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# Correlation effects in ion neutralization scattering with the use of a time-dependent coupled-cluster approach

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We consider the problem of ion neutralization scattering from surfaces. For large kinetic energies, the motion of the ion can be treated classically. The electronic part is assumed to be described by a time-dependent Newns-Anderson Hamiltonian. The ion is supposed to have a closed-shell structure with one empty orbital outside the shell, which can take up, at the most, two electrons from the metal. One can obtain a time-dependent Hartree-Fock (TDHF) solution for this using a procedure suggested earlier. [T. B. Grimley, V. C. Jyothi Bhasu, and K. L. Sebastian, Surf. Sci. 124, 305 (1983)]. We show that this solution is defective in that it predicts that the probability that the ion comes back as a neutral species is always less than 0.5, thus illustrating that one has to include electron correlation in order to describe the process correctly. For this we make use of the time-dependent version of the coupled-cluster approach. In this, one assumes the wave function to have the form $\exp[T_0(t)+T_1(t)+T_2(t)+\ldots]|\Phi_0\rangle$ where $|\Phi_0\rangle$ is a Slater determinant and $T_n(t)$ can create $n$-particle hole excitations in it. We take $T_1(t)$ as a linear combination of all possible single-particle hole-excitation operators while $T_2(t)$ is taken as a linear combination of just those two-particle hole-excitation operators which transfer two electrons to the orbital of the ion from the solid, neglect $T_n(t)$ for $n>2$, and derive differential equations for the matrix elements of the operators $T_1(t)$ and $T_2(t)$. These differential equations are solved numerically to obtain the wave function at any time $t$. New theorems which enable us to calculate all the expectation values that arise in our treatment of the problem are presented. Also, we have derived expressions for the excitation spectrum, produced as a result of the collision, by particles which come back as ions and also by those which have taken up one or two electrons from the solid. The method is applied to the scattering of lithium ions from the Ni(100) surface and also from a Ni surface contaminated with alkali atoms. The calculations show that TDHF theory is not a bad approximation if one is concerned just with the approach of the ion to the surface. But, in treating an ion which leaves the surface, TDHF fails. The predicted values of charge-transfer probabilities are considerably different in the two theories. Also, calculation of the excitation spectrum produced as a result of the collision show that the spectra are much broader for a contaminated surface having a lower work function than for the clean surface.

## I. INTRODUCTION

In the recent past, ion neutralization scattering from metal surfaces has received considerable attention from both experimentalists and theoreticians. The main reason for this is that one can now obtain high-quality experimental data for the scattering of ions from well-defined metal surfaces. If the energy of the ion is sufficiently large, then the motion of the ion can be treated classically, leading to great simplification in the theoretical treatment of the problem. The neutralization can proceed either through a one-electron or a two-electron process. In the first, the ion has an orbital whose energy lies in an occupied band of the metal (usually the conduction band). During the collision, an electron is transferred to this atomic orbital from an occupied orbital of the metal whose energy is not very different; the energy required for (released in) the process is taken from (transferred to) the translational motion of the ion. This is known as the resonance mechanism. The two-electron process is common if the atomic orbital lies far below the conduction band of the metal. Then an electron jumps into the atomic orbital, energy being conserved by the ejection of another electron from the metal. This process is more difficult to treat theoretically than the resonance process.

The resonance process has been observed experimentally for several systems,[1,2] particularly for the scattering of alkali ions from metal surfaces. In this paper we shall be concerned only with this process. There have been several theoretical attacks on the problem. Tully[3] has constructed a theory which is capable of explaining the qualitative features of the process. But an implementation of his theory requires knowledge of many-body wave functions, which are not at all easy to obtain. Bloss and Hone[4] consider a one-particle Hamiltonian and solve approximately the equations of motion for the creation and annihilation operators. Brako and Newns[5] extended this approach. They assume the bandwidth of the metal to be very large and the atomic orbital to be coupled to all the orbitals of the solid with the same strength and obtain expressions for the neutralization probability for scattering from a solid which could be at a nonzero temperature. Muda and Hanawa[6] suggest solving explicitly for expectation values of the form $\langle c_\mu^\dagger(t)c_\nu(t)\rangle$, which are nothing but the bond-order matrices so familiar to the quantum chemist. This procedure is, in our opinion, rather tedious.

Sebastian, Jyothi Bhasu, and Grimley[7] consider another procedure, viz., finding numerically the matrix elements of the time-evolution operator. For one-body Hamiltonians, exact solution can be found. This method is particularly suited for the cases in which the bandwidth is small. This method was applied to the scattering of ions from a linear chain. Also, this method can be applied, under certain assumptions, to scattering from a three-dimensional solid, the computational effort required being the same as that for a linear chain. Furthermore, the possibility of accounting for electronic repulsions, at least partially, using the time-dependent Hartree-Fock approximation was pointed out.[8]

This procedure was further investigated by McDowell[9] who also suggested another procedure similar to those used in studying the effect of vibrational degrees of freedom of the solid on the scattering of atoms from surfaces (see Adelman[10] and Tully.[11]). Inglesfield[12] has calculated the spectrum of excitations produced in the metal when an atom is scattered from its surface. He makes use not of the differential equations but of the integral equations that can be easily obtained from them.

J. Hermann *et al.*[13] have investigated experimentally the scattering of $\mathrm{Li}^+$ ions from the surface of Tungsten and compared the results with that of time-dependent Hartree-Fock (TDHF) approximation, calculated using the method of Grimley *et al.*[8] The probability that the $\mathrm{Li}^+$ ion becomes neutralized by electron transfer to its $2p$ orbital is found to be not in agreement with these results, thus indicating that TDHF is not sufficiently good for the description of the process. Our aim in this paper is to suggest a method for going beyond TDHF. For this we make use of a time-dependent version of the coupled-cluster approach of Coester and Kummel,[14] Cizek,[15] and others.[16] Using this procedure, solutions which take correlation effects into account can be obtained easily. Also, it is possible to calculate the spectrum of excitations produced in the solid by particles that have come out as ions and also by those that have picked up one or two electrons from the solid.

We now give a brief outline of the paper. In Sec. II, we give details of the Hamiltonian that we use. Section III points out a serious defect of the TDHF method, namely, under this method, the probablity that the ion returns as a neutral species is less than 0.5. Section IV introduces and discusses the time-dependent version of the coupled-cluster approach. The problem of extracting useful information from the wave function, once it is in the coupled-cluster form, is considered in Sec. V. We give two theorems which, we believe, are new [Eqs. (23) and (25)]. Another interesting result of this section is Eq. (28). Section VI gives expressions for charge-transfer probabilities and excitation spectra while Sec. VII is concerned with the task of solving the differential equations of the theory numerically. Exact, numerical solution of the equations can be carried out if the solid is represented by a semi-infinite one-dimensional chain. For the semi-infinite three-dimensional solid, the numerical implementation at first appears to be a formidable problem, but a single assumption, regarding the time dependence of the interaction [Eq. (52)] of the orbital of the ion with the orbitals of the solid, reduces the problem exactly to that of scattering from a one-dimensional linear chain. In Sec. VIII we apply the formalism to the scattering of $\mathrm{Li}^+$ ions from the Ni(100) surface. The main conclusions of the paper are in the Sec. IX.

## II. HAMILTONIAN

We consider the scattering of an ion such as $\mathrm{Li}^+$ or $\mathrm{Na}^+$, which has a closed-shell structure, with one empty orbital outside the shell, from the surface of a metal. Including more than one orbital on the ion is not difficult. In the scattering one or two electrons could be transferred to the ion by a resonance (one-electron) process. We assume that the solid can be described by a one-electron Hamiltonian. Because of our neglect of the two-electron terms, we are not able to describe the Auger process that is caused by them. The eigenfunctions of this Hamiltonian shall be labelled by a set of quantum numbers $\underline{k}$. Spin is not included in $\underline{k}$ and is specified by the variable $\sigma$ which can take the values up ($\uparrow$) or down ($\downarrow$). The Hamiltonian for the solid $H_s$, can now be written as

$$H_S=\sum_{\underline{k},\sigma}\epsilon_{\underline{k}}n_{\underline{k}\sigma}\ , \tag{1}$$

where $n_{\underline{k}\sigma}=c^{\dagger}_{\underline{k}\sigma}c_{\underline{k}\sigma}$, $c_{\underline{k}\sigma}(c^{\dagger}_{\underline{k}\sigma})$ represents the annihilation (creation) operator for the orbital $|\underline{k}\sigma\rangle$, which has an energy $\epsilon_{\underline{k}}$. We assume that $|\underline{k}\sigma\rangle$ is normalized according to $\langle\underline{k}'\sigma'|\underline{k}\sigma\rangle=\delta(\underline{k}',\underline{k})\delta_{\sigma'\sigma}$. $\delta(\underline{k}',\underline{k})$ has Dirac $\delta$ functions over the quantum numbers that vary continuously and Kronecker $\delta$ functions over those that vary discretely.

We shall consider ions having energies in the range 200—1000 eV so that the motion of the ion can be treated classically. Furthermore, the ion is assumed to be incident and reflected back in the perpendicular direction. The attractive potential in which the ion moves as a result of its interaction with the solid and any energy loss caused by the collision are both neglected. The ion's distance at any instant $t$, is taken to be $R=R_0+v\,|t|$, where $v$ is the velocity of the ion and $R_0$, a constant (see Sec. IX for further details). $|A\sigma\rangle$ will represent spin orbitals on the ion, the associated operators being $c_{A\sigma}$ and $c^{\dagger}_{A\sigma}$. $|A\sigma\rangle$ is assumed to be orthogonal to $|\underline{k}\sigma\rangle$. The orbital energy of $|A\sigma\rangle$ at large distances from the solid is denoted as $\epsilon^0_A$.

We write the time-dependent Hamiltonian for the electronic part as

$$\begin{aligned}H(t)&=\sum_{\underline{k},\sigma}\epsilon_{\underline{k}\sigma}n_{\underline{k}\sigma}+\sum_{\sigma}\epsilon_A(t)n_{A\sigma}+U(t)n_{A\uparrow}n_{A\downarrow}\\&\quad+\sum_{\underline{k},\sigma}[V_{A\underline{k}}(t)c^{\dagger}_{A\sigma}c_{\underline{k}\sigma}+\mathrm{H.c.}] \qquad (2)\\&=H_0(t)+U(t)n_{A\uparrow}n_{A\downarrow}\ . \qquad (3)\end{aligned}$$

The definition of $H_0(t)$ is obvious from Eq. (3). $\epsilon_A(t)=\epsilon^0_A+I(t)$, where $I(t)$ represents the shifting of the energy of $|A\sigma\rangle$ due to the images. The term $U(t)n_{A\uparrow}n_{A\downarrow}$ represents the Coulombic interaction between electrons of opposite spin in the orbital of the ion. The images make the Coulombic repulsion dependent on the distance of the ion from the surface, which in turn causes $U$ to be time dependent. This Hamiltonian is usually known as the

Newns-Anderson Hamiltonian. The symbol $\sum_{\underline{k}}$ in Eq. (2) and all the equations that follow means that integration has to be performed over all quantum numbers that vary continuously and summation has to be performed over those that take discrete values.

This Hamiltonian, however, neglects the following aspects of the problem. (i) All the dynamics of the atoms in the solid are neglected. (ii) Excitation of plasmons is not considered. Plasmons, however, are included indirectly as we have taken the image interaction into account. (iii) Imagine that $\epsilon_A^0$ is high above the Fermi level $\epsilon_F$ of the metal. Then the orbitals $|A\sigma\rangle$ are unoccupied during the collision so that the electronic system of the solid sees the ion only as a time-dependent potential which can create excitations. The fact that $\epsilon_A^0$ is not high above $\epsilon_F$ can now cause a switching off of this potential by the transfer of an electron.

## III. TIME-DEPENDENT HARTREE-FOCK SOLUTION

At the time $t=-\infty$, the ion is far away from the solid so that $V_{A\underline{k}}(-\infty)=0$ and the wave function for the system is a Slater determinant with all the levels in the solid having an energy less than $\epsilon_F$ being doubly occupied. We denote this state by $|\Phi_0\rangle$. At this time, the net spin of the combined system is zero. Because our Hamiltonian in Eq. (2) has no spin-flipping term, the spin of the combined system has to remain zero at all times. We wish to solve the time-dependent Schrödinger equation,

$$i\frac{\partial}{\partial t}|\psi(t)\rangle=H(t)|\psi(t)\rangle . \tag{4}$$

Because $H(t)$ contains the two-body operator $U(t)n_{A\uparrow}n_{A\downarrow}$, the exact solution of Eq. (4) is not known. One can obtain an approximate solution by the TDHF method in which $H(t)$ is replaced by the one-electron Hamiltonian,

$$H_{\rm HF}(t)=H_0(t)+U(t)(\langle n_{A\uparrow,t}\rangle n_{A\downarrow}+\langle n_{A\downarrow,t}\rangle n_{A\uparrow} -\langle n_{A\uparrow,t}\rangle\langle n_{A\downarrow,t}\rangle) . \tag{5}$$

$\langle n_{A\sigma,t}\rangle$ stands for $\langle\psi(t)|n_{A\sigma}|\psi(t)\rangle$. This solution, however, has the defect discussed below.

Because the initial state is a Slater determinant with identical orbitals for spin-up and spin-down electrons, the wave function at any time $t$, obtained by time evolution under the Hamiltonian of Eq. (5), will also be a Slater determinant with identical orbitals for spin-up and spin-down electrons. This implies

$$\langle n_{A\uparrow,t}\rangle=\langle n_{A\downarrow,t}\rangle . \tag{6}$$

Because the wave function at time $t$ is a *single Slater determinant* and not a linear combination, we have

$$\langle\psi(t)|n_{A\uparrow}n_{A\downarrow}|\psi(t)\rangle=\langle n_{A\uparrow,t}\rangle\langle n_{A\downarrow,t}\rangle . \tag{7}$$

Now we write $|\psi(t)\rangle$ as

$$|\psi(t)\rangle=n_{A\uparrow}n_{A\downarrow}|\psi(t)\rangle+(1-n_{A\uparrow})(1-n_{A\downarrow})|\psi(t)\rangle +[n_{A\uparrow}(1-n_{A\downarrow})+n_{A\downarrow}(1-n_{A\uparrow})]|\psi(t)\rangle . \tag{8}$$

$n_{A\uparrow}n_{A\downarrow}|\psi(t)\rangle$ is that component of the wave function that has two electrons in the atomic orbital of the ion, while $(1-n_{A\uparrow})(1-n_{A\downarrow})|\psi(t)\rangle$ is that which has no electrons in this orbital. $[n_{A\uparrow}(1-n_{A\downarrow})+n_{A\downarrow}(1-n_{A\uparrow})]|\psi(t)\rangle$ has exactly one electron in this orbital, the spin of which can be up or down. The probability that exactly one electron is transferred to the ion at the time $t$ is

$$P_{\rm neu}(t)=\langle\psi(t)|n_{A\uparrow}(1-n_{A\downarrow})+n_{A\downarrow}(1-n_{A\uparrow})|\psi(t)\rangle . \tag{9}$$

Now using Eqs. (6) and (7), we get

$$P_{\rm neu}(t)=2\langle n_{A\uparrow,t}\rangle(1-\langle n_{A\uparrow,t}\rangle) . \tag{10}$$

Because $n_{A\uparrow}$ is an occupation number operator, its expectation value is between zero and unity so that $2\langle n_{A\uparrow,t}\rangle(1-\langle n_{A\uparrow,t}\rangle)$ can have, at most, a value of 0.5, which happens when $\langle n_{A\uparrow,t}\rangle=0.5$. Thus, under the TDHF approximation, the probability that the ion would return as a neutral particle $[=P_{\rm neu}(\infty)]$ is less than or equal to 0.5, in clear contradiction with physical intuition and experimental data. Almost complete neutralization is observed in some experiments.[13] However, if there was one electron with a given spin in the atomic orbital at time $t=-\infty$, then Eq. (6) would not be true and our arguments would not mean inapplicability of TDHF.

## IV. TIME-DEPENDENT COUPLED-CLUSTER APPROACH

The argument given above suggests that one has to look for methods for going beyond the TDHF method. An obvious procedure would be to perform a time-dependent configuration interaction (CI) which, however, is extremely tedious. So we make use of a time-dependent extension of the coupled-cluster approach. The coupled-cluster approach was originated by Coester and Kummel[14] and developed into a powerful tool for molecular electronic structure computations by Cizek *et al.*[15,16] The time-dependent version was used by Hoodbhoy and Negele[17] for applications in nuclear physics and by Schönhammer and Gunnarsson[18] for the calculation of core-hole spectra.

To introduce this procedure, we adopt the following notation. Orbitals of the solid that are occupied in the initial state $|\Phi_0\rangle$ will be referred to as the hole states and denoted by lower case symbols such as $\underline{p}$, $\underline{q}$, etc., while orbitals that are unoccupied in $|\Phi_0\rangle$ will be called the particle states and denoted by upper case symbols such as $\underline{P}$, $\underline{Q}$, etc. The labels $\underline{k}$, $\underline{k}'$, etc. will be used to denote orbitals of the solid which could be particle or hole states, and a summation over such a label will imply summation over all the orbitals of the solid.

Following the idea of the coupled-cluster expansion, we write the wave function as

$$|\psi(t)\rangle=e^{T(t)}|\Phi_0\rangle . \tag{11}$$

Here $T(t)$ is a time-dependent operator, which is assumed to have the form

$$T(t)=T_0(t)+T_1(t)+T_2(t)+\cdots . \tag{12}$$

$T_n(t)$ is an operator that will excite $n$ electrons from hole states to particle states. Using Eq. (11) in Eq. (4) and multiplying by $e^{-T(t)}$ we get

$$i\frac{\partial}{\partial t}T(t)\,|\,\Phi_0\rangle = e^{-T(t)}H(t)e^{T(t)}\,|\,\Phi_0\rangle\ . \tag{13}$$

Taking the matrix elements of this equation with respect to $|\,\Phi_0\rangle$ and the states obtained by creating one, two, etc. particle-hole excitations will lead to a set of coupled nonlinear differential equations for the matrix elements of $T(t)$. As in the time-independent case, this can be done systematically using the diagram techniques of Cizek,[15,19] though for our Hamiltonian it is easier to perform the calculations by the method given below.

In principle, one has to include all $T_n(t)$ which, of course, is not possible. For our problem, we truncate the expansion in (12) at $n=2$ and as even this is rather difficult to handle, we make further approximation in the expression for $T_2(t)$. Thus we take

$$T_1(t) = \sum_{\underline{p},\sigma} T^1_{A\underline{p}}(t)c^\dagger_{A\sigma}c_{\underline{p}\sigma} + \sum_{\underline{P},\underline{p},\sigma} T^1_{\underline{P}\,\underline{p}}(t)c^\dagger_{\underline{P}\sigma}c_{\underline{p}\sigma} \tag{14}$$

$$T_2(t) = \sum_{\underline{p},\underline{q}} T^2_{\underline{p}\,\underline{q}}(t)c^\dagger_{A\downarrow}c^\dagger_{A\uparrow}c_{\underline{p}\uparrow}c_{\underline{q}\downarrow} \tag{15}$$

We have not allowed the matrix elements $T^1_{A\underline{p}}$ and $T^1_{\underline{P}\,\underline{p}}$ to be dependent on the spin. This assures that the system is always in a state with net spin zero. Also, we do not take $T_2(t)$ to have its most general form, rather we take it as a linear combination of just those two-particle hole excitations which are expected to be most important for a correct description of the process, viz., those in which two electrons are transferred to the atomic orbital from the solid. In this transfer, the pair of holes that are left behind also must have a net spin zero, which is assured by taking $T^2_{\underline{p}\,\underline{q}}(t)$ to be symmetric in the indices $\underline{p}$ and $\underline{q}$. As $T_2(t)$ of (15) obeys $T_2(t)^2=0$, we can write the wave function as

$$|\,\psi(t)\rangle = e^{T_0(t)+T_1(t)}[1+T_2(t)]\,|\,\Phi_0\rangle\ . \tag{16}$$

On the right-hand side of (14), one has to calculate quantities of the form $e^{-T(t)}c^\dagger_{\underline{P}\sigma}c_{A\sigma}e^{T(t)}$. We write this as

$$e^{-T(t)}c^\dagger_{\underline{P}\sigma}e^{T(t)}e^{-T(t)}c_{A\sigma}e^{T(t)}$$

and in $e^{-T(t)}c_{A\sigma}e^{T(t)}$, we expand the exponentials to get

$$e^{-T(t)}c_{A\sigma}e^{T(t)} = c_{A\sigma} + [c_{A\sigma}, T(t)]\ . \tag{17}$$

As the particle hole operators, occurring in the expansion of $T(t)$, commute among themselves, only the first power of $T(t)$ remains in Eq. (17). Using equations similar to (17) one can evaluate Eq. (13). On taking matrix elements of this equation with respect to $|\,\Phi_0\rangle$, $c^\dagger_{A\sigma}c_{\underline{p}\sigma}|\,\Phi_0\rangle$, $c^\dagger_{\underline{P}\sigma}c_{\underline{p}\sigma}|\,\Phi_0\rangle$, and $c^\dagger_{A\downarrow}c^\dagger_{A\uparrow}c_{\underline{p}\uparrow}c_{\underline{q}\downarrow}|\,\Phi_0\rangle$, we get the following equations:

$$i\dot{T}_0(t) = 2\sum_{\underline{p}}[\epsilon_{\underline{p}} + T^1_{A\underline{p}}(t)V_{\underline{p}A}(t)]\ , \tag{18}$$

$$i\dot{T}^1_{A\underline{p}}(t) = V_{A\underline{p}}(t) + [\epsilon_A(t)-\epsilon_{\underline{p}}]T^1_{A\underline{p}}(t) + \sum_{\underline{P}} V_{A\underline{P}}(t)T^1_{\underline{P}\underline{p}}(t) + \sum_{\underline{q}} V_{\underline{q}A}(t)[T^2_{\underline{p}\,\underline{q}}(t) - T^1_{A\underline{p}}(t)T^1_{A\underline{q}}(t)]\ , \tag{19}$$

$$i\dot{T}^1_{\underline{P}\,\underline{p}}(t) = (\epsilon_{\underline{P}}-\epsilon_{\underline{p}})T^1_{\underline{P}\,\underline{p}}(t) + V_{\underline{P}A}(t)T^1_{A\underline{p}}(t) - \sum_{\underline{q}} T^1_{\underline{P}\,\underline{q}}(t)V_{\underline{q}A}(t)T^1_{A\underline{p}}(t)\ , \tag{20}$$

$$\begin{aligned} i\dot{T}^2_{\underline{p}\,\underline{q}}(t) = {} & [2\epsilon_A(t)+U(t)-\epsilon_{\underline{p}}-\epsilon_{\underline{q}}]T^2_{\underline{p}\,\underline{q}}(t) + U(t)T^1_{A\underline{p}}(t)T^1_{A\underline{q}}(t) \\ & - \sum_{\underline{p}_1}[2T^1_{Ap_1}(t)V_{p_1A}(t)T^2_{pq}(t) + T^1_{Ap}(t)V_{\underline{p}_1A}(t)T^2_{\underline{p}_1\underline{q}}(t) + T^1_{A\underline{q}}(t)V_{\underline{p}_1A}(t)T^2_{\underline{p}\,\underline{p}_1}(t)]\ . \end{aligned} \tag{21}$$

Because $|\,\psi(-\infty)\rangle = |\,\Phi_0\rangle$, the above equations have to be solved subject to

$$T_0(-\infty) = T^1_{A\underline{p}}(-\infty) = T^1_{\underline{P}\,\underline{p}}(-\infty) = T^2_{\underline{p}\,\underline{q}}(-\infty) = 0 \tag{22}$$

## V. CALCULATING THE MATRIX ELEMENTS

Having solved the above set of differential equations and obtained the wave function in the form $e^{T(t)}|\,\Phi_0\rangle$, how does one compute the expectation values of the operators of interest? For a general $T(t)$ this is an extremely difficult task and there does not exist efficient ways of doing so. This is one of the difficulties that have to be overcome before one uses a general $T(t)$. For the approximate $T(t)$ that we use, this may be done using the formulas derived below.

In this section, symbols such as $\underline{x}$, $\underline{y}$, etc. will stand for spin orbitals which are occupied in the state $|\,\Phi_0\rangle$, while $\underline{X}$, $\underline{Y}$, etc. will stand for spin orbitals that are unoccupied.

We wish to calculate the overlap of the two functions $e^S|\,\Phi_0\rangle$ and $e^W|\,\Phi_0\rangle$, where $S$ and $W$ can create only single-particle excitations and may be written as $S=\sum_{\underline{X},\underline{x}} S_{\underline{X}\,\underline{x}}c^\dagger_{\underline{X}}c_{\underline{x}}$ and $W=\sum_{\underline{X},\underline{x}} W_{\underline{X}\underline{x}}c^\dagger_{\underline{X}}c_{\underline{x}}$. For this, we expand the exponentials in $\langle\Phi_0|\,e^{W^\dagger}e^S\,|\,\Phi_0\rangle$ and use Wick's theorem and diagrammatic techniques. We represent $S$ by the vertex shown in Fig. 1(a), which we refer to as an open vertex. It has one directed line entering it from the left and one leaving it to the left. $W^\dagger$ is represented by the vertex shown in Fig. 1(b) (the dark vertex). All the terms that arise when Wick's theorem is applied to the overlap can be obtained in the following fashion. Imagine that the term contains $n$ $S$ vertices and $m$ $W^\dagger$ vertices. The contractions that arise from Wick's theorem are represented by joining together the associated lines. Due to the contraction of $c^\dagger_{\underline{X}}$ with $c_{\underline{x}}$ or of $c^\dagger_{\underline{x}}$ with $c_{\underline{X}}$ and contractions of two creation operators or two annihilation operators being zero, there is no line joining two $W^\dagger$ vertices or two $S$ vertices. Any line has to start at a

FIG. 1. (a) represents the operator $c_{\underline{X}}^{\dagger}c_{\underline{x}}S_{\underline{X}\,\underline{x}}$ and (b) the operator $W_{\underline{X}\,\underline{x}}^{*}c_{\underline{x}}^{\dagger}c_{\underline{X}}$. Note that particle lines run from right to left and hole lines from left to right.

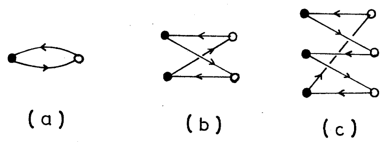

FIG. 2. First three diagrams of $\langle\Phi_0|e^{W^{\dagger}}e^{S}|\Phi_0\rangle_C$. The lines in the figure are to be labeled by particle or hole indices, depending on the direction of the line, and summed over. This is to be done in all the diagrams, wherever we have left a line unlabeled.

$W^{\dagger}$ vertex and end at an $S$ vertex or vice versa. The rules for drawing the diagrams are as follows. (i) Draw $n$ $W^{\dagger}$ vertices and $m$ $S$ vertices such that the $W^{\dagger}$ vertices are on the left and the $S$ vertices on the right (see Fig. 2). (ii) Join together the lines such that there are (a) no lines joining a $W^{\dagger}$ vertex with another $W^{\dagger}$ vertex or an $S$ vertex with another $S$ vertex, (b) the directions of the lines are preserved; (iii) only diagrams which have no free lines need be drawn, and (iv) all possible combinations are to be drawn. To calculate the contribution from a diagram that arises in this fashion, we use the following rules. (i) Each line running from left to right represents a hole line and is to be labelled by a lower case index such as $\underline{x}$, $\underline{y}$, etc. Each line running from right to left is a particle line and is to be labelled by capital letters such as $\underline{X}$, $\underline{Y}$, etc. Each open vertex with lines labelled by $\underline{x}$ and $\underline{X}$ contributes the quantity $S_{\underline{X}\,\underline{x}}$ and if it is a dark vertex then the contribution is $W_{\underline{X}\,\underline{x}}^{*}$. (ii) Each closed loop contributes a factor of $-1$ as does each hole line. (iii) A diagram with $n$ $W^{\dagger}$ and $m$ $S$ vertices has a factor $(n!m!)^{-1}$ associated with it. (iv) Sum over all the lines that are labeled.

The diagrams that arise can be classified as those that are completely connected and those that are not. It is possible to sum the series exactly and express the result only in terms of the connected diagrams. That is,

$$\langle\Phi_0|e^{W^{\dagger}}e^{S}|\Phi_0\rangle=\exp(\langle\Phi_0|e^{W^{\dagger}}e^{S}|\Phi_0\rangle_C)\ . \qquad (23)$$

The subscript $C$ in Eq. (23) means that we need to retain only the connected diagrams. As this result is known in the literature for the case where $S=W$, we shall not give a proof for it. (We have been unable to find a reference where it is proved, but the proof is fairly easy.)

The first three connected diagrams that contribute to $\langle\Phi_0|e^{W^{\dagger}}e^{S}|\Phi_0\rangle_C$ are shown in the Figs. 2(a) to 2(c). These diagrams can be summed to get

$$\langle\Phi_0|e^{W^{\dagger}}e^{S}|\Phi_0\rangle_C=\mathrm{Tr}\ln(\underset{\sim}{I}+\underset{\sim}{W}^{\dagger}\underset{\sim}{S})\ ,$$

so that

$$\langle\Phi_0|e^{W^{\dagger}}e^{S}|\Phi_0\rangle=\det(\underset{\sim}{I}+\underset{\sim}{W}^{\dagger}\underset{\sim}{S})\ . \qquad (24)$$

Here $\underset{\sim}{I}$ denotes the identity matrix. Our result of Eq. (23) is valid even if $S$ and $W$ are general operators of the form given in Eq. (12).

Now we calculate the matrix element $\langle\Phi_0|e^{W^{\dagger}}Be^{S}|\Phi_0\rangle$ of an operator $B$. Using a diagrammatic representation for $B$, one can again represent this matrix element as an infinite series. The series can be summed exactly to get

$$\langle\Phi_0|e^{W^{\dagger}}Be^{S}|\Phi_0\rangle$$
$$=\langle\Phi_0|e^{W^{\dagger}}Be^{S}|\Phi_0\rangle_C\langle\Phi_0|e^{W^{\dagger}}e^{S}|\Phi_0\rangle\ . \qquad (25)$$

As an example, consider the case where $B=c_{\underline{X}}^{\dagger}c_{\underline{x}}$. We represent this operator by the vertex in the Fig. 3(a). The first three diagrams that contribute to $\langle\Phi_0|e^{W^{\dagger}}c_{\underline{X}}^{\dagger}c_{\underline{x}}e^{S}|\Phi_0\rangle_C$ are given in Figs. 3(b)–3(d). Summing the contributions from all such diagrams, taking into account all topologically equivalent diagrams, leads to

$$\langle\Phi_0|e^{W^{\dagger}}c_{\underline{X}}^{\dagger}c_{\underline{x}}e^{S}|\Phi_0\rangle_C=[(\underset{\sim}{I}+\underset{\sim}{W}^{\dagger}\underset{\sim}{S})^{-1}\underset{\sim}{W}^{\dagger}]_{\underline{x}\,\underline{X}}\ . \qquad (26)$$

Representing $c_{\underline{X}}^{\dagger}c_{\underline{Y}}^{\dagger}c_{\underline{y}}c_{\underline{x}}$ by the vertex in Fig. 4(a), one has the diagrams 4(b)–4(e) contributing to the left-hand side of Eq. (26). All these diagrams can be summed exactly to get

$$\langle\Phi_0|e^{W^{\dagger}}c_{\underline{X}}^{\dagger}c_{\underline{Y}}^{\dagger}c_{\underline{y}}c_{\underline{x}}e^{S}|\Phi_0\rangle_C=[(\underset{\sim}{I}+\underset{\sim}{W}^{\dagger}\underset{\sim}{S})^{-1}\underset{\sim}{W}^{\dagger}]_{\underline{x}\,\underline{X}}[(\underset{\sim}{I}+\underset{\sim}{W}^{\dagger}\underset{\sim}{S})^{-1}\underset{\sim}{W}^{\dagger}]_{\underline{y}\,\underline{Y}}-[(\underset{\sim}{I}+\underset{\sim}{W}\underset{\sim}{S})^{-1}\underset{\sim}{W}]_{\underline{x}\,\underline{X}}[(\underset{\sim}{I}+\underset{\sim}{W}^{\dagger}\underset{\sim}{S})^{-1}\underset{\sim}{W}^{\dagger}]_{\underline{y}\,\underline{Y}}\ . \qquad (27)$$

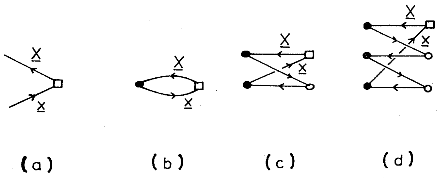

FIG. 3. (a) represents the operator $C_{\underline{X}}^{\dagger}c_{\underline{x}}$. (b) to (d) are the first three diagrams that arise from $\langle\Phi_0|e^{W^{\dagger}}c_{\underline{X}}^{\dagger}c_{\underline{x}}e^{s}|\Phi_0\rangle_C$.

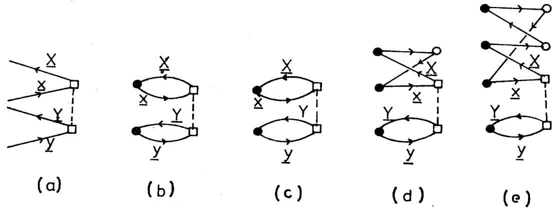

FIG. 4. (a) represents the operator $c_{\underline{X}}^{\dagger}c_{\underline{Y}}^{\dagger}c_{\underline{y}}c_{\underline{x}}$. (b) to (e) are four diagrams that contribute to $\langle\Phi_0|e^{W^{\dagger}}c_{\underline{X}}^{\dagger}c_{\underline{Y}}^{\dagger}c_{\underline{y}}c_{\underline{x}}e^{s}|\Phi_0\rangle_C$.

The first term in this equation is obtained by summing 4(b), 4(d), 4(e), and similar higher order diagrams, while the second term is the result of summing 4(c) and a set of diagrams similar to 4(d) and 4(e). An interesting point about this result is that it can be written in the following form:

$$\mathscr{A}(c_{\underline{X}}^{\dagger}c_{\underline{Y}}^{\dagger}c_{\underline{y}}c_{\underline{x}})=\mathscr{A}(c_{\underline{X}}^{\dagger}c_{\underline{x}})\mathscr{A}(c_{\underline{Y}}^{\dagger}c_{\underline{y}})-\mathscr{A}(c_{\underline{X}}^{\dagger}c_{\underline{y}})\mathscr{A}(c_{\underline{Y}}^{\dagger}c_{\underline{x}}) , \tag{28}$$

where $\mathscr{A}(M)$ means the following expression for any operator $M$:

$$\mathscr{A}(M)=\frac{\langle\Phi_0|e^{W^{\dagger}}Me^{S}|\Phi_0\rangle}{\langle\Phi_0|e^{W^{\dagger}}e^{S}|\Phi_0\rangle}=\langle\Phi_0|e^{W^{\dagger}}Me^{S}|\Phi_0\rangle_C . \tag{29}$$

The result of the Eq. (28) is new, though a special case of it is known. Thus it is true if $\mathscr{A}$ represents taking expectation value with respect to a given Slater determinant.[20]

## VI. EXPRESSIONS FOR CHARGE TRANSFER PROBABILITIES AND EXCITATION SPECTRA

As a result of solving Eqs. (18) to (22) we have the wave function in the form

$$|\psi(t)\rangle=e^{T_0(t)+T_1(t)}[1+T_2(t)]|\Phi_0\rangle .$$

$T_0(t)$ is a constant such that $e^{T_0(t)}$ should normalize this function. Our truncation of expression (12) for $T(t)$ at $n=2$ and the further approximation that we made in $T_2(t)$ causes $e^{T_0(t)}$ not to be equal to the actual normalization constant $N(t)$. This defect can be rectified only by keeping as many terms as possible in the expression for $T(t)$. $N(t)$ contains a time-dependent phase factor which we can safely neglect as we shall not be computing quantities involving $\partial/\partial t$. $N(t)$ can be calculated from

$$|\psi(t)\rangle=N(t)e^{T_1(t)}[1+T_2(t)]|\Phi_0\rangle,\quad \langle\psi(t)|\psi(t)\rangle=1 \tag{30}$$

so that

$$\begin{aligned}N(t)^{-2}&\\ &=\langle\Phi_0|e^{T_1^{\dagger}(t)}[1+T_2^{\dagger}(t)][1+T_2(t)]e^{T_1(t)}|\Phi_0\rangle \qquad (31)\\ &=[1+K(t)]\langle\Phi_0|e^{T_1^{\dagger}(t)}e^{T_1(t)}|\Phi_0\rangle ,\\ K(t)&\\ &=\langle\Phi_0|e^{T_1^{\dagger}(t)}[T_2^{\dagger}(t)+T_2(t)+T_2^{\dagger}(t)T_2(t)]e^{T_1(t)}|\Phi_0\rangle_C .\end{aligned} \tag{32}$$

Using Eq. (24) we get

$$\langle\Phi_0|e^{T_1^{\dagger}(t)}e^{T_1(t)}|\Phi_0\rangle=\{\det[\underset{\sim}{I}+\underset{\sim}{T}{}_1^{\dagger}(t)\underset{\sim}{T}{}_1(t)]\}^2 . \tag{33}$$

The square comes from spin. $\underset{\sim}{T}{}_1^{\dagger}(t)$ is the matrix, whose elements are given by $[\underset{\sim}{T}{}_1(t)]_{A\underline{p}}=T_{A\underline{p}}^1(t)$ and $[\underset{\sim}{T}{}_1(t)]_{\underline{P}\underline{p}}=T_{\underline{P}\underline{p}}^1(t)$. $K(t)$, defined above, can be computed using the methods of the preceding section. The probability $P_{\text{ion}}(t)$ that no electron is transferred to the ion at the time $t$ is the norm of $(1-n_{A\uparrow})(1-n_{A\downarrow})|\psi(t)\rangle$ and is given by

$$\begin{aligned}P_{\text{ion}}(t)=N(t)^2\langle\Phi_0|e^{T_1^{\dagger}(t)+T_2^{\dagger}(t)}&(1-n_{A\uparrow})\\ &\times(1-n_{A\downarrow})e^{T_1(t)+T_2(t)}|\Phi_0\rangle .\end{aligned} \tag{34}$$

The methods of the preceding section lead to

$$P_{\text{ion}}(t)=\frac{(1-\langle n_{A\uparrow,t}\rangle_C)^2}{1+K(t)} , \tag{35}$$

where

$$\begin{aligned}\langle n_{A\uparrow,t}\rangle_C&=\langle\Phi_0|e^{T_1^{\dagger}(t)}n_{A\uparrow}e^{T_1(t)}|\Phi_0\rangle_C\\ &=\{\underset{\sim}{T}{}_1(t)[\underset{\sim}{I}+\underset{\sim}{T}{}_1^{\dagger}(t)\underset{\sim}{T}{}_1(t)]^{-1}\underset{\sim}{T}{}_1^{\dagger}(t)\}_{AA} .\end{aligned} \tag{36}$$

The probability that two electrons are transferred is

$$\begin{aligned}P_{\text{neg}}(t)&=\langle\psi(t)|n_{A\uparrow}n_{A\downarrow}|\psi(t)\rangle\\ &=\frac{\langle n_{A\uparrow,t}\rangle_C+K(t)}{1+K(t)} .\end{aligned} \tag{37}$$

$P_{\text{neu}}(t)$ of Eq. (9) can be evaluated to get

$$P_{\text{neu}}(t)=\frac{2\langle n_{A\uparrow,t}\rangle_C(1-\langle n_{A\uparrow,t}\rangle_C)}{1+K(t)} . \tag{38}$$

Another quantity that is of interest is the spectrum of excitations produced as a result of the collision of the ion with the solid. This is given by a formula used by Muller-Hartmann, Ramakrishnan, and Toulouse;[21] it is

$$\bar{S}(\omega)=\sum_n|\langle\Phi_n|\psi(\infty)\rangle|^2\delta(\omega-E_0+E_n) . \tag{39}$$

In the above, $|\Phi_n\rangle$ are eigenfunctions of the Hamiltonian $H(\infty)$ having eigenvalues $E_n$. From here until the end of this section, the symbols $T_{Ap}^1$, $T_{\underline{P}\underline{p}}^1$, $\underset{\sim}{T}{}_1$, $H$, $K$, $N$, $U$, and $T_{\underline{p}\underline{q}}^2$ will be used to denote the values of these quantities evaluated at the time $t=\infty$. $\bar{S}(\omega)$ can be written as the Fourier transform,

$$\bar{S}(\omega)=\frac{1}{2\pi}\int_{-\infty}^{\infty}S(s)e^{i\omega s}ds , \tag{40}$$

with

$$S(s)=\langle\psi(\infty)|e^{-i(H-E_0)s}|\psi(\infty)\rangle . \tag{41}$$

Explicitly, $H$ is given by

$$H=\sum_{\sigma}\epsilon_A^0 n_{A\sigma}+\sum_{\underline{k},\sigma}\epsilon_{\underline{k}}n_{\underline{k}\sigma}+Un_{A\uparrow}n_{A\downarrow} .$$

$S(s)$ may be written as

$$S(s)=N^2\langle\Phi_0|e^{T_1^{\dagger}}(1+T_2^{\dagger})e^{-iHs}e^{T_1}(1+T_2)e^{iHs}|\Phi_0\rangle . \tag{42}$$

where we have made use of the fact that $|\Phi_0\rangle$ is an eigenfunction of $H$ having the eigenvalue $E_0$. Now defining

$$\begin{aligned}T_1^s&=\sum_{\underline{p},\sigma}T_{A\underline{p}}^{1,s}C_{A\sigma}^{\dagger}C_{\underline{p}\sigma}+\sum_{\underline{P},\underline{p},\sigma}T_{\underline{P}\underline{p}}^{1,s}C_{\underline{P}\sigma}^{\dagger}C_{\underline{p}\sigma} ,\\ T_2^s&=\sum_{\underline{p},\underline{q}}[(e^{-iUs}-1)T_{A\underline{p}}^{1,s}T_{A\underline{q}}^{1,s}+T_{\underline{p}\underline{q}}^{2,s}]c_{A\downarrow}^{\dagger}c_{A\uparrow}^{\dagger}c_{p\uparrow}c_{q\downarrow} ,\end{aligned} \tag{43}$$

$$T^{1,s}_{A\underline{p}}=T^{1}_{A\underline{p}}e^{-i(\epsilon^0_A-\epsilon_{\underline{p}})s},\quad T^{1,s}_{\underline{P}\,\underline{p}}=T^{1}_{\underline{P}\,\underline{p}}e^{-i(\epsilon_{\underline{P}}-\epsilon_{\underline{p}})s}\,,$$
$$T^{2,s}_{\underline{p}\,\underline{q}}=T^{2}_{\underline{p}\,\underline{q}}\exp[-i(2\epsilon^0_A+U-\epsilon_{\underline{p}}-\epsilon_{\underline{q}})s]\,, \tag{44}$$

we get

$$S(s)=N^2\langle\Phi_0|e^{T_1^\dagger}(1+T_2^\dagger)(1+T_2^s)e^{T_1^s}|\Phi_0\rangle$$
$$=N^2(1+K^s)(\det[\underset{\sim}{I}+\underset{\sim}{T}{}_1^\dagger\underset{\sim}{T}{}_1^s])^2\,. \tag{45}$$

Here

$$K^s=\langle\Phi_0|e^{T_1^\dagger}(T_2^\dagger+T_2^s+T_2^\dagger T_2^s)e^{T_1^s}|\Phi_0\rangle_C\,.$$

Using Eqs. (32) and (33) we get

$$S(s)=\frac{1+K^s}{1+K}R_s^2\,, \tag{46}$$

where

$$R_s=\frac{\det(\underset{\sim}{I}+\underset{\sim}{T}{}_1^\dagger\underset{\sim}{T}{}_1^s)}{\det(\underset{\sim}{I}+\underset{\sim}{T}{}_1^\dagger\underset{\sim}{T}{}_1)}\,. \tag{47}$$

The quantity $\bar{S}(\omega)$ in Eq. (40) is the spectrum of all possible excitations and includes excitations in which zero, one or two electrons are transferred to the ion with or without the creation of particle hole excitations in the solid. More interesting quantities, both from experimental and theoretical points of view, are the spectrum of excitations produced by a collision in which (i) no electron is transferred to the ion, (ii) one electron is transferred (the particle returns as a neutral species), and (iii) two electrons are transferred to the ion (it returns with a unit negative charge). These will be denoted by $\bar{S}_{\text{ion}}(\omega)$, $\bar{S}_{\text{neu}}(\omega)$, and $\bar{S}_{\text{neg}}(\omega)$, respectively. The quantities which on Fourier transformation would lead to these will be denoted by $S_{\text{ion}}(s)$, $S_{\text{neu}}(s)$, and $S_{\text{neg}}(s)$. They can also be evaluated easily. Thus $S_{\text{ion}}(s)$ is obtained by replacing $|\psi(\infty)\rangle$ in Eq. (41) by $(1-n_{A\uparrow})(1-n_{A\downarrow})|\psi(\infty)\rangle$. This gives

$$S_{\text{ion}}(s)=\frac{(1-\langle n^s_{A\uparrow}\rangle_C)^2}{1+K}R_s^2\,, \tag{48}$$

$$\langle n^s_{A\uparrow}\rangle_C=\langle\Phi_0|e^{T_1^\dagger}n_{A\uparrow}e^{T_1^s}|\Phi_0\rangle_C$$
$$=\{\underset{\sim}{T}{}_1^s(\underset{\sim}{I}+\underset{\sim}{T}{}_1^\dagger\underset{\sim}{T}{}_1^s)^{-1}\underset{\sim}{T}{}_1^\dagger\}_{AA}\,. \tag{49}$$

Similarly,

$$S_{\text{neu}}(s)=\frac{2\langle n^s_{A\uparrow}\rangle_C(1-\langle n^s_{A\uparrow}\rangle_C)}{1+K}R_s^2\,, \tag{50}$$

and

$$S_{\text{neg}}(s)=\frac{\langle n^s_{A\uparrow}\rangle_C^2+K^s}{1+K}(R_s)^2\,. \tag{51}$$

$S_{\text{neu}}(s)$ and $S_{\text{neg}}(s)$ are obtained by replacing $|\psi(\infty)\rangle$ in Eq. (41) by $[(1-n_{A\uparrow})n_{A\downarrow}+(1-n_{A\downarrow})n_{A\uparrow}]|\psi(\infty)\rangle$ and $n_{A\uparrow}n_{A\downarrow}|\psi(\infty)\rangle$, respectively.

## VII. SOLVING THE DIFFERENTIAL EQUATIONS AND CALCULATING THE MATRIX ELEMENTS

We now have the difficult job of solving numerically the differential equations (18) to (20) to obtain $T_1(t)$ and $T_2(t)$. For scattering from a semi-infinite one-dimensional tight-binding linear chain, this is not difficult. For this system one needs only the energy to specify any given orbital. For a semi-infinite three-dimensional solid one needs at least three quantum numbers, all of which can vary continuously, to specify a given orbital of the solid. We have to solve the differential equations at a selected set of values for each quantum number, which implies that one has $N^3$ $\underline{k}$ points. For $N=10$ this means that we have $\sim 10^6$ differential equations to be solved. This is clearly impossible. However, the following assumption reduces the number of differential equations to $N^2$:[22]

$$V_{A\underline{k}}(t)=\alpha_{\underline{k}}f(t)\,. \tag{52}$$

$f(t)$ is a given function of time, which we assume to be real and $\alpha_{\underline{k}}$ is a complex quantity, which depends on the value of $\underline{k}$.

We can get the solution of Eqs. (19) to (21) by making the following ansatz. Let us assume that we can write

$$T^1_{A\underline{p}}(t)=T^1_A(\epsilon_{\underline{p}},t)\alpha_{\underline{p}}\,,$$
$$T^1_{\underline{P}\,\underline{p}}(t)=T^1(\epsilon_{\underline{P}},\epsilon_{\underline{p}},t)\alpha^*_{\underline{P}}\alpha_{\underline{p}}\,, \tag{53}$$
$$T^2_{\underline{p}\,\underline{q}}(t)=T^2(\epsilon_{\underline{p}},\epsilon_{\underline{q}},t)\alpha_{\underline{p}}\alpha_{\underline{q}}\,,$$

where the quantities $T^1_A(\epsilon_{\underline{p}},t)$, $T^1(\epsilon_{\underline{P}},\epsilon_{\underline{p}},t)$, and $T^2(\epsilon_{\underline{p}},\epsilon_{\underline{q}},t)$ depend only on the energies $\epsilon_{\underline{p}}$, $\epsilon_{\underline{P}}$, and $\epsilon_{\underline{q}}$ and not on the other quantum numbers that specify the states $\underline{p}$, $\underline{P}$, $\underline{q}$, etc. Putting these into Eqs. (19) to (21), we find that if we choose $T^1_A(\epsilon_{\underline{p}},t)$, $T^1(\epsilon_{\underline{P}},\epsilon_{p},t)$, and $T^2(\epsilon_{\underline{p}},\epsilon_{\underline{q}},t)$ to obey Eqs. (54) to (56), then we have the solution of Eqs. (19) to (21):

$$i\dot{T}_A(\epsilon_{\underline{p}},t)=[\epsilon_A(t)-\epsilon_{\underline{p}}]T^1_A(\epsilon_{\underline{p}},t)+f(t)\left[1+\int_{\epsilon_{\underline{P}}>\epsilon_F}d\epsilon_{\underline{P}}\rho(\epsilon_{\underline{P}})T^1(\epsilon_{\underline{P}},\epsilon_{\underline{p}},t)\right.$$
$$\left.+\int_{\epsilon_{\underline{q}}<\epsilon_F}d\epsilon_{\underline{q}}\rho(\epsilon_{\underline{q}})[T^2(\epsilon_{\underline{p}},\epsilon_{\underline{q}},t)-T^1_A(\epsilon_p,t)T^1_A(\epsilon_{\underline{q}},t)]\right]\,, \tag{54}$$

$$i\dot{T}^1(\epsilon_{\underline{P}},\epsilon_p,t)=(\epsilon_{\underline{P}}-\epsilon_{\underline{p}})T^1_{\underline{P}\,\underline{p}}(t)+f(t)T^1_A(\epsilon_{\underline{p}},t)\left[1-\int_{\epsilon_{\underline{q}}<\epsilon_F}d\epsilon_{\underline{q}}\rho(\epsilon_{\underline{q}})T^1(\epsilon_{\underline{P}},\epsilon_{\underline{q}},t)\right]\,, \tag{55}$$

$$i\dot{T}^2(\epsilon_{\underline{p}},\epsilon_{\underline{q}},t)=[2\epsilon_A(t)+U(t)-\epsilon_{\underline{p}}-\epsilon_{\underline{q}}]T^2(\epsilon_{\underline{p}},\epsilon_{\underline{q}},t)+U(t)T^1_A(\epsilon_{\underline{p}},t)T^1_A(\epsilon_{\underline{q}},t)$$
$$-f(t)\left[T^2(\epsilon_{\underline{p}},\epsilon_{\underline{q}},t)\int_{\epsilon_{\underline{p}_1}<\epsilon_F}d\epsilon_{\underline{p}_1}\rho(\epsilon_{\underline{p}_1})T^1_A(\epsilon_{\underline{p}_1},t)+\int_{\epsilon_{\underline{p}_1}<\epsilon_F}d\epsilon_{\underline{p}_1}T^2(\epsilon_{\underline{p}_1},\epsilon_{\underline{q}},t)\rho(\epsilon_{\underline{p}_1})T^1_A(\epsilon_{\underline{p}},t)\right.$$
$$\left.+\int_{\epsilon_{p_1}<\epsilon_F}d\epsilon_{\underline{p}_1}T^2(\epsilon_{\underline{p}},\epsilon_{\underline{p}_1},t)\rho(\epsilon_{\underline{p}_1})T^1_A(\epsilon_{\underline{q}},t)\right]\,. \tag{56}$$

$\int_{\epsilon_{\underline{p}}<q_F} d\epsilon_{\underline{p}} (\int_{\epsilon_{\underline{p}}>\epsilon_F} d\epsilon_{\underline{p}})$ means integration over all energies less (greater) than $\epsilon_F$. In the above equations we have introduced the density of states,

$$\rho(\epsilon)=\sum_{\underline{k}} |\alpha_{\underline{k}}|^2\delta(\epsilon-\epsilon_{\underline{k}}) . \tag{57}$$

$\rho(\epsilon)$ has the information regarding the electronic structure of the solid and is the only quantity one needs to know in order to calculate the neutralization probabilities or the excitation spectrum.

Having obtained $T_1(t)$ and $T_2(t)$ by solving the above differential equations, we have to calculate the expectation values. The problem of working with large dimensional matrices $(N^3\times N^3)$ can also be avoided because of the special structure of $T_1(t)$ and $T_2(t)$ given in Eq. (53). For example, consider $[\underset{\sim}{I}+\underset{\sim}{T}{}_1^\dagger(t)\underset{\sim}{T}{}_1(t)]^{-1}\underset{\sim}{T}{}_1^\dagger(t)$, which occurs in Eq. (36). As the labels on the matrix, $[\underset{\sim}{I}+\underset{\sim}{T}{}_1^\dagger(t)\underset{\sim}{T}{}_1(t)]$, are continuous variables, inverting it amounts to solving the integral equation,

$$\sum_{\underline{q}} [\underset{\sim}{I}+\underset{\sim}{T}{}_1^\dagger(t)\underset{\sim}{T}{}_1(t)]_{\underline{p}\underline{q}} Q_{\underline{q}\underline{p}'}(t)=\delta(\underline{p},\underline{p}') . \tag{58}$$

Putting

$$Q_{\underline{q}\underline{p}'}(t)=\delta(\underline{q},\underline{p}')+\alpha^*_{\underline{q}}\alpha_{\underline{p}'}R(\epsilon_{\underline{q}},\epsilon_{\underline{p}'},t) ,$$

and defining

$$D(\epsilon_{\underline{p}},\epsilon_{\underline{p}'},t)=T_A^{1*}(\epsilon_{\underline{p}},t)T_A^1(\epsilon_{\underline{p}'},t)+\int_{\epsilon''>\epsilon_F} d\epsilon'' T^1(\epsilon'',\epsilon_{\underline{p}},t)^*\rho(\epsilon'')T^1(\epsilon'',\epsilon_{\underline{p}},t) ,$$

we get the solution of Eq. (58) if $R(\epsilon_{\underline{p}},\epsilon_{\underline{q}},t)$ obeys

$$R(\epsilon_{\underline{p}},\epsilon_{\underline{q}},t)+\int_{\epsilon'<\epsilon_F} d\epsilon' D(\epsilon_{\underline{p}},\epsilon',t)\rho(\epsilon')R(\epsilon',\epsilon_{\underline{q}},t)=-D(\epsilon_{\underline{p}},\epsilon_{\underline{q}},t) .$$

This is a simple integral equation which can be solved by selecting $N$ sample points for the energy in the occupied band when this is converted to a matrix equation involving $N\times N$ matrices. All the quantities of interest except the ratio of the determinants in Eq. (47) can be evaluated in a similar fashion. To evaluate the ratio, we write

$$\det(\underset{\sim}{I}+\underset{\sim}{T}{}_1^\dagger\underset{\sim}{T}{}_1^s)=\exp[\operatorname{Tr}\ln(\underset{\sim}{I}+\underset{\sim}{T}{}_1^\dagger\underset{\sim}{T}{}_1^s)] .$$

The use of Eq. (53) in the terms obtained by expanding the logarithm in the exponent leads to

$$\operatorname{Tr}(\underset{\sim}{T}{}_1^\dagger\underset{\sim}{T}{}_1^s)=\int_{\epsilon_p<\epsilon_F} d\epsilon_{\underline{p}}\rho(\epsilon_{\underline{p}})F(\epsilon_{\underline{p}},\epsilon_{\underline{p}},s) , \tag{59}$$

$$\operatorname{Tr}(T_1^\dagger T_1^s)^2=\int_{\epsilon_{\underline{p}}<\epsilon_F} d\epsilon_{\underline{p}}\rho(\epsilon_{\underline{p}}) \int_{\epsilon_{\underline{p}'}<\epsilon_F} d\epsilon_{\underline{p}'}\rho(\epsilon_{\underline{p}'})F(\epsilon_{\underline{p}},\epsilon_{\underline{p}'},s)F(\epsilon_{\underline{p}'},\epsilon_{\underline{p}},s) , \tag{60}$$

etc. $F(\epsilon_{\underline{p}},\epsilon_{\underline{p}'},s)$ is defined by

$$F(\epsilon_{\underline{p}},\epsilon_{\underline{p}'},s)=\exp\left[\frac{is}{2}(\epsilon_{\underline{p}}+\epsilon_{\underline{p}'})\right]\left[T_A^*(\epsilon_{\underline{p}},\infty)T_A(\epsilon_{\underline{p}'},\infty)+\int_{\epsilon_{\underline{P}}>\epsilon_F} d\epsilon_{\underline{P}}T^1(\epsilon_{\underline{P}},\epsilon_{\underline{p}},\infty)^*\rho(\epsilon_{\underline{P}})T^1(\epsilon_{\underline{P}},\epsilon_{\underline{p}'},\infty)e^{-i\epsilon_{\underline{P}},s}\right] . \tag{61}$$

Now we sample a set of energy points $\epsilon_1,\epsilon_2,\ldots,\epsilon_N$ in the occupied band. Then each integral in (59) and (60) can be approximated by a summation over these points. Thus for any function $g(\epsilon)$, we write $\int g(\epsilon)d\epsilon \simeq\sum_{i=1}^N p_i g_i$, $g_i=g(\epsilon_i)$ and $p_i$ are weight factors chosen in such a fashion as to attain a good approximation for the integral. With this, we get

$$\frac{\det[\underset{\sim}{I}+\underset{\sim}{T}{}_1^\dagger\underset{\sim}{T}{}_1^s]}{\det[\underset{\sim}{I}+\underset{\sim}{T}{}_1^\dagger\underset{\sim}{T}{}_1]}\simeq\frac{\det[\underset{\sim}{I}{}_N+\underset{\sim}{A}{}^s]}{\det[\underset{\sim}{I}{}_N+\underset{\sim}{A}{}^s]_{s=0}} , \tag{62}$$

where $(A^s)_{ij}=\sqrt{p_ip_j}F(\epsilon_i,\epsilon_j,s)$ and $\underset{\sim}{I}{}_N$ and $\underset{\sim}{A}{}^s$ are matrices of dimension $N\times N$. To evaluate $F(\epsilon_{\underline{p}},\epsilon_{\underline{p}'},s)$, we again select a set of energies in the unoccupied band and replace the integration in (61) by summation.

## VIII. APPLICATION TO Li$^+$ SCATTERING FROM Ni(100)

We now apply the above formalism to the scattering of Li$^+$ ions from the Ni(100) surface. We assume that the Li$^+$ ion is incident perpendicularly on top of a given Ni atom and assume that its distance from the Ni nucleus at time $t$ is given by $R=R_0+v|t|$, where $R_0=2.6$ a.u. and $v$ is the velocity of the ion. The hopping between the Ni orbitals and the $2s$ orbital of Li is modelled using the Wolfsberg-Helmholtz formula,[23,24] $0.5K(I_{\text{Li}}+I_{\text{Ni}})S$ with $K=1.5$. Here $I_{\text{Li}}$ and $I_{\text{Ni}}$ denote the ionization potentials of lithium and nickel atoms respectively. $S$ is the overlap of the relevant orbitals. Using this formula and assuming that the orbitals on nickel and lithium are described by Slater-type orbitals for the free atoms, with orbital exponents given by Clementi and Rainaldi,[25] one can estimate that the hopping between the Ni $3d$ orbitals and the Li $2s$ orbital is at least 70 times smaller than the hopping between Ni $4s$ and Li $2s$ orbital, for $R>2.6$ a.u. So we make practically no error in neglecting the $3d$ orbitals. We model $f(t)$ in Eq. (52) by putting it equal to the hopping between Ni $4s$ and Li $2s$ orbital calculated using the Wolfsberg-Helmholtz formula. We also have to model the density of states $\rho(\epsilon)$ in Eq. (57), which actually represents the fact that the Ni atom on which the Li$^+$ ion is incident is bonded to other atoms in the solid. We assume that it has the form

$$\rho(\epsilon)=\frac{1}{2\pi\beta^2}[4\beta^2-(\epsilon-\epsilon_F)^2]^{1/2} . \tag{63}$$

Here $\beta$ is a parameter, defined by the relationship $4\beta=$ the $s$ bandwidth. For Ni we take it to be 2.84 eV. The ionization potential of the Ni atom is 7.633 eV and that of the Li atom is 5.390 eV. The Coulombic repulsion $U$ for the free Li atom can be estimated as the difference of the electron affinity and ionization potential of Li to be 4.790 eV. The image interaction between the Ni surface and a charge which is kept at a distance of $R$ a.u. from the plane formed by the first layer of Ni atoms is taken to be given by $-1/(4R)$ in atomic units. Not that this does not diverge as the minimum possible value for $R$ is $R_0$ in our problem. Thus if the ion is at a distance $R$, then the orbital energy is $\epsilon_A(R)=\epsilon_A^0+I(R)$, where $I(R)=1/4R$. The Coulombic interaction between two electrons in the $2s$ orbital of Li at this distance is $U(R)=U-2I(R)$. The $R$ dependence of $\epsilon_A(R)$ and $I(R)$ can be converted to time dependences as we know $R$ as a function of time. The Ni(100) surface is taken to have a work function of 5.1 eV. We take the $s$ band to be half-filled. We have calculated the neutralization probabilities for the scattering of Li ions having an energy in the range 250 to 1000 eV.

Figure 5 shows the occupation number of the affinity orbital of the ion ($\langle n_{A\uparrow,t}\rangle$) as a function of time, calculated using the TDHF method and the coupled-cluster theory (CCT). The ion is closest to the surface at the time zero. For $t<0$ the ion is approaching the surface and in this region, the predictions of the two theories are not very different. This is a common feature of all the calculations reported in this paper. The reason for this is that the occupation number of the affinity orbital of the ion is still not very large and hence the two-electron term is not expected to be of importance. For $t>0$, however, the behavior of $\langle n_{A\uparrow,t}\rangle$ is roughly the same in the two theories, but the predicted value of $\langle n_{A\uparrow,\infty}\rangle$ in CCT (0.137) is approximately four times the TDHF result (0.0345) indicating that correlation effects are important in the final outcome of the scattering. Figures 6 and 7 show the probabilities of transferring zero, one, or two electrons as a function of time according to the TDHF theory and CCT. As before, the two results are not very different for $t<0$. Both theories predict that two-electron transfer has a low probability ($1.16\times10^{-3}$ in TDHF and $4.1\times10^{-4}$ in CCT). The predicted value of neutralization probability in TDHF ($6.58\times10^{-2}$) is approximately $\frac{1}{4}$ the CCT value ($2.6\times10^{-1}$). A rough estimate of the error that we make in truncating $T(t)$, as in Eq. (14), and neglecting all the higher-order $T_n(t)$ can be obtained by comparing $\exp[\mathrm{Re}T_0(\infty)]/N(\infty)$ with unity. For the calculations reported above, it was found that $|e^{\mathrm{Re}T_0(\infty)}/N(\infty)-1|<0.015$ indicating that the approximation that we use is reasonable.

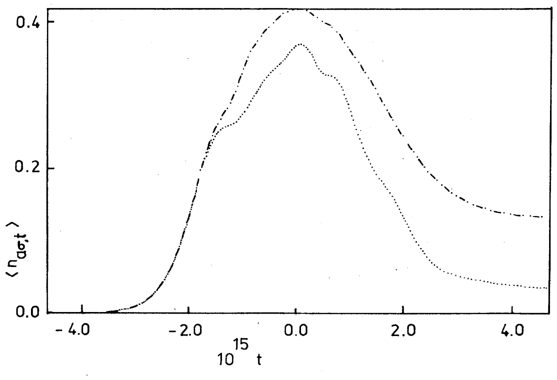

FIG. 5. Occupation number $\langle n_{A\uparrow},t\rangle$ of the affinity orbital of the ion as a function of time. Time is in units of seconds in all the figures. · · · · is the TDHF result and ··— the CCT one. The kinetic energy of the Li$^+$ ion is 1000 eV.

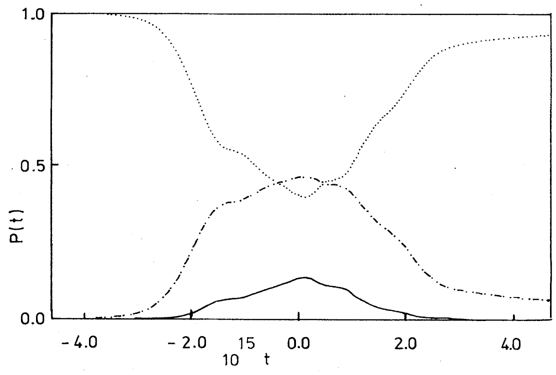

FIG. 6. Probability of transferring zero (· · · ·), one (··—), and two (——) electrons as functions of time, according to the TDHF theory. The kinetic energy of the Li$^+$ ion is 1000 eV.

There have been experiments in which the scattering of the ion takes place from a surface which has a fraction of a monolayer of alkali atoms deposited on it. One can model this deposition simply by changing the work function of the solid, if the coverage of the adsorbed alkali atoms is small. Figures 8 and 9 report the results of a calculation where we have assumed the decrease in the work function to be $0.5\beta$ (i.e., the work function is now 3.68 eV). One immediately notices that charge transfer is much more probable now. In CCT the probability of single-electron transfer takes a maximum value of 0.77 while in TDHF it always remains less than 0.5, in accor-

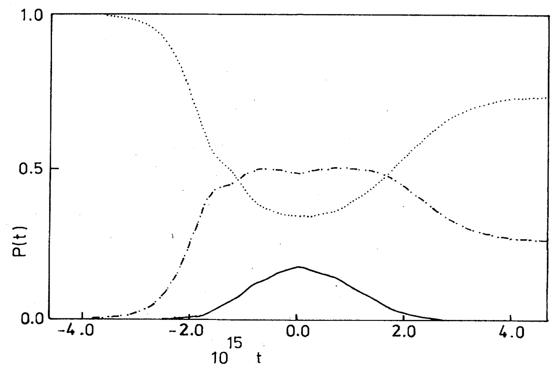

FIG. 7. Probability of transferring zero (· · · ·), one (··—), and two (——) electrons as functions of time, according to the CCT theory. The kinetic energy of the Li$^+$ ion is 1000 eV.

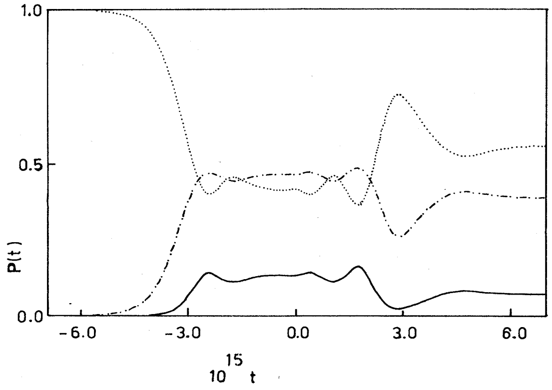

FIG. 8. Probability of transferring zero (· · · ·), one (··—), and two (——) electrons as functions of time, according to the TDHF theory, for Li$^+$ ions having a kinetic energy of 500 eV. To simulate the effect of depositing small amounts of Li on the surface, we have changed the work function of the metal to 3.68 eV.

dance with our expectation of Sec. III. The affinity orbital of the ion lies below the Fermi level if the ion is far away. As one brings the ion close to the surface, the image interaction causes the energy of this orbital to go up and eventually cross the Fermi level. For a clean Ni surface this occurs at about 10 Å and for the alkali deposited case at about 2.5 Å. The effect of this crossing is seen clearly in Fig. 9. The ion is at this distance at the time $-3\times10^{-15}$ s, and until this time the probability of single-electron transfer is steadily increasing.

When the ion is brought still closer, the affinity orbital goes above the Fermi level as a result of which the probability of finding one electron on the ion decreases. It is interesting that the probability of transferring two electrons, however, steadily increases as one approaches the surface. This can be traced to the following reason. A configuration having only one electron on the ion has an electronic energy $\epsilon_A(R)$, while a configuration with two electrons has $2\epsilon_A(R)+U(R)=2\epsilon_A^0+U$. That is, the electronic energy of the two-electron configuration is independent of the distance of the ion from the surface. The crossing of $\epsilon_A(R)$ with the Fermi level tends to reduce the weight of configurations having one electron on the ion by two mechanisms: (i) by transferring electrons back to the metal and (ii) by getting one more electron from the metal. In practice, both happen (though the second is more in Fig. 9) leading to an increase in the weights of configurations which have zero or two electrons on the ion. The predicted values of single-electron transfer (0.382 in TDHF and 0.165 in CCT) and two-electron transfer ($6.63\times10^{-2}$ in TDHF and 0.318 in CCT) are very different. For this calculation, $|e^{\mathrm{Re}T_0(\infty)}/N(\infty)-1|=0.247$, indicating that the solution is not as good as in the previous case.

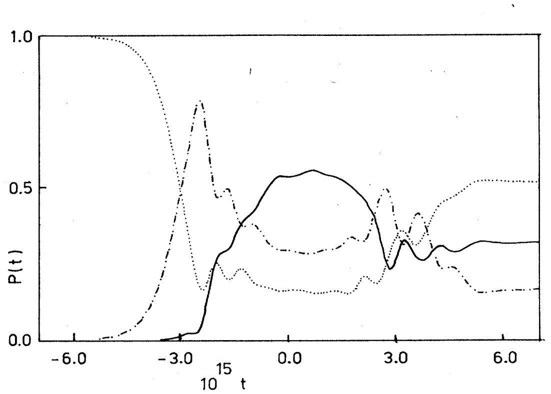

FIG. 9. Probability of transferring zero (· · · ·), one (··—), and two (——) electrons as functions of time, according to the CCT theory, for Li$^+$ ions having an energy of 500 eV. To simulate the effect of depositing small amounts of Li on the surface, we have changed the work function from 5.1 to 3.68 eV.

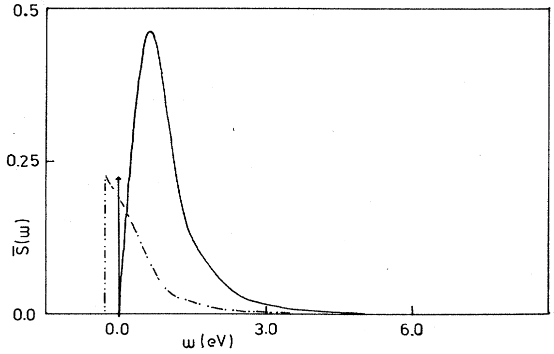

FIG. 10. The spectrum of excitations produced as a result of the collision of the ion with the surface, according to CCT. —— is the excitation spectrum produced by those ions which have taken up zero electrons from the surface [$\bar{S}_{\mathrm{ion}}(\omega)$], while ··— is that produced by ions which have taken up one electron from the surface [$\bar{S}_{\mathrm{neu}}(\omega)$]. Note that $\bar{S}_{\mathrm{neu}}(\omega)$ has nonzero value even for $\omega<0$ because of the fact that if the ion is far away from the surface the ionic orbital has an energy less than that of the Fermi level of the metal. The straight line at $\omega=0$ represents a $\delta$ function at that point having a strength 0.239. The kinetic energy of the Li$^+$ ion is 1000 eV.

In Figs. 10 and 11, we give the spectrum of excitations produced as a result of the collision for the two cases that we considered above, viz., clean and alkali deposited Ni

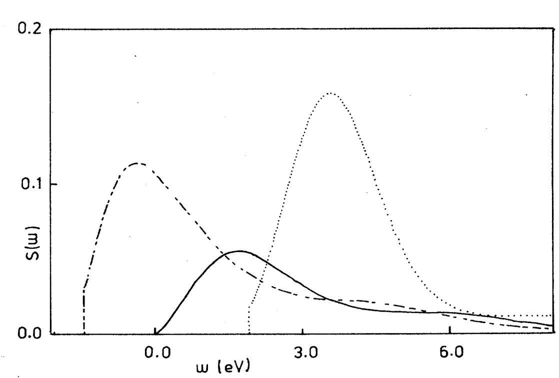

FIG. 11. The difference between this diagram and the previous one is that we have changed the work function to 3.68 eV and that the kinetic energy of the Li$^+$ ion is now only 500 eV. · · · · represents the excitation spectrum produced by particles which come back as negatively charged Li$^+$ ions [$\bar{S}_{\mathrm{neg}}(\omega)$].

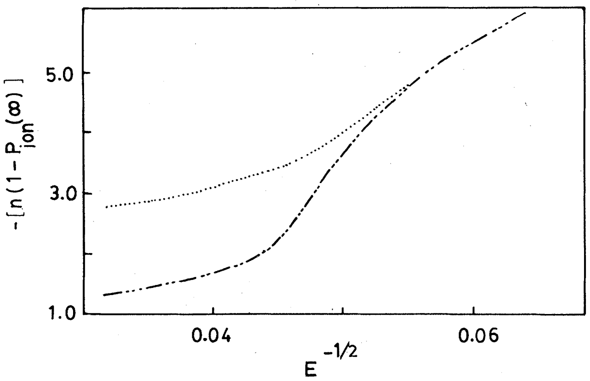

FIG. 12. $-\ln[1-P_{\text{ion}}(\infty)]$ against $1/\sqrt{E}$, for scattering from clean Ni surface. · · · · is the TDHF result and ··— is the CCT one. $E$ is in eV.

surfaces. The vertical line in both the figure at $\omega=0$ represent Dirac $\delta$ functions, the height being equal to the strength of the $\delta$ function. This strength gives the probability of elastic scattering. The excitation spectra extend into the region $\omega<0$ due to the reason that the affinity orbital on the ion lies below the Fermi level if the ion is far away from the surface. The main conclusion to be drawn from the two figures is that the spectrum of excitations produced in the solid is much broader if the crossing of the affinity level occurs in a region near the solid than in the case where it occurs at a large distance. Note also that in the Fig. 11 we report results for a $\text{Li}^+$ ion kinetic energy of 500 eV. For a kinetic energy of 1000 eV, the spectrum would be even broader.

We now consider the dependence of the outcome of scattering on the velocity of the particle, for the case of scattering from a clean Ni surface. Calculations showed charge-transfer probabilities at the distance of the closest approach to be almost independent of the velocity of the particle. This implies that nonadiabaticity is not important for $t<0$. Even though at large distances the affinity orbital is below the Fermi level, at distances over which the transfer of electron does not have a vanishingly small probability it is above the Fermi level. Hence, for very low velocities the outcome of the scattering will be $\text{Li}^+$ ion with unit probability. The deviation from this at finite velocities, measured by $1-P_{\text{ion}}(\infty)$ is expected to have the functional form $\exp(-\text{constant}/v_\perp)$, where $v_\perp$ is the velocity of the ion perpendicular to the surface. To verify this, we have made a plot of $-\ln[1-P_{\text{ion}}(\infty)]$ against $1/\sqrt{E}$ in Fig. 12. The result is approximately a straight line at energies less than 350 eV. The TDHF results, plotted in the same figure, show a similar behavior.

## IX. CONCLUSIONS

We have considered the problem of ion neutralization scattering from the surface of a metal using a time-dependent Newns-Anderson Hamiltonian. For an ion with a closed-shell structure, the time-dependent Hartree-Fock solution was shown to be defective in that it predicted that the probability of neutralization should always be less than 0.5. We suggest that the time-dependent extension of coupled-cluster theory is a possible alternative. We have applied it to the problem and derived some interesting new theorems that are required for the application. The usefulness of the procedure is illustrated by applying it to the scattering of Li ions from the Ni(100) surface. The predictions of the TDHF and CCT are very different in the calculations that we have done for this system. However, the calculations also showed that TDHF is not a bad approximation if one is concerned with the region in which the ion is approaching the surface. We have simulated the effect of depositing small amounts of alkali atoms on the surface by simply decreasing the work function of the surface. In this case the affinity level of the ion crosses the Fermi level of the metal at a shorter distance than for the pure Ni surface. Correspondingly, we find the charge-transfer probabilities to be higher and the spectrum of excitations produced in the solid as a result of the collision to be broader.

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