Many-electron theory of charge transfer in ion-surface scattering

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(Received 15 December 1987)

A treatment of the time-dependent Anderson-Newns model of ion-surface scattering is formulated by using many-electron wave functions. In its fullest generality, the formalism allows various charge-exchange mechanisms to be described on an equal footing. Within the local-time approximation, the subsidiary set of equations governing resonance transfer can easily be solved numerically. As a specific application, the case of Li^+ impinging on cesiated W is investigated. Comparison between the calculated results and those obtained using Hartree-Fock wave functions show the former to be in better agreement with experimental data.

I. INTRODUCTION

The mechanisms involved in charge transfer during the scattering of ions or atoms from solid surfaces have become the subject of much investigation by both theorists and experimentalists. A popular theoretical starting point has been the time-dependent Anderson-Newns (TDAN) model,[1] although most studies have neglected the effect of the intra-atomic Coulomb repulsion. Among those who have not ignored this interaction, Yoshimori et al.[2,3] used the Hartree-Fock approximation in order to obtain a set of nonlinear integral equations, which could be solved numerically for the electron occupation numbers. The qualitative behavior of the results was unchanged, to a certain extent, by the time dependence of the repulsive Coulomb integral U and the atom's ionization level.

Another Hartree-Fock treatment of the TDAN model was formulated by Grimley et al.[4] in terms of the time-evolution operator, resulting in a set of coupled integrodifferential equations. However, application of this theory to the formation of the excited neutral product $Li^0(2p)$, during Li^+ scattering from alkali-covered polycrystalline tungsten surfaces,[5] led to the conclusion that the Hartree-Fock approximation is unable to reproduce the experimental findings. Moreover, in a subsequent paper,[6] Sebastian cast doubts on the overall reliability of the Hartree-Fock approximation and concluded that the effect of electron correlation must be included. Sebastian[7] has made some progress in this direction, extending the method of Grimley et al.[4] beyond Hartree-

Fock by making use of the fact that the time-evolution operator for a two-electron Hamiltonian can be expressed as a functional average of the time-evolution operator for a one-electron Hamiltonian. However, no numerical results for the method have been reported, making it difficult to evaluate the technique thoroughly. A second approach, taken by Sebastian,[6] involved a time-dependent version of the coupled-cluster technique[8,9] which produced markedly different results from Hartree-Fock.

Kasai and Okiji[10] also developed the TDAN model beyond Hartree-Fock by means of the Heisenberg equations of motion within the wide-band limit.[11] One effect of the Coulomb interaction that was noticed was an increase in the expectation value of the neutral state at the expense of the ionized ones.

A major point of concern regarding the widespread use of single-configuration restricted Hartree-Fock wave functions to treat the charge-transfer problem is the fact that such wave functions do not give an adequate description of dissociation;[12] to do so, multiconfiguration wave functions have to be used. Since the scattering of an atom or ion from a surface can be considered as a dissociation process, it seems likely that no treatment of surface-charge transfer, based on single-configuration wave functions, can be completely satisfactory. Hence, it is necessary to develop a theory based on many-electron multiconfigurational wave functions. Moreover, such a theory is also required in order to properly describe the two-electron process of Auger neutralization. This fact was recognized a decade ago by Tully,[13] and was the basis for his *classical path equations* describing ion neutraliza-

tion at surfaces, a theory similar in motivation to that presented here. More recently, in his previously mentioned coupled-cluster technique,[6] Sebastian took a rather different, but related, approach to the problem and wrote the wave function in terms of particle-hole excitations on the Slater determinant representing the initial state of the system.

In this article, a theory of surface-charge transfer, based on many-electron wave functions, is presented within the framework of the TDAN model. The formalism allows the Coulomb interaction term to be included, without resorting to the Hartree-Fock approximation. The general formulation is given in Sec. II, and an approximate method of solution, using the local-time approximation[14] is outlined in Sec. III. In Sec. IV, the theory is applied to the scattering of Li^+ from cesiated W(110), while Sec. V contains a summary.

II. MANY-ELECTRON EQUATIONS

In the variation of constants method for solving the time-dependent Schrödinger equation (in atomic units)

$$i\frac{\partial\psi}{\partial t}=H(t)\psi , \tag{1}$$

the many-electron wave function ψ is written as a linear combination of time-independent orthonormal functions ψ_i, i.e.,

$$\psi(t)=\sum_i a_i(t)\psi_i . \tag{2}$$

The time-dependent coefficients satisfy

$$i\dot{a}_i=\sum_j H_{ij}(t)a_j , \tag{3}$$

with

$$H_{ij}(t)=\langle \psi_i | H(t) | \psi_j \rangle ,$$

and, if ψ_0 is chosen to equal $\psi(-\infty)$, then (3) must be solved subject to the initial conditions $a_i(-\infty)=\delta_{i0}$.

For (2) to be rigorously correct, the set of functions $\{\psi_i\}$ should be complete, but, since this is impossible in practice, the set must be truncated. Therefore, the first step in defining any model which makes use of this method is to designate the truncated set. The second and final step is to specify the matrix elements H_{ij}; in effect, this defines H implicitly.

Consider an atom, with an empty valence orbital ω_0, being scattered from a metal surface. In this process, one electron, or two electrons of opposite spins, may be transferred from the appropriate metal band into the orbital ω_0 by resonance transfer. Initially, at $t=-\infty$, the wave function is that of the metal band. Suppose the filled part of the band can be represented by m doubly occupied one-electron orbitals $\{\phi_i\}_{i=1,\ldots,m}$ and the unfilled part by v empty orbitals $\{\phi_\mu\}_{\mu=m+1,\ldots,m+v}$. [In this paper, lower case Roman (Greek) indices refer to occupied (unoccupied) metal orbitals, while upper case Roman indices designate the full set of $m+v$ metal orbitals.] Thus, ψ_0 is the Slater determinant

$$\psi_0= | \phi_1\bar{\phi}_1 \cdots \phi_m\bar{\phi}_m | . \tag{4}$$

The wave function for the transfer of an electron from ϕ_i to ω_0 is

$$\psi_{i0}=\frac{1}{\sqrt{2}}\{ | \phi_1\bar{\phi}_1 \cdots \phi_i\bar{\omega}_0 \cdots | + | \phi_1\bar{\phi}_1 \cdots \omega_0\bar{\phi}_i \cdots | \} . \tag{5}$$

There are m of these functions $(i=1,2,\ldots,m)$ to consider. Note that the particular combination of Slater determinants in (5) is chosen to ensure that the total spin remains zero, although it would be possible to treat each term in (5) separately. It would be necessary to do so in order to discuss magnetic effects.

Similarly, wave functions for the transfer of two electrons to ω_0 will be

$$\psi_{i0k0}=\frac{1}{\sqrt{2}}\{ | \cdots \phi_i\bar{\omega}_0 \cdots \omega_0\bar{\phi}_k \cdots |$$
$$+ | \cdots \omega_0\bar{\phi}_i \cdots \phi_k\bar{\omega}_0 \cdots | \} \quad (i<k) ,$$
$$\psi_{i0i0}= | \cdots \phi_{i-1}\bar{\phi}_{i-1}\omega_0\bar{\omega}_0\phi_{i+1}\bar{\phi}_{i+1} \cdots | . \tag{6}$$

It is convenient in (6) to distinguish between the case where both electrons come from the same metal orbital and that where they are transferred from two different metal orbitals.

The functions (4)–(6) will comprise the major components of the wave function. The most important secondary effect will arise when an electron, having been transferred from an occupied orbital ϕ_i to ω_0, moves back at a later time into an unoccupied metal orbital ϕ_μ. Effectively, therefore, the electron is excited from ϕ_i to ϕ_μ, and this is represented by the wave function

$$\psi_{i\mu}=\frac{1}{\sqrt{2}}\{ | \cdots \phi_i\bar{\phi}_\mu \cdots | + | \cdots \phi_\mu\bar{\phi}_i \cdots | \} . \tag{7}$$

There are mv wave functions of this type.

Rewriting (2) in terms of this truncated set of $mv+\frac{1}{2}(m^2+3m)+1$ functions gives

$$\psi=a_0(t)\psi_0+ \sum_{i=1}^m b_i(t)\psi_{i0}$$
$$+ \sum_{i=1}^j \sum_{j=1}^m c_{ij}(t)\psi_{i0j0}+ \sum_{i=1}^m \sum_{\mu=m+1}^{m+v} d_{i\mu}(t)\psi_{i\mu} . \tag{8}$$

Notice in (8) that only one valence orbital of the atom is considered. More orbitals and, hence, more functions in (8) would be required to consider excitation processes such as that suggested recently by Kawai et al.[15] Similarly, if more than one metal band is involved in the transfer of electrons, then more metal orbitals have to be introduced.

To make use of (3), it is necessary to have orthonormal and time-independent functions. Unfortunately, because the atom is moving relative to the metal surface (which is assumed fixed), the position coordinates of the atomic nucleus will depend on t as, therefore, will ω_0, since it is defined relative to the nucleus. Thus, ω_0 will not be orthogonal to the metal orbitals for all values of t. Howev-

er, the overlap between ω_0 and the $\{\phi_i\}$ and $\{\phi_\mu\}$ should be small enough to neglect and, in so doing, the functions in (8) can be treated as orthonormal. Furthermore, it can be assumed that some of the more important aspects of the time dependence of ω_0 can be allowed for by factoring them out into the coefficients $b_i(t)$ and $c_{ij}(t)$, and by suitable choice of the matrix elements.

Within the basis set of functions, represented by Eqs. (4)–(7), the Hamiltonian is assumed to have Anderson-Newns form

$$H = \sum_{k,\sigma} \varepsilon_k c_{k\sigma}^\dagger c_{k\sigma} + \sum_\sigma \varepsilon_0(t) c_{0\sigma}^\dagger c_{0\sigma}$$
$$+ U(t) c_{0+}^\dagger c_{0+} c_{0-}^\dagger c_{0-} + \sum_{k,\sigma} v_k V(t)(c_{k\sigma}^\dagger c_{0\sigma} + c_{0\sigma}^\dagger c_{k\sigma}) ,$$

$$(9)$$

where the c's are appropriate creation and annihilation operators, with the index σ being for spin. In (9), ε_k is the time-independent energy of the metal orbitals (both occupied and unoccupied), $\varepsilon_0(t)$ is the energy of the atomic orbital ω_0, and $U(t)$ the effective Coulomb repulsion integral between two electrons with opposite spins in the orbital ω_0. By allowing ε_0 and U to be time dependent, image forces and many-body effects in the atom-surface interaction are allowed for. Aside from this, the interaction is assumed to be one-electron in character, coupling ω_0 to each of the metal orbitals, occupied and unoccupied. This coupling has the form $v_k V(t)$, i.e., a common time-dependent factor $V(t)$ times a constant v_k, depending only on the metal orbital and related to the surface density of states, and it gives rise to the last terms in (9).

Using (9), the diagonal elements of H with respect to the basis functions are

$$E_0 = \langle \psi_0 | H | \psi_0 \rangle = 2 \sum_{i=1}^m \varepsilon_i ,$$

$$E_i = \langle \psi_{i0} | H | \psi_{i0} \rangle = E_0 - \varepsilon_i + \varepsilon_0(t) ,$$

$$E_{i0k0} = \langle \psi_{i0k0} | H | \psi_{i0k0} \rangle$$
$$= E_0 - \varepsilon_i - \varepsilon_k + 2\varepsilon_0(t) + U(t) ,$$

$$E_{i\mu} = \langle \psi_{i\mu} | H | \psi_{i\mu} \rangle = E_0 - \varepsilon_i + \varepsilon_\mu .$$

$$(10)$$

The nonzero matrix elements linking the basis functions are

$$\langle \psi_0 | H | \psi_{i0} \rangle = \sqrt{2} v_i V(t) ,$$

$$\langle \psi_{i\mu} | H | \psi_{i0} \rangle = v_\mu V(t) ,$$

$$\langle \psi_{k0l0} | H | \psi_{i0} \rangle = (v_l \delta_{ik} + v_k \delta_{il}) V(t) ,$$

$$\langle \psi_{i0i0} | H | \psi_{i0} \rangle = \sqrt{2} v_i V(t) .$$

$$(11)$$

Substituting into (3) leads to the following set of coupled first-order differential equations:

$$\dot{a}_0 = -iE_0 a_0 - i\sqrt{2} V(t) \sum_j v_j b_j , \tag{12a}$$

$$\dot{b}_k = -i\sqrt{2} v_k V(t) a_0 - i[E_0 + \varepsilon_0(t) - \varepsilon_k] b_k - i\sqrt{2} v_k V(t) c_{kk} - iV(t) \left[\sum_{j<k} v_j c_{jk} + \sum_{j>k} v_j c_{kj} \right] - iV(t) \sum_\mu v_\mu d_{k\mu} , \tag{12b}$$

$$\dot{c}_{kk} = -i\sqrt{2} v_k V(t) b_k - i[E_0 - 2\varepsilon_k + 2\varepsilon_0(t) + U(t)] c_{kk} , \tag{12c}$$

$$\dot{c}_{kl} = -iv_l V(t) b_k - iv_k V(t) b_l - i[E_0 - \varepsilon_k - \varepsilon_l + 2\varepsilon_0(t) + U(t)] c_{kl} \quad (k < l) , \tag{12d}$$

$$\dot{d}_{k\mu} = -iv_\mu V(t) b_k - i(E_0 - \varepsilon_k + \varepsilon_\mu) d_{k\mu} . \tag{12e}$$

III. APPROXIMATE SOLUTIONS

In principle, Eqs. (12) could be solved as a set of coupled linear equations. However, the large number of equations involved makes this a difficult and time consuming numerical problem. Therefore, as a first attempt to investigate the type of solution produced by this method, a number of simplifying assumptions, which lead to fairly tractable equations, are introduced.

Firstly, the number of equations involved can be considerably reduced by neglecting the excitation functions $\psi_{k\mu}$, i.e., by setting $d_{k\mu} = 0$. These functions represent a reionization channel, which is second order in character, and so their omission is unlikely to change the results qualitatively. Quantitatively, their neglect will lead to an overestimation of the neutralization probability. After making this approximation, and integrating (12c) and (12d), the functions c_{kk} and c_{kl} can be eliminated from

(12b), which becomes the integrodifferential equation

$$\dot{b}_k = -i\sqrt{2} v_k V(t) a_0 - i(E_0 + \varepsilon_0 - \varepsilon_k) b_k$$

$$- V(t) \sum_j v_j^2 e^{-iE_{jk} t} \int_{-\infty}^t V(u) e^{iE_{jk} u} b_k(u) du$$

$$- V(t) v_k \sum_j v_j e^{-iE_{jk} t} \int_{-\infty}^t V(u) e^{iE_{jk} u} b_j(u) du , \tag{13}$$

where

$$E_{jk} = E_0 - 2I + U_0 - \varepsilon_j - \varepsilon_k .$$

Implicit in (13) is the assumption that the time dependencies of ε_0 and U are such that $2\varepsilon_0 + U$ is time independent, which will be the case when ε_0 and U have the semiclassical forms

$$\varepsilon_0(t) = I + F(t)$$

and

$$U(t) = U_0 - 2F(t) ,$$

where

$$F(t) = [4(v \mid t \mid + R_0)]^{-1} ,$$

v being the ion's velocity. $I = \varepsilon_0(-\infty)$ and $U_0 = U(-\infty)$ are the ionization level and effective Coulomb repulsion of the ion at infinite separation from the surface, respectively.

As a final step, we introduce a variant of the local-time approximation,[14,16] which has been used successfully in the Hartree-Fock theory of charge transfer. In this approximation, the functions $b_j(u)$ in the integrals in (13) can be taken outside the integrals as $b_j(t)$. The justification is that, in many cases, the oscillation of the exponential in $\sum_j v_j^2 e^{iE_{jk}(u-t)}$ enables this factor to be approximated by a δ function. Thus, (13) becomes

$$\dot{b}_k = -i\sqrt{2}v_k V(t)a_0 - R_k(t)b_k(t) - \sum_{j=1}^{m} Q_{kj}(t)b_j(t) ,$$

$$(14)$$

where

$$R_k(t) = i[E_0 + \varepsilon_0(t) - \varepsilon_k] + V(t) \sum_{j=1}^{m} v_j^2 e^{-iE_{jk}t} I_{jk}(t)$$

$$(15)$$

and

$$Q_{kj}(t) = V(t)v_k v_j e^{-iE_{jk}t} I_{jk}(t) ,$$

$$(16)$$

with

$$I_{jk}(t) = \int_{-\infty}^{t} V(u)e^{iE_{jk}u} du .$$

$$(17)$$

The m equations (14), plus (12a), constitute a linear sys-

tem which can be solved numerically. Upon doing so, the probability P^+ of the outgoing particle being a positive ion is

$$P^+ = \mid a_0(\infty) \mid^2 .$$

The probability of it being neutral is

$$P^0 = \sum_k \mid b_k(\infty) \mid^2 ,$$

while P^-, for the negative product, is

$$P^- = 1 - P^0 - P^+ .$$

IV. APPLICATION TO Li⁺ SCATTERING FROM Cs/W(110)

To illustrate the use of the theory of the preceding sections, we consider the scattering of positive Li ions from cesiated W(110). Experimentally, the three products Li^+, Li^0, and Li^- have all been observed, but the proportions differ as the incident energy E and work function ϕ are varied.[17-19] The excited neutral state $Li^0(2p)$ has also been detected,[5] but as its fraction is believed to be always less than 3%, we shall ignore it here. The chosen system has the advantage that all electron exchanges, which can occur, do so by means of resonance transfer, so that Auger transitions need not be considered.

Equations (12a) and (14) were solved numerically for an ion striking a one-dimensional tight-binding chain of W atoms. Previous work[20] has shown that this is a satisfactory model for an ion colliding with a metal surface. In the calculations reported here, satisfactory convergence of the results was achieved with a chain of 40 atoms.

The energy-level diagram for Li^+-Cs/W is shown in Fig. 1. The W band center α, measured from the vacuum level, is -5 eV, while the d-band width 4β is 7 eV (i.e., $\beta = 1.75$ eV). The Fermi level ε_F of W(110) is allowed to
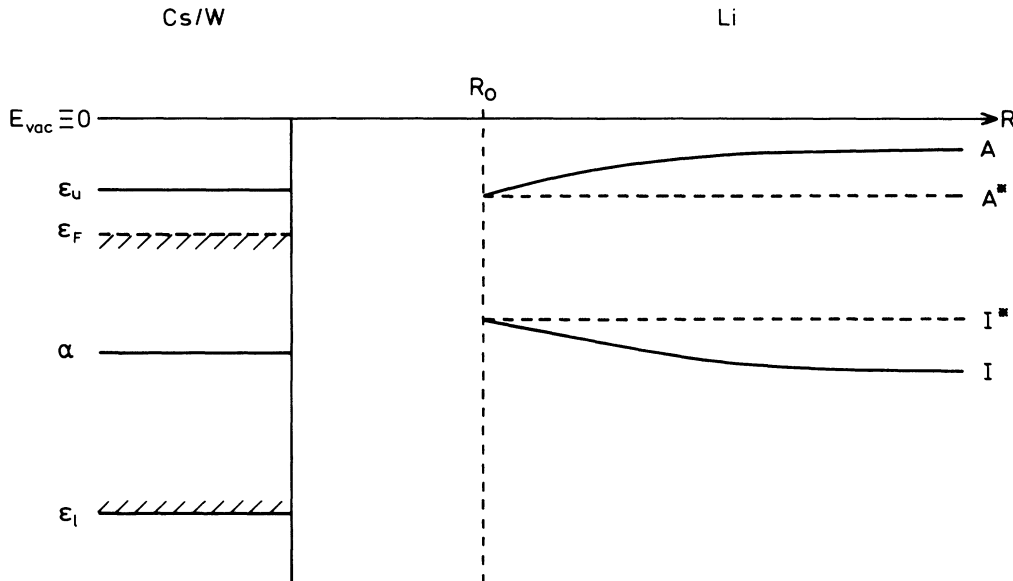
FIG. 1. Energy level diagram for Li^+-Cs/W system. Energies are in eV.

vary from -5 eV, for a clean surface, to -1.5 eV to simulate saturation with Cs adatoms. The presence of adsorbed Cs could be explicitly modeled, as has been done for Na-Na/W using the molecular-orbital method,[21] but for present purposes, merely varying ε_F should suffice. The ionization and affinity levels of isolated Li are $I = -5.392$ eV and $A = -0.616$ eV, respectively. Because of the image interaction, the ionization level I (affinity level A) of the Li ion is shifted upwards (downwards) by 1.0466 eV to I^* (A^*), at the assumed minimum ion-surface separation of $R_0 = 3.44$ Å. The interaction potential is here taken to have the customary form

$$V(t) = V_0 e^{-\lambda|t|},$$

where the parameter λ is related to the ion's velocity by $\lambda = v\gamma$, with γ having an assumed value of 0.5 a.u. (Ref. 4). The interaction strength V_0 is assumed to be equal to $\frac{1}{2}\beta = 0.875$ eV.

Resonance electron transfer can occur when an ion energy level is aligned with the occupied part of the metal band. As is obvious from Fig. 1, the position of the Fermi level and the amount of shift in the ionization and affinity levels are the significant factors in determining the relative fractions of the various products. Indeed, as has been noted in other studies,[4,21] a particular ion orbital can be expected to have significant occupation only if its energy is below the Fermi level, at the ion's closest approach to the surface. On this basis, the Li ionization level should always be occupied except for the lowest Fermi energies, i.e., clean or sparsely covered surfaces. Conversely, the affinity level should be occupied only for densely covered surfaces.

Calculated fractions of Li^+, Li^0, and Li^-, as functions of work function ϕ, are shown in Figs. 2(a)–(c) for three different incident energies along with the associated experimental data.[17,19] It is readily apparent that the general qualitative behavior of the curves is the same for all values of E. For ϕ less than about 3.5, P^+ is virtually constant, while for large ϕ it is a monotonically increasing, almost linear function. On the other hand, P^- is essentially zero for high work functions and monotonically decreasing for low work functions. P^0 has a relative maximum at some intermediate value of ϕ. Thus, for each value of E, there is a critical value of ϕ (ϕ_c, say), which defines two separate areas of behavior on the graph. For $\phi > \phi_c$, the region of low surface coverage by Cs adatoms, the Li^- fraction is negligible, because the affinity level is situated too far away from the occupied part of the band. Also, the Li^0 fraction increases in almost direct proportion to surface coverage (i.e., decreasing values of ϕ). Such a dependency on the number of adsorption sites indicates that they are acting as neutralization centers for the incoming ions. In the region of high surface coverage ($\phi < \phi_c$), the Li^+ fraction is approximately constant, because the states becoming occupied, as ϕ decreases, are far away from the ionization level and thus largely unreactive towards it, making P^+ virtually independent of changes in ϕ. As coverage increases, the amount of Li^- increases at the expense of Li^0, because the affinity level is more closely aligned with occupied
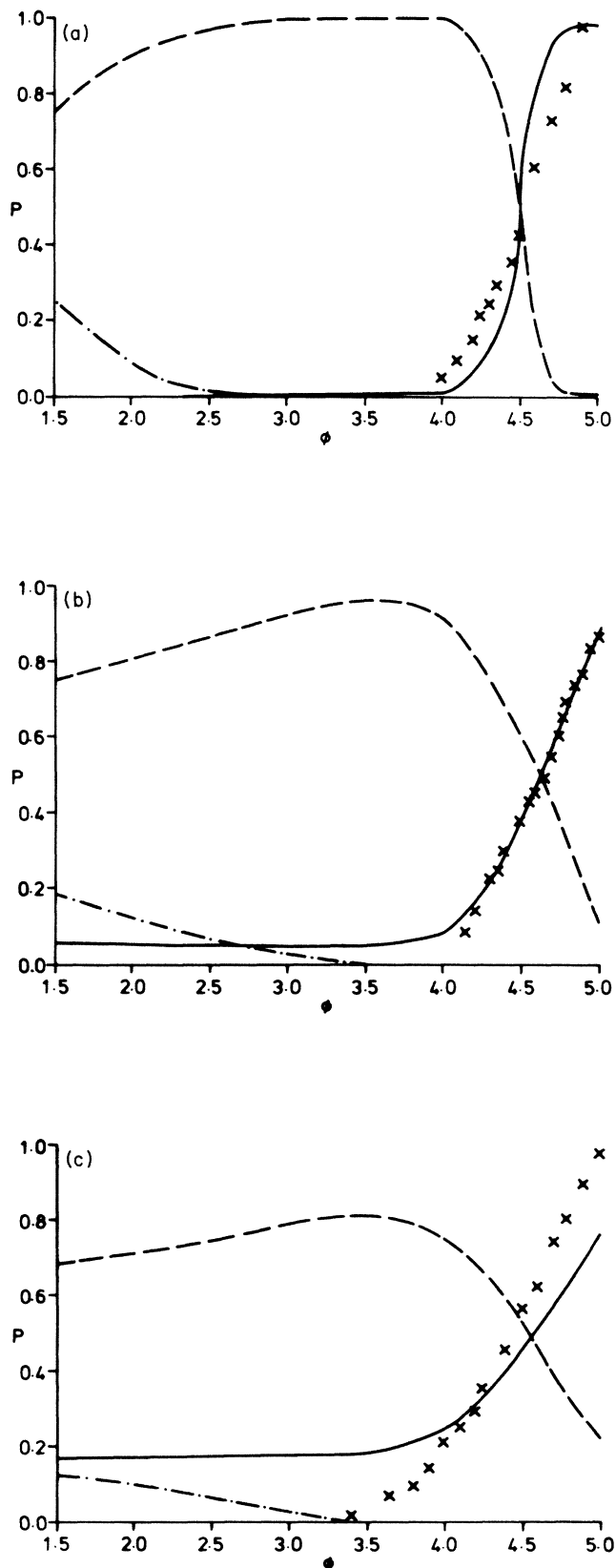

FIG. 2. Many-electron theoretical results for P^+ (———), P^0 (— — —), and P^- (—·—) vs ϕ. Experimental values of P^+ are denoted by $\times$. Graphs correspond to $E =$ (a) 100, (b) 400, and (c) 1000 eV.

states, making electron transfer into it more probable.

Comparison of the theoretical results with the experimental ones, for large ϕ, shows generally satisfactory agreement, the best fit being for $E=400$ eV. All of the experimental curves exhibit the roughly linear behavior found theoretically, although the slopes for $E=100$ and 1000 are not as good as could be wished for. Despite the fact that experimental values of P^+ for low ϕ are not available, it would seem that the corresponding theoretical values, when $E=400$ and 1000, are too high and should, in fact, be approximately zero. In this situation, because of the high surface coverage by Cs adatoms, it would appear that collisions between incoming Li^+ ions and Cs may be having a substantial effect on the final Li^+ population, acting to neutralize more of them than is predicted by the current model. Thus, more satisfactory results might be obtained in the low ϕ region, by explicit inclusion in the model of the presence of Cs adatoms, rather than by reliance solely on the work function.

Unrestricted Hartree-Fock molecular-orbital results, corresponding to Fig. 2(c), are shown in Fig. 3. Comparison is made somewhat difficult by the fact that Li^- production was not considered in this molecular-orbital calculation because the inclusion of the Coulomb term, using the unrestricted Hartree-Fock approximation, did not lead to satisfactory convergence in our numerical procedure. Thus, in Fig. 3, U is effectively infinite, because, at most, one electron can be transferred to the ion. With this in mind, the qualitative behavior of the two graphs is very roughly the same, although quantitatively the differences are considerable. The many-electron treatment is clearly in better agreement with the experimental data, but both methods fail for low ϕ, giving Li^+ fractions which are much too high. The molecular-orbital results could undoubtedly be improved for low ϕ including the Coulomb repulsion term, and perhaps, also, by some adjustment of the parameters, specifically V_0 and R_0. We have made similar comparisons for $E=100$ and 400, and the conclusions are essentially the same.

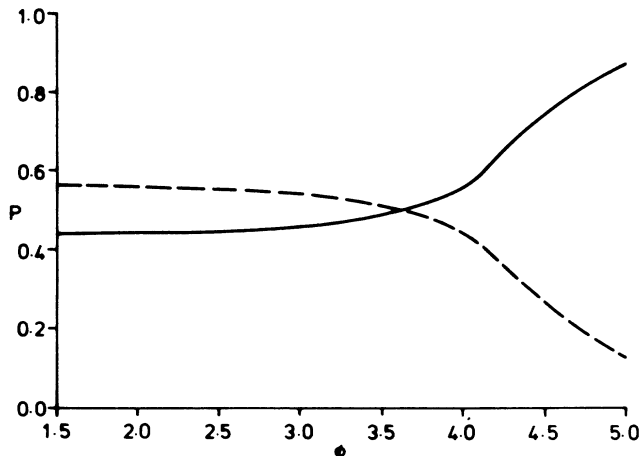Ionized and neutral fractions, calculated using the

many-electron technique, are shown in Figs. 4(a) and (b) as functions of E, for cesium-saturated ($\varepsilon_F=-2$ eV) and clean ($\varepsilon_F=-5$ eV) surfaces, respectively. Experimental data from Ref. 5 are also given in Fig. 4(a). For a low work function [Fig. 4(a)], Li^0 is the majority product at all incident energies, and significant amounts of Li^- are formed. For a high work function [Fig. 4(b)], Li^+ is always the majority product, and Li^- production is negligible. The calculated fractions are monotone functions of E and are almost linear in the low ϕ case. For a Cs-saturated surface, I^* is aligned with the center of the occupied part of the band, making electron transfer into it highly probable (i.e., low P^+). However, faster-moving (high E) ions have a shorter effective interaction time at the surface, giving them a better chance of escaping neutralization (or negative ionization) than slower ions, hence producing the monotone increasing behavior of the P^+ versus E curve. The situation for the clean surface [Fig. 4(b)] is more complicated because the ionization level is initially 0.392 eV below the Fermi level, but shifts above it as the ion approaches the surface. As a result, one does not expect the probability of charge transfer (i.e., P^0) to be particularly large, as is indeed the case. Moreover, for those ions which do become neutralized,
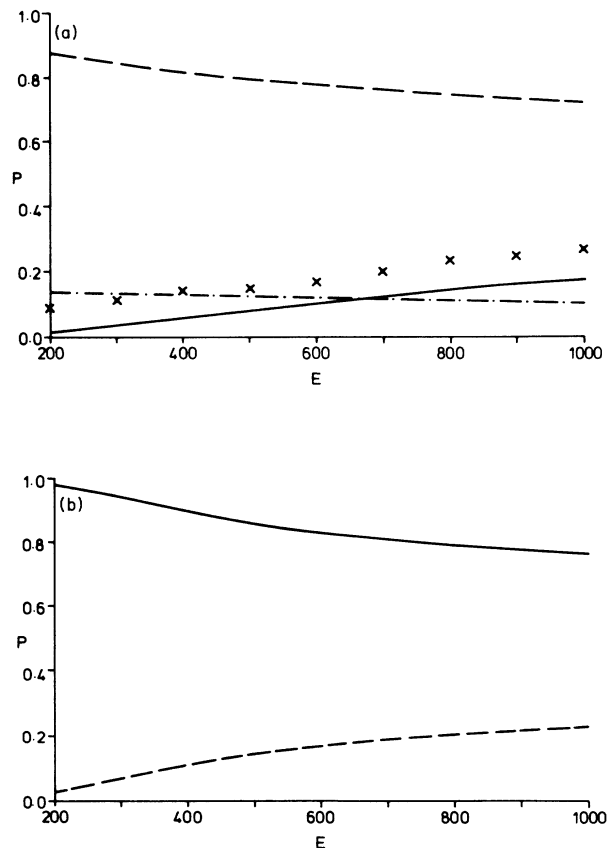

FIG. 3. Molecular-orbital theoretical results for P^+ (———) and P^0 (— — —) vs ϕ, with $E=1000$ eV.

FIG. 4. Many-electron theoretical results for P^+ (———), P^0 (— — —), and P^- (— $\cdot$ —) vs E. Experimental values of P^+ are denoted by $\times$. Graphs correspond to $\phi=$(a) 2 and (b) 5 eV. In (b), $P^-<0.025$ for all E.

the possibility of reionization exists; viz., the recently acquired electron may be transferred back into the unoccupied solid orbital from which it came. Such a double-charge transfer is more likely to occur for a slower-moving ion simply because of its longer interaction time at the surface.

The qualitative comparison between the theoretical and experimental Li^+ fractions in Fig. 4(a) is quite good in that both are monotonically increasing functions of E. Both give Li^+ as the minority product, but the theory predicts values about 50% of the experimental ones. The reason for this discrepancy is unclear, although a possible cause could lie in the angle of incidence of the incoming ions. The experimental results were for an angle of 82°, while the theoretical ones were for normal incidence. On the other hand, the experimental results of Fig. 2 were also obtained using a large reflection angle (75°) and yet are in much better agreement with the theoretical calculations. A study of parallel velocity effects, in the many-electron formulation of the problem, might help to clarify their importance (cf. the analysis of Easa and Modinos[22]).

Figure 5 gives the molecular-orbital results corresponding to the many-electron ones of Fig. 4. As before, Li^- production was neglected, which is unimportant for the clean surface because the amount of Li^- is negligible. The many-electron results are clearly in better agreement with experiment. Both methods show the same qualitative behavior for P^+ and P^0 (i.e., increasing or decreasing functions of E), but quantitatively, the agreement between them is much better for the clean surface [Fig. 5(b)] than for the saturated one [Fig. 5(a)] (presumably as a result of the inadequate treatment of the Coulomb term in the molecular-orbital method), and for lower incident energies.

V. SUMMARY

A many-electron theory of charge transfer between ions and solid surfaces has been presented. Although only resonance transfer has been considered here, the method should be versatile enough to allow Auger transitions, nonadiabatic processes, excitations, etc., to be considered on an equal footing by appropriate choice of basis functions and a many-electron Hamiltonian. Because of the large number of coupled differential equations which must be solved, it was useful to introduce two approximations which had the effect of making numerical calculations more tractable and, indeed, very straightforward. One involved the neglect of the excitation terms and the
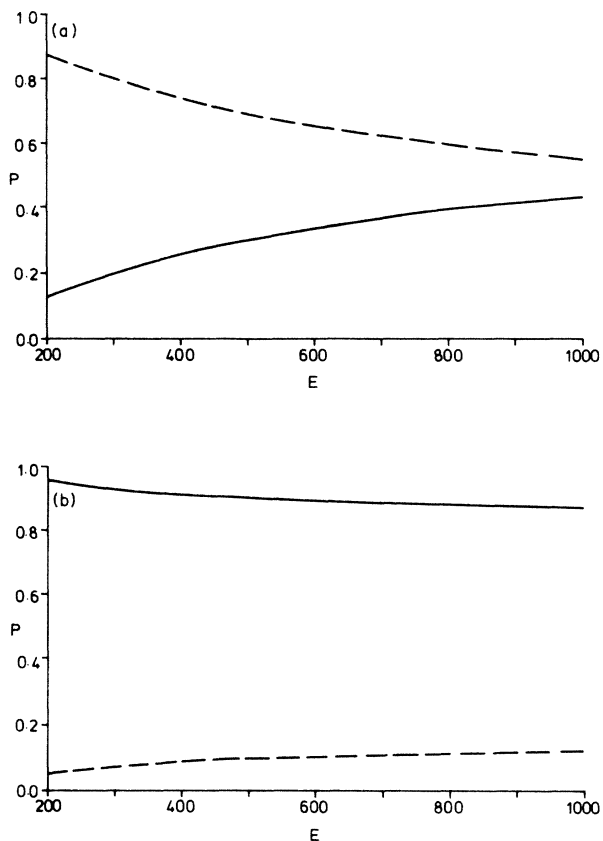

FIG. 5. Molecular-orbital theoretical results for P^+ (——) and P^0 (— — —) vs E, where $\phi=$(a) 2 and (b) 5 eV.

other invoked the local time approximation to remove the functions b_j from the integrals in (13).

The formalism developed here has been applied to the scattering of Li^+ from Cs/W, and the results compared with those of the molecular-orbital technique and with experimental values. The many-electron theory was seen to be the more reliable, generally being in good qualitative agreement with experiment.

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