Charge exchange in many-body time-dependent processes

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Dynamical processes involving charge exchange betwen atoms and solid surfaces are studied within an Anderson-Newns model. We performed a perturbative treatment of the correlation term starting from a time-dependent Hartree-Fock basis, and calculated the probabilities of the final atomic charge states by using the Green-function formalism for irreversible processes. We analyzed the negative-ion fraction, assuming an Anderson symmetric case, and considering the electronic correlation effects up to a second perturbative order, for two "extreme" model systems: the two-level one, and a solid within the wideband approximation.

I. INTRODUCTION

Electronic charge exchange between atoms and solid surfaces taking place in processes like atom-surface collisions, desorption, and secondary-ion emission, represents a typically nonadiabatic phenomenon.[1-6] In all these processes there is an atom moving at low or moderate velocities which interacts with the surface, having, far from this, nonzero probabilities of being in ionized or excited states. The main objective of any theoretical model for a description of these phenomena is the calculation of the outgoing-atom charge-state probabilities. In recent years, the work done on the subject has grown rapidly, following two main lines. One approach is to consider a description of the substrate in which an equation of motion for fermionic operators within an Anderson-Newns model is formulated;[6-9] the other approach is to support, on a cluster, a representation of the system in which a dynamical wave-function formalism may be used.[10-12] The electron-electron interaction is neglected in almost all the theoretical models, making possible the resolution of the problem in a simpler way. Although this approach is an oversimplification, the probabilities obtained in this way present a qualitative agreement with experimental data concerning the adatom velocity, the substrate work function, the temperature, and other similar parameters. Nevertheless, the intraatomic correlation should be taken into account, because it affects the adatom electronic states as they approach the atomic limit. Thus the calculation of the different final-charge-state probabilities makes sense only when all the possible ionization channels for the atom are treated on an equal footing in the dynamical evolution description of a system, where the intra-atomic Coulomb repulsion is present.

Several approaches have been used to treat the problem including the effects of the correlation terms, although a good understanding has still not been achieved.[13,14] An exact calculation of the Anderson-Newns Hamiltonian for a small four-atom cluster has been performed,[15] showing in this case that for large values of the correlation parameter, the negative and positive ionizations may be treated as independent processes as long as the adatom level is either empty or singly occupied. The single-occupation assumption is equivalent to the limit of an infinite correlation parameter.[13] In a tight-binding formulation where the dynamical wave function is solved through an equation of motion for the evolution operator, the double occupation can be partially suppressed by considering adequate energy shifts.[16]

In the present work, we perform a perturbative treatment of the correlation term within the Keldysh formalism.[17] Taking the Hartree-Fock time-dependent solution as the zeroth-order approximation, we arrive at a perturbative expansion of the dynamical wave function including the successive correction terms due to the intraatomic correlation. In a Green-function formalism, this involves a calculation of the self-energies by a perturbation theory, starting from a time-dependent Hartree-Fock basis. Explicit expressions of the self-energies calculated up to a second order in the correlation parameter are given. The atomic charge-state probabilities are obtained from the asymptotic behavior of average values of fermionic operators taken at different times.

This is, from our point of view, an interesting formulation of the problem which allow us to treat those cases where negative and positive ionizations play equivalent roles, i.e., for small values of the correlation parameter.

In Sec. II A we describe how to calculate the different charge-state probabilities within an Anderson-Newns model, using the Keldysh formalism. The perturbative scheme for treating the intra-atomic correlation is developed in Sec. II B. In Sec. III we apply this formalism to a two-atom chain, and to an atom-solid system described in the wide-band limit. In Sec. IV we discuss the results.

II. THEORY

A. Use of the Keldysh formalism for calculating atomic charge-state probabilities

Starting with the Anderson-Newns Hamiltonian

$$H = \sum_{i,j} E_i n_{i\sigma} + E_A \sum_{\sigma} n_{A\sigma} + U \sum_{\sigma} n_{A\sigma} n_{A-\sigma}$$
$$+ \sum_{i,\sigma} V_{iA}(c_{i\sigma}^{\dagger} c_{A\sigma} + c_{A\sigma}^{\dagger} c_{i\sigma}) , \qquad (1)$$

where $V_{iA}(t)$ is a time-dependent interaction between substrate (i) and adatom (A) levels, E_i, E_A being the respective energies, and U is the intra-atomic Coulomb interaction assumed constant in the present case. In Eq. (1), $c^{\dagger}, c$ are the usual creation and annihilation Fermi operators, respectively, therefore $n = c^{\dagger}c$; and σ indicates the spin projection.

We are interested in the probability calculation of the different charge states of the atom far from the solid surface, that is when the interaction $V_{iA}(t)$ tends to zero. Let us consider the correlation function of the two Heisenberg operators $c_{A\sigma}(t)$ and $c_{A\sigma}^{\dagger}(t')$:

$$\langle c_{A\sigma}^{\dagger}(t') c_{A\sigma}(t) \rangle = \langle \psi_0 | c_{A\sigma}^{\dagger}(t') c_{A\sigma}(t) | \psi_0 \rangle . \qquad (2)$$

Going over to operators in the Schrödinger representation we can write

$$\langle c_{A\sigma}^{\dagger}(t') c_{A\sigma}(t) \rangle = \langle \psi^N(t') | c_{A\sigma}^{\dagger} U(t',t) c_{A\sigma} | \psi^N(t) \rangle , \qquad (3)$$

where $|\psi^N(t')\rangle = U(t',t_0)|\psi_0\rangle$ is the time-dependent wave function for the N-electron system, and $U(t',t)$ is the time evolution operator. Introducing in (3) the complete basis set of eigenstates for the system with $N-1$ electrons at the initial time t_0, $|\psi_{\alpha}^{N-1}\rangle$, and taking into account that $|\psi_{\alpha}^{N-1}(t)\rangle = U(t,t_0)|\psi_{\alpha}^{N-1}\rangle$ denotes the time evolution of the $(N-1)$-electron system when it is assumed to be in the eigenstate $|\psi_{\alpha}^{N-1}\rangle$ at time t_0, we can rewrite Eq. (3) as

$$\langle c_{A\sigma}^{\dagger}(t') c_{A\sigma}(t) \rangle = \sum_{\alpha} \langle \psi^N(t') | c_{A\sigma}^{\dagger} | \psi_{\alpha}^{N-1}(t') \rangle$$
$$\times \langle \psi_{\alpha}^{N-1}(t) | c_{A\sigma} | \psi^N(t) \rangle . \qquad (4)$$

Going over to the expansion of the time-dependent wave function for the system with $N(N-1)$ electrons in Slater determinants $D_i^{N(N-1)}$, which is a good basis set to describe the uncoupled atom-substrate limit:

$$|\psi^N(t)\rangle = \sum_i a_i(t) D_i^N \exp(-iE_i^N t) ,$$
$$|\psi_{\alpha}^{N-1}(t)\rangle = \sum_j b_j^{\alpha}(t) D_j^{N-1} \exp(-iE_j^{N-1} t) , \qquad (5)$$

$E_i^{N(N-1)}$ being the total energies corresponding to the many-body states $D_i^{N(N-1)}$; and assuming time values in the asymptotic limit, that is, t and t' sufficiently large as to justify a zero coupling between adatom and substrate, we have that

$$\sum_{\alpha} b_j^{\alpha}(\infty) b_{j'}^{\alpha}(\infty) = \delta_{jj'} \qquad (6)$$

and consequently

$$\langle c^{\dagger}c \rangle_{t,t' \to \infty} = \sum_{i,j} |a_i(\infty)|^2 \exp[i(E_j^{N-1} - E_i^N)(t-t')]$$
$$\times |\langle D_i^N | c_{A\sigma}^{\dagger} | D_j^{N-1} \rangle|^2 . \qquad (7)$$

For each value of i the sum over j reduces to only one term which corresponds to

$$|D_j^{N-1}\rangle = c_{A\sigma} |D_i^N\rangle .$$

The energy differences $E_i^N - E_j^{N-1}$ give E_A for all the configuration states D_i^N having one electron in the atomic state; and $E_A + U$ for all these having two electrons in the atomic state. Then, we can write the final expression as

$$\langle c^{\dagger}c \rangle_{t,t' \to \infty} = \sum_i |a_i^{\sigma}|^2 \exp[-iE_A(t-t')]$$
$$+ \sum_j |a_j|^2 \exp[-i(E_A + U)(t-t')] . \qquad (8)$$

Thus $\sum |a_i^{\sigma}|^2$ represents the probability of having one electron with spin projection σ, while $\sum |a_j|^2$ is the probability of having two electrons, in the adatom far from the substrate, irrespectively of the substrate electronic configurations involved.

Therefore, from the asymptotic behavior of the correlation function of the operators $c_{A\sigma}^{\dagger}(t')$ and $c_{A\sigma}(t)$, taken at different instants of time, we can extract the probabilities of the charge states of the atom.

Average values of operators can be evaluated using the diagrammatic technique introduced by Keldysh to deal with nonequilibrium problems.[17] Without entering into details, for which the reader is refered to Ref. 17, a Dyson equation in a matrix form is obtained:

$$\mathbf{G} = \mathbf{G}_0 + \mathbf{G}_0 \mathbf{\Sigma} \mathbf{G} , \qquad (9)$$

where $\mathbf{G}$, $\mathbf{G}_0$, and $\mathbf{\Sigma}$ are 2×2 matrices defined as follows:

$$\mathbf{G} = \begin{bmatrix} G^{++} & G^{+-} \\ G^{-+} & G^{--} \end{bmatrix}, \quad \mathbf{\Sigma} = \begin{bmatrix} \Sigma^{++} & \Sigma^{+-} \\ \Sigma^{-+} & \Sigma^{--} \end{bmatrix} . \qquad (10)$$

$\mathbf{G}_0$ can be referred either to the system without interactions, or to the system including some interactions treated in an exact way. In this case we are looking for average values of the operators $c_{A\sigma}^{\dagger}$ and $c_{A\sigma}$ at different times; then the functions $G^{\alpha\beta}$ are defined as

$$G^{+-}(t,t') = i \langle 0 | U(t_0,t') c_{A\sigma}^{\dagger} U(t',t) c_{A\sigma} U(t,t_0) | 0 \rangle ,$$
$$G^{-+}(t,t') = -i \langle 0 | U(t_0,t) c_{A\sigma} U(t,t') c_{A\sigma}^{\dagger} U(t',t_0) | 0 \rangle , \qquad (11)$$
$$G^{++}(t,t') = \Theta(t-t') G^{-+}(t,t') + \Theta(t'-t) G^{+-}(t,t') ,$$
$$G^{--}(t,t') = \Theta(t-t') G^{+-}(t,t') + \Theta(t'-t) G^{-+}(t,t') .$$

Only G^{+-} and G^{-+} are independent functions. Explicit reduction of Eq. (10) to two independent equations is carried through the canonical transformation:

$$\mathcal{A} = \begin{bmatrix} 1 & -1 \\ 1 & 1 \end{bmatrix} (\mathbf{A}/2) \begin{bmatrix} 1 & 1 \\ -1 & 1 \end{bmatrix} .$$

Thus the functions $\mathbf{G}$ and $\mathbf{\Sigma}$ become

$$\mathscr{G}=\begin{bmatrix} 0 & G^a \\ G^r & F \end{bmatrix}, \quad \mathscr{V}=\begin{bmatrix} \Omega & \Sigma^r \\ \Sigma^a & 0 \end{bmatrix}, \tag{12}$$

where retarded and advanced functions are defined as

$$G^r=G^{++}-G^{+-}, \quad G^a=G^{++}-G^{-+}, \tag{13}$$

both functions containing equivalent information; one is the Hermitian conjugate of the other. The function F is given by

$$F=G^{++}+G^{--} \tag{14}$$

and the new self-energies are related to the old ones by means of the relations

$$\Sigma^r=\Sigma^{++}+\Sigma^{+-},$$
$$\Sigma^a=\Sigma^{++}+\Sigma^{-+}, \tag{15}$$
$$\Omega=\Sigma^{++}+\Sigma^{--}.$$

The components of the Dyson equation can now be written as

$$G^a=G_0^a+G_0^a\Sigma^aG^a,$$
$$G^r=G_0^r+G_0^r\Sigma^rG^r, \tag{16}$$
$$F=F_0(1+\Sigma^aG^a)+G_0^r(\Omega G^a+\Sigma^rF).$$

The asymptotic behaviors of $F(t,t')$ and $G^{a(r)}(t,t')$ allow one to determine the probabilities for the different charge states of the atom when it is far from the surface, in accordance with Eq. (8):

$$G^a(t\to\infty, t'\to\infty)=-i\{A_1\exp[-iE_A(t-t')]$$
$$+A_2\exp[-i(E_A+U)(t-t')]\},$$
$$\tag{17}$$
$$F(t\to\infty, t'\to\infty)=i\{B_1\exp[-iE_A(t-t')]$$
$$+B_2\exp[-i(E_A+U)(t-t')]\},$$

where

$$A_1=P_\sigma+P^+,$$
$$A_2=P_{-\sigma}+P^-,$$
$$B_1=P_\sigma-P^+, \tag{18}$$
$$B_2=P^--P_{-\sigma},$$

P^+, $(P_\sigma+P_{-\sigma})$, and P^- being the probabilities of having, respectively, zero, one, and two electrons in the atomic state. This is an important result which shows that the asymptotic behaviors of G^a and F related with a given spin projection operator determine the probabilities for all the possible atomic-state electronic configurations.

B. Perturbative treatment of the electronic correlation term

Since we are interested in the weak-correlation regime, i.e., for small values of the parameter U, we perform a perturbative treatment calculation up to the second order in U. The zeroth-order Hamiltonian $H_0(t)$ describes the dynamical evolution of the system in the Hartree-Fock approximation. This means that

$$H(t)=H_0(t)+H_p, \tag{19}$$

with

$$H_0(t)=\sum_{i,\sigma} E_i n_{i\sigma}+\sum_\sigma (E_A+U\langle n_{A-\sigma}\rangle)n_{A\sigma}$$
$$+\sum_{i,\sigma} V_{iA}(t)(c_{i\sigma}^\dagger c_{A\sigma}+c_{A\sigma}^\dagger c_{i\sigma})-U\langle n_{A_\uparrow}\rangle\langle n_{A_\downarrow}\rangle,$$
$$\tag{20}$$
$$H_p=U(n_{A_\uparrow}-\langle n_{A_\uparrow}\rangle)(n_{A_\downarrow}-\langle n_{A_\downarrow}\rangle).$$

The dynamical wave function can be written as

$$|\psi(t)\rangle=|\psi_0(t)\rangle+|\delta\psi(t)\rangle, \tag{21}$$

$\psi_0(t)$ being the solution of

$$[H_0(t)-i\partial/\partial t]|\psi_0(t)\rangle=0. \tag{22}$$

The zeroth-order wave function $\psi_0(t)$ is a Slater determinant built with dynamical one-electron states $\{X_n(t)\}$, which describe the time evolution from the initially occupied molecular orbitals $\{\phi_n(t_0)\}$; this means

$$|\psi_0(t)\rangle=\det\{X_n(t)\}=U(t,t_0)|\psi_0(t_0)\rangle$$
$$=U(t,t_0)\det\{\phi_n(t_0)\}.$$

Then it is also verified that

$$|X_n(t)\rangle=U(t,t_0)|\phi_n(t_0)\rangle. \tag{23}$$

We consider the following expansion for $\delta\psi(t)$:

$$|\delta\psi\rangle=\sum_\alpha c_\alpha(t)|\psi_\alpha(t)\rangle, \tag{24}$$

where $\{\psi_\alpha(t)\}$ is a complete basis set for the N-electron system in an independent-particle model; it includes the time evolution of the ground level ψ_0 and of all the possible excitations which can be constructed from the molecular-orbital basis set at time t_0. Solving the time-dependent Schrödinger equation, with $H(t)$ given by (19) and $\psi(t)$ by (21), and introducing also Eq. (24), we arrive at the following expression for the coefficient $c_\beta(t)$ in a second perturbative order:

$$c_\beta^2(t)=-i\int^t d\tau\langle\psi_\beta(\tau)|H_p|\psi_0(\tau)\rangle-\sum_\alpha\int^t d\tau\langle\psi_\beta(\tau)|H_p|\psi_\alpha(\tau)\rangle\int^\tau d\tau'\langle\psi_\alpha(\tau')|H_p|\psi_0(\tau')\rangle \tag{25}$$

and for the time-dependent wave function we have

$$\psi(t)=\psi_0(t)-i\sum_\alpha\psi_\alpha(t)\int^t d\tau\langle\psi_\alpha(\tau)|H_p|\psi_0(\tau)\rangle-\sum_\alpha\psi_\alpha(t)\sum_\beta\int^t d\tau\langle\psi_\alpha(\tau)|H_p|\psi_\beta(\tau)\rangle\int^\tau d\tau'\langle\psi_\beta(\tau')|H_p|\psi_0(\tau')\rangle. \tag{26}$$

Within this perturbative scheme the Dyson equation (9) involves Green functions $G_0^{\alpha\beta}$ referred to the Hartree-Fock time evolution, and self-energies $\Sigma^{\alpha\beta}$ which take into account higher-order corrections due to the electronic correlation. A second-order calculation leads to the following expressions for $\Sigma^{\alpha\beta}$:

$$\Sigma_U^{+-}(t,t') = -U^2 G_{0\sigma}^{+-}(t,t')G_{0-\sigma}^{+-}(t,t')G_{0-\sigma}^{-+}(t',t) ,$$

$$\Sigma_U^{-+}(t,t') = -U^2 G_{0\sigma}^{-+}(t,t')G_{0-\sigma}^{-+}(t,t')G_{0-\sigma}^{+-}(t',t) ,$$

$$\Sigma_U^{++}(t,t') = -\Sigma^{-+}(t,t'), \quad t>t' ,$$

$$\Sigma_U^{--}(t,t') = -\Sigma^{+-}(t,t'), \quad t>t' , \qquad (27)$$

$$\Sigma_U^{++}(t,t') = -\Sigma^{+-}(t,t'), \quad t<t' ,$$

$$\Sigma_U^{--}(t,t') = -\Sigma^{-+}(t,t'), \quad t<t' .$$

Going back to the Dyson equations (16) for $G^a(t,t')$ and $F(t,t')$, and assuming the electronic correlation as a perturbation over a time-dependent system of independent particles, we can write them as

$$G^a = G_0^a + G_0^a \Sigma_U^a G^a , \qquad (28)$$

$$F = F_0(1+\Sigma_U^a G^a) + G_0^r(\Omega_U G^a + \Sigma_U^r F) . \qquad (29)$$

On the other hand, $G_0^{r(a)}$ and F_0 are solutions of the following Dyson equations:

$$G_0^{r(a)} = g_0^{r(a)} + g_0^{r(a)}\Sigma_v^{r(a)}G_0^{r(a)} ,$$

$$F_0 = f_0(1+\Sigma_V^a G_0^a) + g_0^r(\Omega_V G_0^a + \Sigma_V^r F_0) , \qquad (30)$$

where $g_0^{r(a)}$ and f_0 refer to the system without interactions, and Σ_V, Ω_V are the self-energies corresponding to the one-body time-dependent potential $V_{iA}(t)$. By introducing in Eqs. (28) and (29) the expressions of G_0 and F_0 given by (30), we get

$$G^{r(a)} = g_0^{r(a)} + g_0^{r(a)}(\Sigma_V^{r(a)} + \Sigma_U^{r(a)})G^{r(a)} ,$$

$$F = g_0^r(\Sigma_V^r + \Sigma_U^r)F + g_0^r(\Omega_V + \Omega_U)G^a$$

$$\qquad + f_0(1+\Sigma_V^a G^a + \Sigma_U^a G^a) . \qquad (31)$$

Finally, it is possible to write Eqs. (31) in differential form:

$$g_0^{-1}G^a = \delta(t-t') + (\Sigma_V^a + \Sigma_U^a)G^a ,$$

$$g_0^{-1}F = (\Sigma_V^r + \Sigma_U^r)F + (\Omega_V + \Omega_U)G^a , \qquad (32)$$

where we have used the differential operator g_0^{-1}:

$$g_0^{-1}g_0 = \delta(t-t'), \quad g_0^{-1}f_0 = 0 .$$

Dyson equations written in the differential form show the independence on the initial distribution given through f_0. Thus solutions of Eqs. (32) are determined uniquely and independently of the distribution at $t = -\infty$.

In summary, we calculate $G^a(t,t')$ through the differential equations (32) in the following way: fixing t' at a sufficiently large time, we evaluate $G^a(t,t')$ for t going from t' to a negative value t_0; and then $F(t,t')$ is integrated for t values going from t_0 to t'. The calculation

of $F(t,t')$ at each instant of time only requires the knowledge of F for times before.

III. APPLICATION OF THE FORMALISM

We apply this formalism to the calculation of the probabilities of negative- and positive-ion emission for two "extreme" cases: a two-atom chain, and an atom adsorbed in a solid within the wide-band limit.[8]

For simplicity we restrict ourselves to the so-called Anderson symmetric model, in which $E_A = -U/2$; and we also consider a restricted Hartree-Fock for the time evolution of the zeroth-order wave function $\psi_0(t)$, then having

$$\langle n_{A\sigma}(t) \rangle^{\mathrm{RHF}} = \langle n_{A-\sigma}(t) \rangle^{\mathrm{RHF}} = 0.5 .$$

From the motion equations which result for $F_0(t,t')$ and $G_0^r(t,t')$ the following expressions for $\Sigma_V^r(t,t')$ and $\Omega_V(t,t')$ are obtained:

$$\Sigma_V^r(t,t') = -i\Theta(t-t')\sum_k \zeta_{kA}(t,t') ,$$

$$\qquad (33)$$

$$\Omega_V(t,t') = i\left[\sum_{k \text{ occupied}} \zeta_{kA}(t,t') - \sum_{k \text{ empty}} \zeta_{kA}(t,t')\right] ,$$

where the function $\zeta_{kA}(t,t')$ is defined as

$$\zeta_{kA}(t,t') = V_{kA}(t)V_{kA}(t')\exp[-i(\varepsilon_k - \varepsilon_A)(t-t')] ,$$

$$\qquad (34)$$

k states being the substrate eigenstates; and $\varepsilon_A = E_A + U\langle n_{A-\sigma}(t)\rangle$, which, in the Anderson symmetric case and for a restricted Hartree-Fock, is equal to zero for any instant of time.

The functions $G_0^{\alpha\beta}(t,t')$ are obtained through the following relations:[8]

$$G_0^{+-}(t,t') = i\sum_{k \text{ occupied}} G_{Ak}^r(t,-\infty)G_{Ak}^a(-\infty,t') ,$$

$$G_0^{-+}(t,t') = -i\sum_{k \text{ empty}} G_{Ak}^r(t,-\infty)G_{Ak}^a(-\infty,t') , \qquad (35)$$

$$G_0^r(t,t') = -i\Theta(t-t')\sum_k G_{Ak}^r(t,-\infty)G_{Ak}^a(-\infty,t') .$$

Here there is involved only the calculation of the function $G_{Ak}^{a(r)}(t,-\infty)$, which for a one-body time-dependent potential, is straightforward.

Let us write these all quantities for the two cases that we are going to analyze.

A. Two-atom chain

Taking the time-dependent interaction as

$$V(t) = \begin{cases} V_0, & t<0 \\ V_0\exp(-\lambda t), & t>0 , \end{cases}$$

the expressions (33)–(35) give in this case

$$\Sigma_V^r(t,t') = -i\Theta(t-t')V(t)V(t') ,$$

$$\Omega_V(t,t') = 0 ,$$

$$G_0^{+-}(t,t')=(i/2)\exp\{i[f(t)-f(t')]\} \ ,$$

$$G_0^{-+}(t,t')=(-i/2)\exp\{-i[f(t)-f(t')]\} \ ,$$

$$G_0^r(t,t')=-i\Theta(t-t')\cos[f(t)-f(t')] \ ,$$

where

$$f(t)=\begin{cases} V_0t, & t<0 \\ V_0[1-\exp(-\lambda t)]/\lambda, & t>0 \ . \end{cases}$$

The self-energies (27) associated with the intra-atomic Coulomb repulsion U result to be

$$\Sigma_U^{+-}(t,t')=(-iU^2/8)\exp\{3i[f(t)-f(t')]\} \ ,$$

$$\Sigma_U^{-+}(t,t')=(iU^2/8)\exp\{-3i[f(t)-f(t')]\} \ .$$

Then, according to Eqs. (15), we have

$$\Sigma_U^r(t,t')=(-iU^2/4)\cos\{3[f(t)-f(t')]\} \ ,$$

$$\Omega_U(t,t')=(-U^2/4)\sin\{3[f(t)-f(t')]\} \ .$$

B. Wide-band limit

The usual approximations involved in the wide-band limit of the noninteracting theory[6,8] are

$$V_{kA}(t)=V_k u(t) \ ,$$

$$\Delta(\varepsilon)=\pi\rho(\varepsilon)\langle|V_k|^2\rangle_{\varepsilon_k=\varepsilon} \ ,$$

ρ being the density of states of the electron gas and $\Delta(\varepsilon)$ is assumed to be independent of the energy ε. For $u(t)$ we consider

$$u(t)=\begin{cases} 1, & t<0 \\ \exp(-\lambda t), & t>0 \ . \end{cases}$$

Expressions (33)–(35) give the following results in this case:

$$\Sigma_V^r(t,t')=-i\Theta(t-t')2\Delta|u(t)|^2\delta(t-t') \ ,$$

$$\Omega_V(t,t')=\lim_{\eta\to 0}\frac{(-2\Delta/\pi)u(t)u(t')(t-t')}{[(t-t')^2+\eta^2]} \ ,$$

$$G_0^{+-}(t,t')=(i\Delta/\pi)\int_{-\infty}^0 d\varepsilon\, f(t,\varepsilon)f^*(t',\varepsilon) \ ,$$

$$G_0^{-+}(t,t')=(-i\Delta/\pi)\int_0^\infty d\varepsilon\, f(t,\varepsilon)f^*(t',\varepsilon) \ ,$$

the function $f(t,\varepsilon)$ being

$$f(t,\varepsilon)=\int_{-\infty}^\infty d\tau\, u(\tau)\exp(-i\varepsilon\tau)G_0^r(t,\tau) \ ,$$

with $G_0^r(t,\tau)$ given by

$$G_0^r(t,\tau)=-i\Theta(t-\tau)\exp\left[-\int_\tau^t \Delta|u(x)|^2 dx\right] \ .$$

The self-energies $\Sigma_U^{r(a)}$ and Ω_U are calculated in terms of $G_0^{\alpha\beta}$ according to Eqs. (15) and Eqs. (27).

IV. RESULTS AND DISCUSSION

The limiting cases[18,19] in which (i) correlation equals zero, (ii) adatom decoupled from the substrate, and (iii) bandwidth equals zero (two-level system), are all included exactly in our formalism. In the stationary limit, i.e., a constant atom-substrate coupling, the second-order approximation of the spectral density of local single-particle excitations for the nondegenerate symmetric Anderson model[20,21] is also recovered.
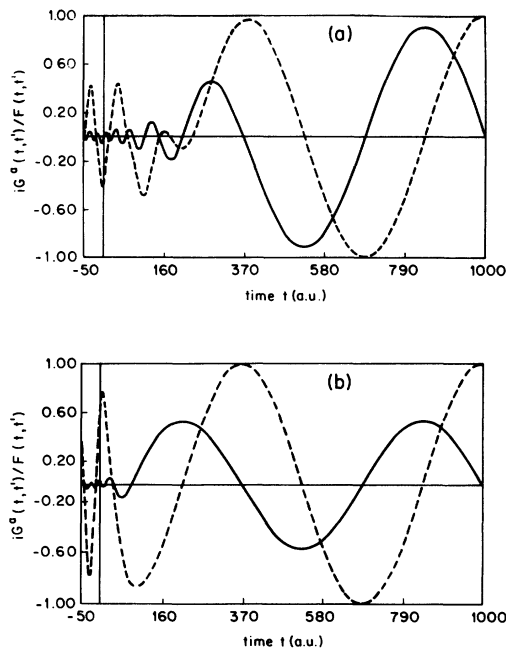

FIG. 1. Time-dependent behavior of $iG^a(t,t')$ (— — —) and $F(t,t')$ (———) for the two-level system. $V=0.1$ a.u., $\lambda_0=1$ a.u., $U=0.02$ a.u.; and atom velocities $v=$(a) 0.01 a.u., (b) 0.025 a.u.
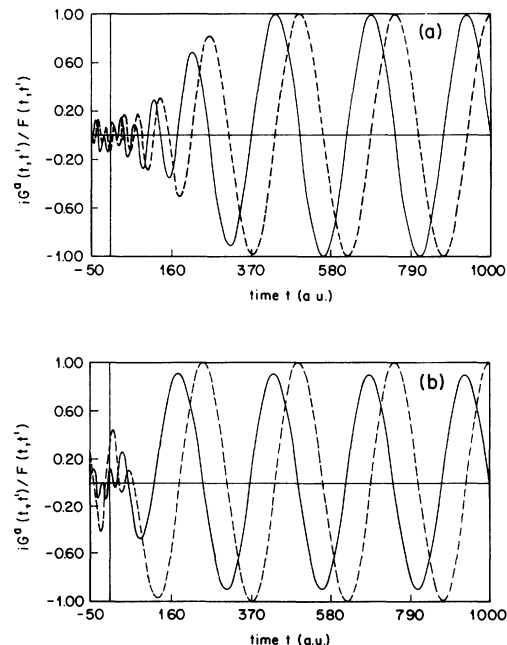

FIG. 2. The same as in Fig. 1, but with $U=0.05$ a.u.

We obtained the following asymptotic behaviors of $G_a(t,t')$ and $F(t,t')$:

$$[G^a(t,t')]_{t,t'\to\infty} = -i\cos[U(t-t')/2] \ ,$$

$$[F(t,t')]_{t,t'\to\infty} = -B\sin[U(t-t')/2]$$

$$\text{with } B = P_\sigma + P_{-\sigma} - P^- - P^+ \ .$$

These are the expected behaviors for the spin restricted and symmetric case where $P_\sigma = P_{-\sigma}$ and $P^+ = P^-$. According to expressions (18), the negative (positive) ionization probability is given by

$$P^{-\ (+)} = (1-B)/4 \ .$$

Figures 1–3 show the behaviors of $G_a(t,t')$ and $F(t,t')$ as functions of time ($t'\to\infty$), for different sets of parameters and for the two analyzed cases: the two-level system and the wide-band solid limit. In all the cases the atom-substrate coupling decreases exponentially as $\exp(-\lambda_0 vt)$, with $\lambda_0 = 1$ a.u. From these figures we can see the oscillatory behavior for large values of time t with a period equal to $4\pi/U$, with amplitudes which for $G_a(t,t')$ are always equal to unity, while for $F(t,t')$ these depend on the velocity, the correlation parameter, and the interaction strength. Asymptotically $G_a(t,t')$ and $F(t,t')$ are out of phase in $\pi/2$. All these characteristics are a good test for the numerical integration of the Dyson equations. Also, the continuous functions along the time obtained for both, G_a and F, show a perfect matching between the different coupling regimes going from V_{ia} to zero.
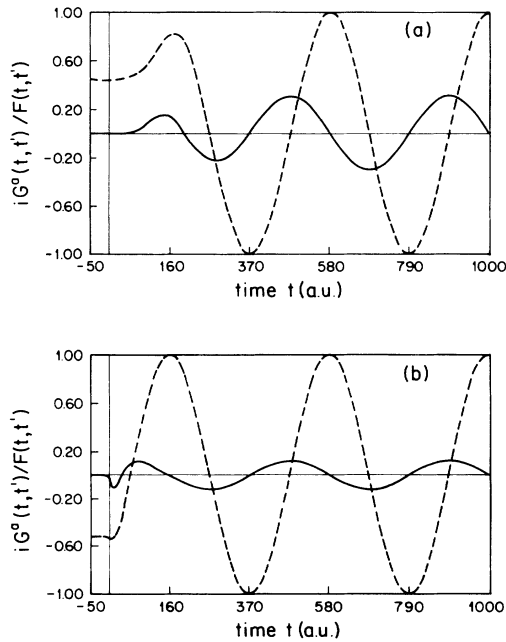

FIG. 4. $F(t,t')$ as a function of t for the wide-band approximation. $\Delta = 0.2$ a.u., $\lambda_0 = 1$ a.u., $v = 0.0125$ a.u., and U equals 0.02 a.u. (——), 0.03 a.u. (— — —), 0.05 a.u. (—·—·—·).

In Figs. 4 and 5 we show, in the wide-band solid case, the time-dependent behavior of $F(t,t')$ for three different values of U, and for three different values of velocity, respectively. The remaining parameters in each case are fixed.

The negative ionization probability as a function of the inverse of the atom velocity is shown in Figs. 6 and 7 for Δ values of 0.2 and 0.05 a.u., respectively, and for various U values in each case. We can observe from these figures that the negative ionization probability is slightly dependent on U and velocity. In order to understand the U and velocity dependence of the negative ionization probability, it is necessary to take into account the relevant features contained in the Anderson model for the symmetric case. There is a Coulomb energy U for two electrons on the adsorbate site, and the energy of the two-electron adsorbate state is equal to the Fermi energy. Taking the bandwidth to infinity leaves only two independent parameters: U and the hybridization width Δ. The adsorbate spectral density has Lorentzian side peaks centered at energies $(+U/2)$ and $(-U/2)$ of width Δ, and a central Kondo peak at the Fermi level of width T_k (Kondo temperature). This T_k is found to be given by the expression[21,22]

$$T_k = (1+1/2u)0.515u^{1/2}\Delta\exp(-\pi^2 u/8) \ ,$$

FIG. 3. Time-dependent behavior of $iG^a(t,t')$ (— — —) and $F(t,t')$ (——) for the wide-band approximation. $\Delta = 0.2$ a.u., $\lambda_0 = 1$ a.u., $U = 0.03$ a.u.; and atom velocities $v =$ (a) 0.01 a.u., (b) 0.05 a.u.
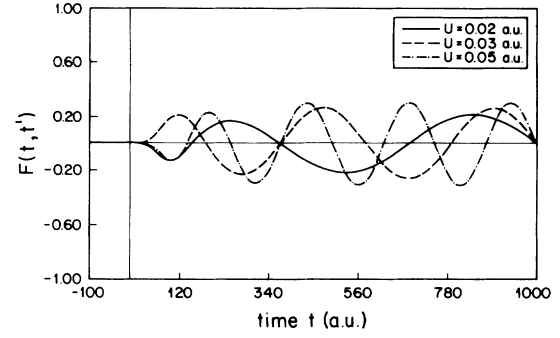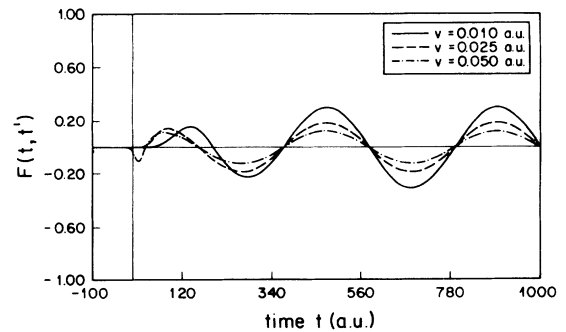

FIG. 5. The same as in Fig. 4, but with $U = 0.03$ a.u., and v equals 0.01 a.u. (——), 0.025 a.u. (— — —), 0.05 a.u. (—·—·—·).
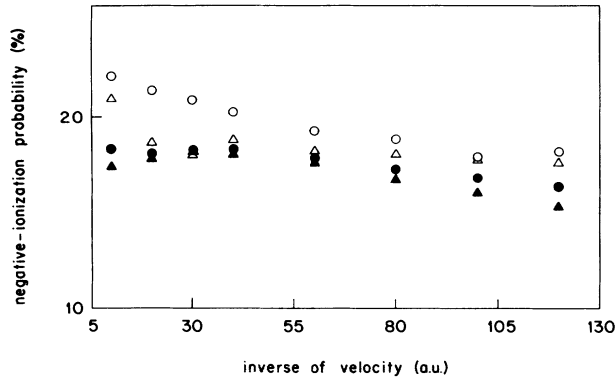
FIG. 6. Negative ionization probability vs inverse of atom velocity. $\Delta=0.2$ a.u. and $U=0.03$ a.u. ($\bigcirc$); 0.05 a.u. ($\triangle$); 0.2 a.u. ($\bullet$); 0.3 a.u. ($\blacktriangle$).

FIG. 7. The same as in Fig. 6, but with $\Delta=0.05$ a.u. and $U=0.025$ a.u. ($\bullet$); 0.05 a.u. ($\triangle$); 0.1 a.u. ($\bigcirc$).

where $u=U/(\pi\Delta)$. The two side peaks can be understood as lifetime-broadened resonances corresponding to local quasiparticles with energies $(+U/2)$ and $(-U/2)$, while the Kondo peak reflects those many-body effects which cannot be given a simple interpretation.

For $u \ll 1$ the split between the three peaks is diminished, it being a good approximation to think of them as merging into a single broadened peak centered at the Fermi level. This corresponds to the Hartree-Fock limit situation. For $u \gg 1$ the Kondo peak becomes a very sharp resonance at the Fermi level which accommodates a very small fraction of localized electrons, but gives rise to enormous enhancements of low-temperature thermodynamic and transport quantities.[21] This makes an important difference with the limit $u=\infty$ in which the adsorbate density of states around the Fermi level is zero.

The mechanism of charge transfer in the dynamical process for this kind of system can be viewed as a resonant tunneling of electrons through the potential barrier between atom and solid. If only the two side peaks which correspond to a local quasiparticle with lifetime $1/\Delta(z)$ were present, one would expect strong variations in the negative ionization probability with the correlation parameter U and with the atom velocity v. The reason is that, the larger is the relation U/Δ, the smaller becomes the tail of the broadened peak centered at $U/2$ around the Fermi energy. This leads to a decreasing negative emission as long as U/Δ grows at constant velocity. For a constant value of U, a larger velocity implies a shorter interaction distance from the surface, and therefore a larger width of the broadened side peaks. This should be reflected in a growing ionization probability with the atom velocity. However, the presence of the Kondo
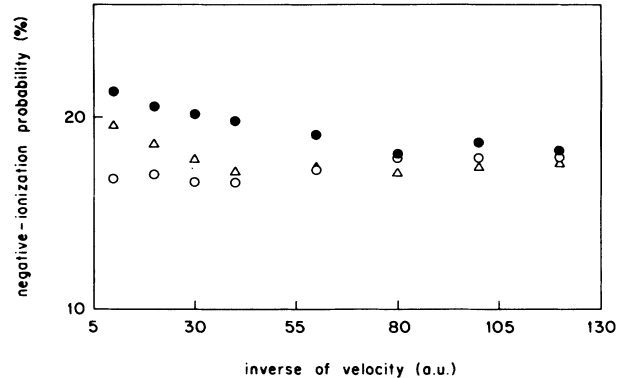
peak, as a resonance at the Fermi energy, introduces important changes in this picture. This resonance favors strongly the negative ionization, leading to very smooth U and v dependences.

The second-order perturbation theory in the stationary case gives the exact spectral density for $u < 1.2$, and for larger values it predicts a qualitatively correct structure.[22] It seems natural to expect a similar validity range for the dynamical process of charge transfer based on a resonant tunneling mechanism.

In summary, our formalism reproduces the stationary one for a constant coupling, and describes correctly the limiting cases of $U=0$ and $\Delta=0$. For finite values of U/Δ the behavior of the negative ionization probability with U and v is consistent with the presence of the characteristic resonance at the Fermi level, known as the Kondo peak, for the symmetric Anderson case. Our formalism also gives the exact ionization probabilities for a zero-bandwidth solid (two-level system), where it is known that second-order perturbation theory reproduces the exact self-energy in the static case.

The aim of this work was only to present the formalism and some straightforward applications of it. We think it opens interesting possibilities for treating dynamical charge-transfer processes with correlation effects. Further works on more realistic model systems are in progress.

ACKNOWLEDGMENTS

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