate of its width could be obtained directly by using Eq. (15) instead of Eq. (18) for the rate Γ_{00}. Note that, for Auger neutralization $\rho(\mathcal{E})$ of Eqs. (15) and (18) is a two-electron density of states; i.e., a convolution of the product of two ordinary density-of-states functions.[4]

In the illustrative calculations reported in Sec. III we do not attempt an *a priori* calculation of the Auger rate Γ_{00}, but instead assume a simple phenomenological form suggested by Hagstrum.[7,8]

D. Nonadiabatic collisions

If the adiabatic approximation is not applicable, the simplifications of the previous section are not valid. We could still derive a formal expression for $\dot{a}_0$ involving a complex effective potential as in Eq. (16). However, it would be an integro-differential equation with a nonlocal potential, and it is not obvious how to obtain even approximate solutions.

We proceed in an alternative direction. We note that nonadiabatic effects are likely to be important only when there exist near-resonant channels that are strongly coupled to the incident channel. This is borne out experimentally by the absence of oscillatory intensities in ion-surface scattering when no near-resonant surface levels are present.[10-17] We consequently assume that we can pick out those specific channels which are likely to participate in nonadiabatic behavior. We assume that they will be relatively localized electronic states, and describe them as discrete states imbedded in continua; i.e., resonance states.

We consider the simplest case where no excited states of the ion are populated. We expand the total electronic wave function Φ as in Eq. (5), where the sum over discrete states includes φ_0, the ground state of the ion, and one or a small number of φ_d, $d \neq 0$, describing specific localized surface electronic levels. The amplitudes of each of the discrete states are then given by the finite set of coupled equations, Eq. (13). Therefore, once the real and imaginary electronic interactions $W_{dd'}$, W_{dc}, $\Delta_{dd'}$ and $\Gamma_{dd'}$ have been obtained from Eqs. (7), (14), and (15), Eqs. (13) can be solved numerically along any prescribed trajectory to obtain the ion survival probability $|a_0|^2$. Calculation of the probability of formation (destruction) of electronically excited ions or neutrals can be achieved simply by including the appropriate states among the basis functions φ_d. Effects due to collective excitations (e.g., surface plasmons) and electron-phonon interaction can, in principle, also be described correctly within this formalism.

Equations (13)–(15) can be simplified by assuming, as in the previous section, that $\rho(\mathcal{E})$ and W_{dc} vary slowly with energy $\mathcal{E}$. Under this assumption, we obtain

$$i\hbar \dot{a}_d(t) = -\tfrac{1}{2} i\Gamma_{dd}(t)a_d(t) + \sum_{d\neq d'} a_{d'}(t)W_{dd'}(t)\exp\left\{-\frac{i}{\hbar}\int_0^t [W_{d'd'}(t') - W_{dd}(t')]dt'\right\}, \tag{21}$$

where $\Gamma_{dd}(t)$ is again given by a golden-rule expression,

$$\Gamma_{dd}(t) = 2\pi\rho_d[W_{dd}(t)]\,|W_{dc}(t)|^2 . \tag{22}$$

In obtaining Eq. (21) we have made the additional assumption that cross terms $\Gamma_{dd'}$ vanish. This amounts to assuming that each discrete state φ_d decays independently into its own continuum with an appropriate density of states ρ_d. It would be hardly any more difficult to retain the cross terms $\Gamma_{dd'}$, but omission of them is almost certainly justified in most situations, and the resulting set of equations, Eq. (21), has a more direct physical interpretation. The population of discrete state φ_d is altered by two processes. The first is destruction through interaction with the continuum, determined by the width Γ_{dd} of Eq. (22). The second is via transition to or from other discrete states, determined by the off-diagonal interaction $W_{dd'}$ of Eq. (7), with the energy discrepancy $W_{dd} - W_{d'd'}$ accounted for by nuclear motion. Thus Γ_{00}, which determines the direct (adiabatic) neutralization of the ion, is expected to be dominated by the Auger process and can be obtained as described in Sec. II C. Γ_{dd}, determining destruction of a hole created by removal of an electron from a localized surface state, may have contributions from Auger processes and delocalization; i.e., hopping to neighboring sites. In favorable circumstances Γ_{dd} can be estimated directly from the experimental bandwidth determined, for example, by photoelectron spectroscopy. Calculation of the off-diagonal coupling $W_{dd'}$ will, in general, require knowledge of the symmetry and spatial extent of the atomic and surface electronic wave functions.

The major assumption required to derive the final expressions, Eqs. (21) and (22), is that the density of states function $\rho(\mathcal{E})$ varies smoothly with energy $\mathcal{E}$. We invoke this assumption in two places, first to obtain Eq. (12) and then to reduce Eqs. (13)–(15) to the simple form, Eqs. (21) and (22). We know, of course, that the density of electronic states in a solid is by no means a smoothly varying function. For example, the surface states thought to be responsible for the oscillatory structure in He$^+$-solid scattering, i.e., levels bound by 20 eV or so relative to the Fermi level, will be very narrow bands corresponding to strongly localized atomiclike states. In the present theory we describe such localized states as one or more discrete levels imbedded in a smooth continuum. Underlying this discussion is the question of irreversibility. If the continuum acts purely as a sink, then its effects can be described by a local dissipative potential, as we have done. If there can be transitions from the continuum back to discrete states, then the complex potential must become nonlocal; i.e., exhibit memory. We avoid this by redefining basis functions in such a way that irreversible effects are encompassed by discrete states and the new continuum acts as a pure sink. This ultimately is the justification for invoking local complex potentials in Eqs. (13), (19), and (21), as well as for eliminating cross terms $\Gamma_{dd'}$. It is evident that careful consideration must go into the selection of basis functions in order that they accurately reflect the basic physics of the process to be studied.

E. Prescription of classical trajectories

The assumption that nuclear motion evolves according to classical mechanics is almost certainly accurate for all of the types of processes considered here, even for light ions (protons) and low energies (of order 1 eV). This has been demonstrated convincingly for gas-phase collisions.[21] Criteria for the validity of the classical path method have been described[21,29] and should be satisfied equally well in gas-phase or gas-surface collisions. The only qualitatively new feature that may arise in the latter is the possibility of diffraction effects arising from the periodicity of the surface. Even these can be accurately reproduced by appropriate combination of the quantum-mechanical principle of superposition with an essentially classical-mechanical description of nuclear motion.[30,31]

Prescriptions for obtaining the required classical trajectories can range from very simple to very complicated, depending primarily on the energy of the collision. At low energies (thermal up to ~10 eV), trajectories are very sensitive to detailed chemical interactions among the atoms. In such situations, one can imagine constructing an accurate multidimensional potential energy hypersurface describing these interactions, and then numerically integrating the classical equations of motion for the colliding atom and responding solid atoms along this hypersurface, in conjunction with the coupled equations, Eqs. (13). A great many trajectories along the hypersurface might be required in order to adequately sample over initial position and direction of the colliding particle and the thermal motion of the solid. In some cases it might also require defining several potential energy hypersurfaces, one corresponding to each electronic state included in the expansion, Eq. (5), and allowing trajectories to hop back and forth between hypersurfaces. All of these techniques have become almost routine in descriptions of gas-phase collision processes involving small molecules.[21,32,33]

Fortunately, at higher collision energies (greater than about 50 eV), much of this work is unnecessary. Two major simplifications occur. First, the various potential energy hypersurfaces corresponding to different electronic states are sufficiently similar compared to nuclear kinetic energies that only a single effective interaction potential is required to determine the trajectory $\vec{R}(t)$. Second, since the course of the trajectory is determined almost entirely by short-range repulsions between atoms, only binary atom-atom forces need to be employed. There are a variety of parametrized forms for binary interactions that should be suitable, including Born-Mayer[34,35] and screened Coulomb.[36,37] Thus we can solve Eqs. (13) along a trajectory obtained by following the motion of the ion as it bumps into spherical solid atoms one at a time; i.e., we can append the integration of Eqs. (13) to the standard computer codes that have been developed to simulate ion-solid scattering.[37-40] These computer simulations can incorporate multiple scattering effects, the thermal motion of the solid, etc.

Investigation of oscillatory ion-surface backscatter intensities is simpler yet. The experiments measure the intensity of the "surface peak" arising from specular reflection of the ion by an individual surface atom through a particular scattering angle θ. Thus only a single ion-atom trajectory is required for any initial energy E and scattering angle θ.

III. APPLICATION TO He$^+$ BACKSCATTERING

In this section we employ the theory just described to calculate intensities of He$^+$ ions scattered from Cd, Ga, Pb, In, Sn, and Sb surfaces at collision energies between 300 and 2500 eV. We apply the theory in a very primitive way, using interaction strengths computed from hydrogenic functions and an empirically obtained Auger rate. The resulting backscatter intensities as a function of energy are not quantitatively accurate, but qualitative agreement with experiment is sufficiently good to demonstrate the validity of the theory and to shed light on the various mechanisms of ion neutralization at surfaces.

We will compare with the experiments of Rusch and Erickson[13] and Tolk *et al.*[11] These experiments measured the intensity of the surface peak arising from reflection of the He$^+$ by a single surface atom. As mentioned above, for any scattering angle θ and collision energy E we require only a single trajectory determined from a binary ion-atom interaction potential. In the calculations reported here we have employed a screened Coulomb potential, using the Moliere approximation to the Thomas-Fermi screening function.[37] Along with the numerical integration to obtain the trajectory, we solve the coupled equations, Eqs. (19) or (21), which determine the time evolution of the electronic motion.

The intensity of backscattered ions $I(E, \theta, \phi)$ is proportional to the differential cross section $\sigma(E, \theta)$ times the ion survival probability $P_s(E, \theta, \phi)$,

$$I(E, \theta, \phi) \propto \sigma(E, \theta) P_s(E, \theta, \phi) , \qquad (23)$$

where $\sigma(E, \theta)$ is determined from the Moliere potential and

$$P_s(E, \theta, \phi) = |a_0(t \to \infty)|^2 . \qquad (24)$$

A. He$^+$-Cd

We use He$^+$-Cd scattering as an example to illustrate the anticipated behavior produced by a nearly adiabatic neutralization process. Since there are no near-resonant electronic states of Cd, we obtain a_0 from Eq. (19). We assume that the neutralization rate Γ_{00} can be approximated by the simple form proposed by Hagstrum[7]

$$\hbar^{-1}\Gamma_{00} = A \exp(-as) , \qquad (25)$$

where s is the perpendicular distance to the surface as defined in Fig. 1. The resulting neutralization probability turns out to depend strongly on the ratio A/a, but is almost totally independent of the individual values of A and a. Thus for all of the calculations reported here we have elected to keep

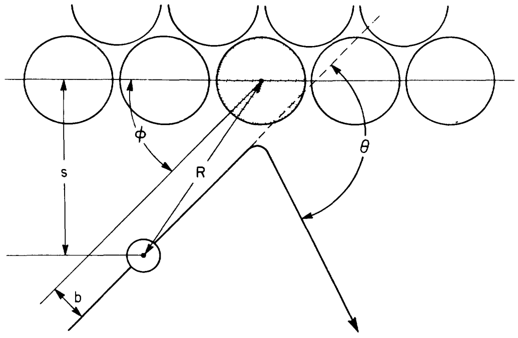

FIG. 1. Definition of orientation angle ϕ, scattering angle θ, radial distance R, and perpendicular distance s.

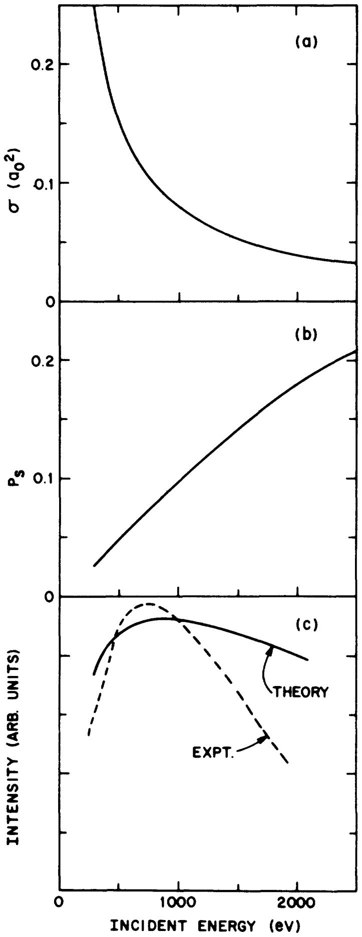

FIG. 2. (a) Differential cross section σ as a function of collision energy for He$^+$-Cd binary collision obtained from Moliere potential with $\theta = 90°$. (b) He$^+$ ion survival probability P_s for collision with Cd surface with $\theta = 90°$ and $\phi = 45°$. (c) Calculated He$^+$-Cd ion scattering intensity obtained from the product of σ and P_s (solid curve), compared with experimental results of Ref. 13 (dashed curve).

the parameter α fixed at the more or less typical value of 1.3 Å^{-1}.

The parameter A was chosen for the He$^+$-Cd case to give reasonable agreement with the overall shape of the experimental intensity versus collision energy curve. The results are shown in Fig. 2. Figure 2(a) shows the monotonically decreasing differential cross section $\sigma(E, \theta)$ computed from the Moliere potential. The ion survival probability $P_s(E, \theta, \phi)$ of Eq. (24) increases monotonically for this simple case, as shown in Fig. 2(b). The scattered ion intensity obtained from Eq. (23) thus peaks at some intermediate value of energy, as shown in Fig. 2(c). While the general shapes of the calculated and experimental intensity curves are similar, quantitative agreement is poor and there is no value of the parameter A that will give much improvement. The disagreement may arise from several sources, including inadequacy of the simple expression Eq. (25) for the neutralization rate, inaccuracy of the Thomas-Fermi-Moliere potential, and experimental difficulties associated with the variation of ion detection efficiencies with energy. In addition, the experiments measure the height of the surface peak with no background correction while the calculations correspond more nearly to the area of the peak with background subtracted. The importance of experimental difficulties is indicated by the fact that ion intensity versus energy curves measured in different laboratories usually have considerably different shapes, particularly at low energies. These problems would have to be addressed if a meaningful quantitative comparison of theory and experiment were to be attempted. For the present, however, we will be satisfied with qualitative comparisons; the experimental and calculated intensity curves of Fig. 2 are both smooth and peak in the middle.

The results of Fig. 2 were obtained with the parameter A chosen to be 2.8×10^{15} sec^{-1}. This corresponds to a ratio A/a of 2.2×10^{7} cm/sec, which falls somewhere in the middle of estimates ranging from 1.2×10^{6} to 9×10^{8} cm/sec obtained for this quantity by other groups.[41]

For all of the remaining calculations reported in this paper, the parameters A and a of Eq. (25) were taken to be unchanged from the values used in the He$^+$-Cd calculation. There is no reason to expect that Auger neutralization rates will be even approximately the same for different solid materials, and we could have achieved considerably better agreement with experiment by readjusting these parameters. On the other hand, since we are not seeking quantitative agreement here it was thought preferable to leave these parameters unchanged so that any differences in computed scattered ion intensities could be attributed directly to nonadiabatic effects.

B. He^+-Ga

Gallium has a $3d$ level bound by approximately 22 eV with respect to the vacuum level.[42] This is sufficiently close to the 24.5-eV ionization potential of He to make Ga a likely candidate to exhibit near-resonant charge-transfer effects. In order to compute ion scattering intensities for this case, we have added a single discrete channel to describe the $3d$ Ga level. Thus we must solve two coupled equations of the form of Eq. (21).

We approximate the various interactions appearing in Eq. (21) in very crude ways. The energy difference $W_{11} - W_{00}$ is taken to be

$$W_{11} - W_{00} \simeq W_{11}(s=\infty) - W_{00}(s=\infty) + e^2/4s\,, \tag{26}$$

i.e., the energy splitting is equal to the asymptotic splitting (22.–24.5 eV) corrected by the bare image potential.

The off-diagonal interaction W_{01} is assumed to arise solely from the exchange interaction; i.e., from charge transfer. We approximate this by the expression

$$W_{12} \simeq \tfrac{1}{2}[W_{00}(s=\infty) + W_{11}(s=\infty)]\langle \varphi_0 | \varphi_1 \rangle\,. \tag{27}$$

The wave function φ_0 describing an electron on He is taken to be a $1s$ hydrogenic function with a binding energy of 24.5 eV. Similarly, the wave function ϕ_1 describing an electron in the surface is taken to be hydrogenic with the appropriate n, l, and m quantum numbers and binding energy; i.e., $3d_{z^2}$ with $E_b = 22$ eV for Ga. The overlap term appearing in Eq. (27) was evaluated exactly using these hydrogenic functions.

The only other parameter required to apply the theory to He^+-Ga scattering is the width Γ_{11} of the $3d$ gallium level. A width of 0.048 eV has been computed for the corresponding state in Ge.[43] Ga is expected to be similar, so we have used this value in the present calculation. We note, however, that variation of Γ_{11} from 0 to 0.15 eV produces only relatively minor changes in the computed scattering intensitites. This insensitivity to the hole lifetime in this case is a result of the fact that the lifetime is unusually long for the $3d$ state of Ga; 0.048 eV corresponds to a lifetime of order 10^{-14} sec which is long compared to the He^+-surface collision time, except for energies below 300 eV or so. Some electronic states in solids are considerably broader than 0.048 eV and, as discussed below, this could have a significant effect on ion-surface scattering intensities, particularly at low energies.

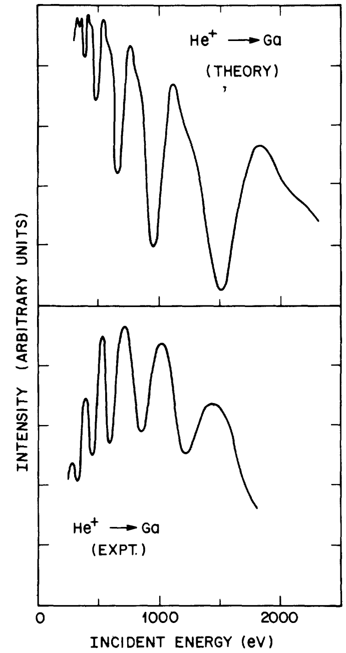

FIG. 3. Calculated He^+-Ga backscatter intensity for $\theta = 90°$, $\phi = 45°$ (top), compared with experimental results of Ref. 13 (bottom).

All input for the He^+-Ga calculations was obtained from known properties with the exception of the Auger neutralization rate for which the He^+-Cd parameters were employed. The input, of course, is very crude, but it should suffice to provide an idea of the importance of near-resonant nonadiabatic effects. The resulting He^+ backscatter intensities are compared in Fig. 3 with the experimental results of Rusch and Erickson[13] for the Ga surface peak of GaN.

Agreement is far from quantitative. Much better agreement with the overall shape of the envelope can be obtained by increasing the Auger rate parameter A by about a factor of 2. This does not improve the matchup between experimental and theoretical oscillation peak positions. The discrepancies are not surprising considering the very approximate nature of the interaction potentials employed in the calculation. The important point is that both experiment and theory show oscillations. We consider this result, and those presented below, to be conclusive proof that, first, the oscillatory intensities observed in ion-surface scattering do arise from a near-resonant charge exchange mechanism and, second, the theory developed in this paper is capable of reproducing the important features of this process.

C. He^+-Pb

We have applied the theory to He^+-Pb scattering in exactly the same way as for He^+-Ga. The Auger

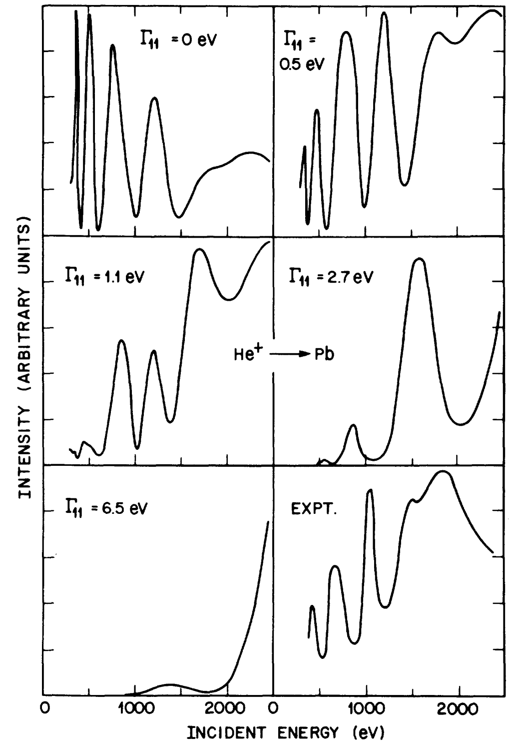

FIG. 4. Calculated He^+-Pb backscatter intensity for $\theta = 90°$ and $\phi = 45°$, and for various values of the Pb-5*d* width, compared with experimental results of Ref. 44.

parameters a and A were taken unchanged from their He^+-Cd values. The ion-surface interactions were obtained from Eqs. (26) and (27), with the near-resonant level in Pb a 5*d* state lying 25 eV below the vacuum level.

The calculated He^+ scattering intensities are shown in Fig. 4 for several values of the unknown Pb-5*d* hole width, Γ_{11}. Results are shown to be quite sensitive to the width. For $\Gamma_{11} = 0.5$ eV, the calculated ion scattering spectrum is in good qualitative agreement with the experimental results of Tolk *et al.*[11,44] also shown in Fig. 4. Even the irregular features of these spectra are quite similar. These irregularities were speculated to arise from the fact that the 5*d* level in Pb is split due to spin-orbit coupling into two levels separated by about 2 eV. However, the irregular behavior is reproduced by the present two-state calculation (one surface state) which neglects the spin-orbit coupling, so this effect must arise, as with Ga, from the detailed variation of interaction potentials with distance.

D. Other systems

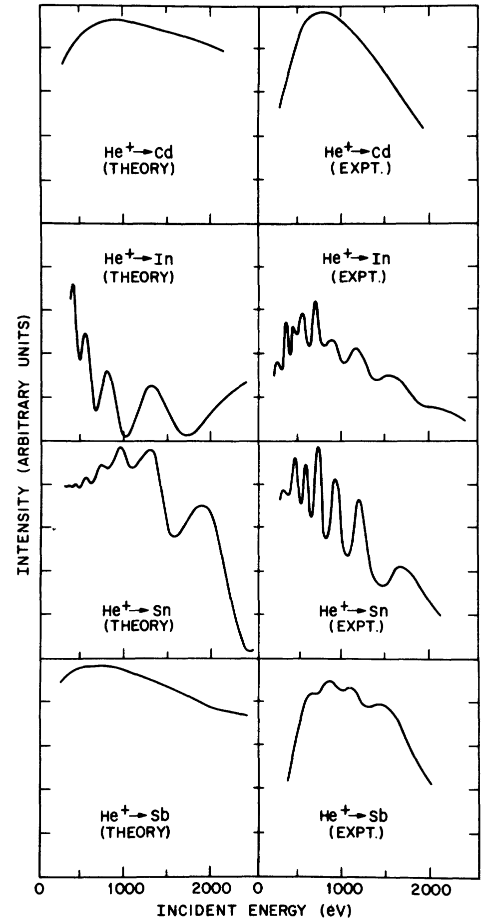

FIG. 5. He^+ scattering intensities for Cd, In, Sn, and Sb targets for $\theta = 90°$ and $\phi = 45°$. Left: calculated. Right: experimental results of Ref. 13.

Figure 5 shows calculated and experimental[13] ion scattering intensities for He^+ incident on the sequence of fourth-row elements Cd, In, Sn, and Sb. The values of the Auger parameters were again fixed at the He^+-Cd values and Eqs. (26) and (27) were used to estimate the interaction potentials. The energies with respect to the vacuum level of the 4*d* levels in Cd, In, Sn, and Sb are 13, 20, 28, and 36 eV, respectively. Thus In and Sn are near-resonant cases, whereas the Cd and Sb levels are at least 10 eV off resonance. The hole widths, which are expected to be small for these states, were taken to be zero to avoid arbitrariness.

Both the calculated and experimental He^+ scattering intensities are shown in Fig. 5 to be smooth for Cd and highly oscillating for In and Sn. The experimental results exhibit slight oscillating behavior for He^+-Sb, whereas the calculated intensities show only barely perceptible wiggles for this case.

The general features of the experimental results are correctly reproduced by the theory. In detail, comparison between experiment and theory is terrible. Considering the very crude way in which input to the theory was approximated, this disagreement should not be unexpected. Perhaps it is more surprising that the He^+-Ga and He^+-Pb are in such good agreement. Nevertheless, the results presented here demonstrate that the basic physical processes responsible for ion-neutralization at surfaces can be correctly described by the present theory.

IV. DISCUSSION

We have developed a theory of ion neutralization at surfaces which encompasses both resonant and nonadiabatic mechanisms. Application of the theory in a primitive form to scattering of helium ions by a variety of surface materials has shown that both mechanisms can be important and can have effects that are qualitatively different and experimentally discernable. The calculations demonstrate conclusively that the oscillatory intensities recently observed in, e.g., He^+-Ga and He^+-Pb scattering[10,11,13] result from a nonadiabatic near-resonant charge exchange process.

The calculations presented here were performed in an essentially *a priori* way with the only adjustable parameter held fixed for all cases. However, they utilized very approximate interaction potentials and the results, although in qualitative agreement with experiment, are not quantitatively accurate. A program to implement more accurate interactions based on Hartree-Fock atomic wave functions with inclusion of spin-orbit effects is now in progress. Even in the crude form applied here, the theory can provide useful information about the existence of irregular or oscillatory ion backscatter intensities, the dependence of ion intensities on the identity of the target material and incident ion, and possibly the lifetimes of near-resonant levels in the solid. The interesting angular dependences[11] and isotope effects[14] observed recently can be addressed by simply integrating the same set of coupled equations with the same interactions, but along different ion trajectories.

The theory can be applied to a variety of gas-surface collision phenomena in addition to ion backscattering intensities. The effects of nonadiabatic processes on the intensity and energy distribution of Auger emission in INS can be investigated. Photoemission arising from neutralization of ions into excited states can be described. Excitation and deexcitation processes involving neutral species, although not neutralization processes, are encompassed by the theory.

Our object is not merely to account for previous experimental observations, but to learn new information and to suggest new experiments. Several possibilities for new experiments come to mind immediately. For example, observation of oscillatory Auger emission intensities as a function of collision energy in near-resonant systems may be feasible. A similar effect may arise in optical radiation. The theory can be helpful in suggesting promising candidates for these effects. A study of the correlation of ion-surface scattering intensities with the lifetimes of near-resonant states in the solid appears fruitful. Finally, preliminary calculations indicate that population of the $2p$ or $3p$ state of He upon impact of 1-keV He^+ with a variety of metal and semiconductor surfaces should be anisotropic; i.e., optical emission from these excited states should exhibit strong linear polarization.

It is our hope that the present theory can provide a framework for utilizing experimental results to obtain fundamental information about the nature of surfaces and their interaction with gases. We have discussed above how energies, lifetimes, symmetries and densities of surface states can influence ion neutralization. Information about these properties can in many cases be extracted from experimental measurements. Rusch and Erickson[13] have shown that ion-surface scattering intensities can be sensitive to the environment of the surface atom probed. This effect is due at least partly to alteration of the energy, lifetime, etc., of surface states so analysis of experiments may reveal, for example, how a surface state is effected by chemical bonding to an absorbed species.

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