Dynamical screening effects in surface ionization: Application to C_{60}

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We study the positive ionization probability $P^+(E_c)$ of a carbon atom sputtered from a C_{60} target at energy E_c. As the atom leaves the target molecule its atomic level progressively decouples from the target levels. This can be described by means of the Anderson Hamiltonian with time-dependent parameters. We discuss some attempts published in the literature for solving this kind of time-dependent problem. In our C_{60} study we first use an approximate boson technique. Then we present a numerical exact solution of the Schrödinger equation. The dimension of the N-electron determinant basis is controlled by verifying that an increase of the basis size does not change the results. The exact and approximate (boson approximation) calculations are compared. The aspect of the $P^+(E_c)$ curves is globally the same, i.e., a power-law dependence. The difference between the two approaches is that the exponent is constant in the approximation and is (slowly) varying with E_c in the exact calculation. This power-law dependence agrees with typical experimental results on similar systems. We show that our $P^+(E_c)$ dependence is obtained because we take into account the excitations which appear in the whole electronic structure, particularly on the target levels, during the decoupling process.

I. INTRODUCTION

The positive or negative ionization probability of atoms sputtered from a metallic target is a problem which has received much attention in the last two decades.[1-16] As the atom leaves the metal surface the exchanges of electrons between it and the continuum can be described by means of the Anderson Hamiltonian with time-varying $E_1(t)$ and $\beta_1(t)$ parameters, where $E_1(t)$ is the atomic-level energy of the emitted atom (in this paper we will only consider one electronic state per ejected or target atom) and $\beta_1(t)$ is the coupling energy to the continuum. A positive-ionization problem will be described by a decreasing $E_1(t)$ function and a negative ionization problem by the reverse situation. When the ejected and target atoms are of the same type (homonuclear systems) the following Hamiltonian can be written:

$$H(t) = \beta \sum_{i,j \text{ neigh}} c_i^\dagger c_j + E_{at} \sum_i c_i^\dagger c_i + \delta E_1(t) c_1^\dagger c_1$$

$$+ \delta\beta_1(t) \sum_{j \text{ neigh} 1} (c_1^\dagger c_j + c_j^\dagger c_1) , \qquad (1)$$

where $E_1(t) = E_{at} + \delta E_1(t)$ and $\beta_1(t) = \beta + \delta\beta_1(t)$. We also assume that atom 1 is equally distant from all its neighbors j during the whole process. Let us call t_0 the initial decoupling time $[\delta E_1(t) = \delta\beta_1(t) = 0$ for $t < t_0]$ and $H_0 = H(t_0)$ the initial Hamiltonian:

$$H_0 = \beta \sum_{i,j \text{ neigh}} c_i^\dagger c_j + E_{at} \sum_i c_i^\dagger c_i . \qquad (2)$$

If we put H_0 under its diagonal form

$$H_0 = \sum_k \varepsilon_k c_k^\dagger c_k \qquad (3)$$

with $c_j = \sum_k a_k^j c_k$, the Hamiltonian 1 becomes

$$H(t) = \sum_k \varepsilon_k c_k^\dagger c_k + \delta E_1(t) c_1^\dagger c_1 + \sum_k \delta\beta_k(t) c_1^\dagger c_k$$

$$+ \delta\beta_k^*(t) c_k^\dagger c_1 , \qquad (4)$$

where

$$\delta\beta_k(t) = \delta\beta_1(t) \sum_{j \text{ neigh} 1} a_k^j .$$

The extension of Hamiltonian (1) or (4) to the case where the emitted atom is different from the target will be discussed below.

The question to be solved is to follow the evolution with time of the population $n_1(t)$ on atom 1. This problem enters a large class of processes which may receive the generic name of "response of a fermion gas to a time-varying localized potential." In this category we also find the many-electron effects appearing in core-level photoemission processes. In this last phenomenon a core-level electron is ejected and, as a consequence, a positive localized potential suddenly appears which scatters the valence electrons. Various works[17-24] have shown that the screening of the localized hole is far from adiabaticity and many excitations accompanying the main transition are created in the valence band. This leads to important deviations of the photoemitted electron spectrum from the one-electron (or adiabatic) spectrum. The treatment of core-level photoemission problems can be undertaken in the sudden-limit formalism. It is no longer the case of surface ionization where the time dependence is continuous which greatly increases the mathematical difficulties.

In Sec. II we will describe some attempts made for solving this problem. In this section we also present a boson approximate method. Then we develop in Sec. III an exact numerical treatment of the Schrödinger equation and discuss its results.

Let us now briefly describe the particular system which

<u>53</u>   11 242

will be studied and introduce our main approximations. We examine a finite system, C_{60}, which is interesting for various reasons. Indeed, SIMS[22−25] (secondary ion mass spectrometry) or high-velocity ion-cluster collision[26] experiments have already been achieved on C_{60} solid targets. Moreover, the photoemission of the K core level has already been studied from an experimental[27,28] and theoretical point of view.[29,30] We will only consider the π levels with one π electron per atom. This means that we neglect the creation of excitations on the σ levels which are far from the Fermi level. We will also limit ourselves to only one spin direction. This approximation is usual in this kind of work.[5,7,8,10,11]

For a given spin direction the atom 1 population passes from 0.5 inside C_{60} (all the atoms are equivalent) to a larger value outside. As the atom 1 level is getting deeper and deeper it is completely merged in the Fermi sea and the final adiabatic population $n_{1,\text{adia}}(t=\infty)$ (on a given spin direction) is one:

$$n_{1,\text{adia}}(t=\infty)=1$$

and the ionization probability zero $P^+(0)=0$. We will call positive ionization probability the deviation from adiabaticity:

$$P^+(E_c)=n_{1,\text{adia}}(\infty)-n_1(\infty)=1-n_1(\infty) . \tag{5}$$

II. PREVIOUS SOLUTIONS OF THE PROBLEM

At time t, the state will be described by the N-electron wave function $|\Psi(t)\rangle$. By introducing the evolution operator we can write

$$|\Psi(t)\rangle=U(t,t_0)|\Psi(t_0)\rangle , \tag{6}$$

where $|\Psi(t_0)\rangle$ is the initial wave function. The population on atom 1 is given by

$$n_1(t)=\langle \Psi(t)|c_1^\dagger c_1|\Psi(t)\rangle . \tag{7}$$

If we introduce $H_1(t)$ the perturbative part of Hamiltonian (4) by

$$H_1(t)=H(t)-H_0 , \tag{8}$$

we may write $U(t,t_0)$ as a perturbative development

$$U(t,t_0)=\sum_{p=0}^{\infty} U_p(t,t_0) \tag{9}$$

with

$$U_p(t,t_0)=(-i)^p\int_{t_0}^{t}dt_1\int_{t}^{t_1}dt_2\cdots$$
$$\times\int_{t}^{t_{p-1}}dt_p$$
$$\times\mathscr{H}_1(t_1)\cdots\mathscr{H}_1(t_p) \tag{10}$$

in which

$$\mathscr{H}_1(t)=e^{iH_0t}H_1(t)e^{-iH_0t} . \tag{11}$$

In principle, the previous formalism allows one to calculate the $n_1(t)$ variation. However, a low-order perturbation treatment is not well adapted to the problem since the variation of the coupling parameter is large, opposite to its initial value $[\delta\beta_1(t=-\infty)=\beta]$. Only a summation of the perturbative series to all orders would give a convenient solution. Let us mention a case where a perturbation treatment may be useful. Indeed, when one considers heteronuclear systems such as AlM or CuM dilute alloys (where the dilute element M is a transition metal $M=$Ti, V, . . . , Ni), the measured M ionization probability strongly depends on the nature of M. For example, in the AlM series two maxima occur for $M=$Cr and Fe.[3,4] This phenomenon is reminiscent of a similar effect occurring in the resistivities of these alloys versus M. The effect is explained by the alloy electronic structure and the presence of a virtual bound state centered on atom M. It is thus interesting to describe precisely the first stage of the decoupling, say up to a time t_1 larger but close to t_0 ($t_1\gtrsim t_0$), since one may expect that during this short period the alloy electronic structure will play a large part. Of course, in this kind of approach the decoupling process after this first stage is supposed to be nearly equivalent for all the alloys of a series. From a theoretical point of view Eqs. (6)–(11) and the Hamiltonian H_0 can be used. The only change is that in H_0 the level 1, which will correspond to the M dilute element, will present diagonal and nondiagonal terms different from the matrix elements. A perturbative treatment to first order[3,4] shows that the nonadiabatic character at time t_1 given by

$$n_{1,\text{adia}}(t_1)-n_1(t_1)$$

varies with M in the same way as the measured ionization probability.

In our present work, the same Hamiltonian $H(t)$ is used but we rewrite it as in the analytical models developed for bulk systems.[5−13] The main difference from formula (4) is that now we directly introduce $\beta_1(t)$ instead of $\delta\beta_1(t)$. Then a new Hamiltonian H_0' is introduced which describes all the levels except level 1 at time $t<t_0$, hence

$$H_0'=\beta\sum_{i,j\neq 1\text{ neigh}} c_i^\dagger c_j+E_{\text{at}}\sum_{i\neq 1} c_i^\dagger c_i . \tag{12}$$

Its diagonal form is

$$H_0'=\sum_k \tilde{\varepsilon}_k\tilde{c}_k^\dagger\tilde{c}_k , \tag{13}$$

where

$$c_j=\sum_k \tilde{a}_k^i c_k . \tag{14}$$

$H(t)$ becomes

$$H(t)=\sum_k \tilde{\varepsilon}_k\tilde{c}_k^\dagger\tilde{c}_k+E_1(t)c_1^\dagger c_1$$
$$+\sum_k \tilde{\beta}_k(t)c_1^\dagger\tilde{c}_k+\tilde{\beta}_k^\dagger(t)\tilde{c}_k^\dagger c_1 \tag{15}$$

with

$$\tilde{\beta}_k(t) = \beta_1(t) \sum_{j \text{ neigh } 1} \bar{a}_k^j . \tag{16}$$

We see that $\tilde{\beta}_k(t)$ decreases with time for $t > t_0$ while in Eq. (4) the time-dependent coupling term $\delta\beta_k(t')$ was increasing with time. Moreover, $E_1(t) = E_{\text{at}}$ and $\tilde{\beta}_k(t) = \tilde{\beta}_k(t_0)$ for $t < t_0$.

For $t > t_0$, we will take the same $\beta_1(t)$ variation as in other works:[5-13]

$$\beta_1(t) = \beta \quad t < t_0 ,$$
$$\beta_1(t) = \beta e^{-\eta(t-t_0)} , \quad t > t_0 . \tag{17}$$

Previous studies of the C_{60} molecules show that β is of the order of -1 and -1.5 eV;[29] we will use here $\beta = -1.25$ eV. Some parameters are known which will help us to determine $E_1(t)$. The difference between the ionization potential of C_{60} (Ref. 31) and C gives the total decrease of the E_1 function:

$$E_1(\infty) - E_1(t_0) = E_1(\infty) - E_{\text{at}} = -[\text{IP(C)} - \text{IP}(C_{60})]$$
$$= -(11.2 - 7.6)$$
$$= -3.6 \text{ eV} .$$

By letting $E_1(\infty) = 0$ (which becomes the energy origin) we get

$$E_1(t_0) = E_{\text{at}} = 3.6 \text{ eV} .$$

For simplicity we take for $E_1(t)$ the same time dependence as for $\beta_1(t)$, then

$$E_1(t) = E_{\text{at}}, \quad t < t_0 ,$$
$$E_1(t) = E_{\text{at}} e^{-\eta(t-t_0)}, \quad t > t_0 . \tag{18}$$

If we use the previous numerical β value, we see that $E_{\text{at}} = 2.9|\beta|$.

The first approach of the problem that we intend to present is a boson approximation. For doing this it is useful to discuss the sudden limit case where $H(t)$ passes suddenly from H_0 to $H(\infty)$. In our formulation this is obtained for $\eta \rightarrow \infty$. Physically this could correspond to the ejection of a very fast atom though at such velocities other processes, not examined here, would interfere, for example the excitation of σ electrons.

In the sudden limit the probability that the ith excited state of $H(\infty)$, with wave function $|\Psi_{fi}\rangle$, be occupied at $t = \infty$ is given by

$$\alpha_i = |\langle \Psi_0 | \Psi_{fi} \rangle|^2 , \tag{19}$$

where $|\Psi_0\rangle$ is the wave function at the origin time t_0. For each ith state we calculate the population n_{1i} and, at the end of the process, the total population on atom 1 is given by

$$n_1(\infty) = \sum_i \alpha_i n_{1i} . \tag{20}$$

This calculation gives the simple result $n_1(\infty) = 0.5$ and, from Eq. (5), $P_{\text{sud}}^+ = 0.5$ which means that the ejected atom keeps the population it had in the target (0.5 per

spin direction). Another characteristic of the results is that the significant α_i terms ($\alpha_i > 10^{-4}$) are obtained for final states containing only one electron-hole pair.

Let us now describe the boson approximation. The Hamiltonian $H(t)$ is modified by replacing an electron-hole creation operator $a_{k_>}^\dagger a_{k'_<}$ (where $k_>$ and $k'_<$ are, respectively, electrons, $31 \le k_> \le 60$, and holes, $1 \le k' \le 30$, labels) by a boson creation operator $b_i^\dagger$ with energy E_i. For defining the hole and electron state we choose the final Hamiltonian $H(\infty)$. Then each boson corresponds to an excited state of $H(\infty)$, the E_i value is the corresponding excitation energy with respect to the $H(\infty)$ ground-state energy. The interest of this transformation is that the time-dependent term in $H(t)$ becomes a single operator term. At time t, the boson Hamiltonian in its new form is written

$$H_B(t) = \sum_i E_i(b_i^\dagger b_i + \tfrac{1}{2}) + V_i(t)(b_i^\dagger + b_i) . \tag{21}$$

As is explained in the Müller-Hartmann, Ramakrishnan, and Toulouse paper[32] by writing $H_B(t)$ some terms of the fermion Hamiltonian are omitted which are expected to be of little importance for the systems under consideration. A control of the boson technique will be given in this paper in the next section where an exact solution is also developed.

We will see later how the $V_i(t)$ terms have been fixed. We may say here that, as $V_i(t)$ is deduced from the $\beta_1(t)$ and $E_1(t)$ parameters, its time dependence is the same; by letting $t_0 = 0$ we will write

$$V_i(t) = V_i, \quad t < 0 ,$$
$$V_i(t) = V_i e^{-\eta t}, \quad t > 0 . \tag{22}$$

The boson state $|\Phi(t)\rangle$ is given by

$$|\Phi(t)\rangle = U_B(t,0)|\Phi_0\rangle ,$$

where $|\Phi_0\rangle$ is the ground state of $H_B(0)$. An analytical expression for $U_B(t,0)$ can be obtained:[32]

$$U_B(t,0) = \exp\left[i \sum_i \varphi_i(t,0)\right]$$
$$\times \exp\left\{-\sum_i [f_i(t,0)b_i^\dagger - f_i^*(t,0)b_i]\right\} , \tag{23}$$

where $\varphi_i(t,0)$ is a real function which disappears later in the calculation and

$$f_i(t,0) = i \int_0^t V_i(t') e^{iE_i t'} dt' . \tag{24}$$

The overlap between $|\Phi(t)\rangle$ and the final ground state $|\Phi_{f0}\rangle$ is

$$\langle \Phi_{f0} | U(t,0 | \Phi_{i0} \rangle . \tag{25}$$

If we call U_v the canonical transformation which transforms $\tilde{H}(\infty)$ in $\tilde{H}(0)$ we have

$$|\Phi_{i0}\rangle = U_v |\Phi_{f0}\rangle ,$$

with

$$U_v = \exp \sum_i (V_i b_i^\dagger - V_i^* b_i)/E_i \tag{26}$$

and (25) becomes

$$\langle \Phi_{f0}|U(t,0)U_v|\Phi_{f0}\rangle \; .$$

The probability of finding at $t = \infty$ the system in the ground state of the final Hamiltonian is given by

$$|\langle \Phi(\infty)|\Phi_{f0}\rangle|^2 = |\langle \Phi_{f0}|U(\infty,0)U_v|\Phi_{f0}\rangle|^2 \tag{27}$$

which becomes after some calculations

$$|\langle \Phi(\infty)|\Phi_{f0}\rangle|^2 = 1 - \sum_i g_i \tag{28}$$

with

$$g_i = \left[\frac{V_i}{E_i}\right]^2 \left[1 - \frac{E_i^2}{E_i^2 + \hbar^2 \eta^2}\right] \; . \tag{29}$$

Up to now the V_i values have not been fixed. For doing it let us apply the previous model to the sudden limit ($\eta \to \infty$); then (29) gives

$$g_{i,\text{sud}} = \left[\frac{V_i}{E_i}\right]^2 \; . \tag{30}$$

This quantity strictly corresponds to α_i given by (19) in the fermion description; thus we may write

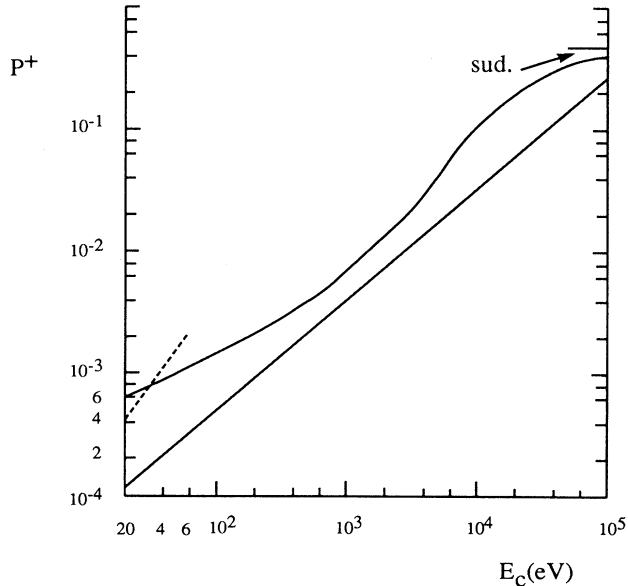$$\left[\frac{V_i}{E_i}\right]^2 = |\langle \Psi_0|\Psi_{fi}\rangle|^2 \tag{31}$$

FIG. 1. Variation of the ionization probability P^+ vs the emission energy E_c. The upper curve is the exact solution of the Schrödinger equation, the lower curve is the bosonization method. The dotted lines give experimental values of P^+ for Cu^+ emitted from the Cu target (see Ref. 12). We also give the value of the sudden limit $P^+ = 0.5$ for $E_c \to \infty$, noted by symbol "sud."

and the g_i values [given by (29)] can be calculated. As before the population on atom 1 is given by

$$n_i(\infty) = \sum_i g_i n_{1i} \; . \tag{32}$$

Our results for various η values are shown in Fig. 1 where we have drawn P^+ versus the kinetic energy E_c related to η by

$$E_c = \tfrac{1}{2}mv_\perp^2 = \tfrac{1}{2}m(\gamma^{-1}\eta)^2 \; , \tag{33}$$

where $v_\perp$ is the normal ejection velocity and $\eta = \gamma v_\perp$ where γ^{-1} is a characteristic distance from the surface of about 2 Å; along the γ^{-1} distance the β value decreases by an order of magnitude.

We observe that P^+ increases as a $v_\perp$ power (roughly as $v_\perp^2$). This behavior is reminiscent of the observed experimental behavior, shown also in Fig. 1, for another one electron per atom system (Cu^+ sputtered from a Cu target). We may notice that the boson approximation gives the exact results in the two opposite limits $v_\perp \to \infty$ or 0 corresponding, respectively, to $\eta \to \infty$ and $\eta \to 0$. In the first one our solution gives the exact sudden limit. In the second case we obtain $g_i = 0$ for any $i \neq 0$, $P^+ = 0$, and $|\langle \Psi(\infty)|\Psi_{f0}\rangle|^2 = 1$ which means that the evolution of the system is perfectly adiabatic.

III. EXACT SOLUTION

In this paper we present the results of an exact numerical solution of the Schrödinger equation:

$$i\hbar \frac{d|\Psi(t)\rangle}{dt} = H(t)|\Psi(t)\rangle \; . \tag{34}$$

We developed $|\Psi(t)\rangle$ on a basis of 60-electron determinants which are eigenfunctions of the final $H(\infty)$ Hamiltonian. This basis includes the ground state $|\Psi_{f0}\rangle$ and a variable number of $|\Psi_{fi}\rangle$ excited states. Most of the results presented here are obtained with basis 1 where the $|\Psi_{fi}\rangle$ states are selected by the condition

$$|\langle \Psi_{f0}|\Psi_{fi}\rangle| > 0.05 \; . \tag{35}$$

By replacing the 0.05 limit in (35) by 0.01 we increase the basis dimension (basis 2) which will be used later. The order of the system of differential equations (which is twice the basis size) is, respectively, 24 for basis 1 and 68 for basis 2.

In our basis each $|\Psi_{fi}\rangle$ state, $i = 0,1,\ldots$, is characterized by a given set of 30 numbers that we may call $1(i)$, $2(i),\ldots,30(i)$, which describes the distribution of the 30 spin $\uparrow$ electrons on the 60 possible levels (let us recall that in this one-electron model we only consider one spin direction, see Sec. I). In fact, as we already see, only excited states with one electron-hole pair are selected by the conditions of type (35); then our $|\Psi_{fi}\rangle$ states can be characterized by two numbers $k'(i)$ and $k(i)$ giving, respectively, the hole and electron labels. This is done in Table I. The total spin $\uparrow$ electron energy is for $|\Psi_{fi}\rangle$,

$$\mathcal{E}_i = \varepsilon_{1(i)} + \varepsilon_{2(i)} + \cdots + \varepsilon_{30(i)} \; ,$$

TABLE I. Characteristics of the $n_1(t)$ calculation for $\eta=2.4\times10^{15}$ s^{-1} ($E_c=1.44\times10^4$ eV). The i values label particular 60-electron states of the basis, $i=0$ is the ground state of $H(\infty)$. These states have the largest weights in the $|\psi(t=\infty)\rangle$ development with basis 1. $\mathcal{E}_i$ is the total energy of ↑ electrons in β units, $E_i=\mathcal{E}_i-\mathcal{E}_0$ is the excitation energy in β units ($\beta<0$). We give in line 2 the hole, $k'(i)$, and electron, $k(i)$, labels of the electron-hole $k'(i)\rightarrow k(i)$ pairs. Lines 5 and 6 give the square of the weights in, respectively, the basis-1 and basis-2 calculations. We observe that though the basis-2 dimension is increased, almost the same values are obtained for each i state. Lines 7 and 8 give the square of the weights for two times, respectively, $t_1=0.25\times10^{15}$ s and $t_2=10^{-15}$ s.

i	0	1	2	3	4	5	6
$k'(i)\rightarrow k(i)$		26→31	17→31	10→31	5→31	2→31	2→50
$\mathcal{E}_i$	48.097	47.475	46.837	46.098	45.569	45.336	43.307
E_i	0	−0.622	−1.260	−1.999	−2.528	−2.761	−4.790
$t=\infty$	0.724	0.031	0.028	0.155	0.011	0.023	0.014
$t=\infty$	0.712	0.036	0.031	0.147	0.009	0.020	0.015
t_1	0.505	0.020	0.016	0.329	0.027	0.077	0.008
t_2	0.740	0.031	0.026	0.146	0.009	0.024	0.011

where the ε_j values are the one-electron eigenenergies of Hamiltonian $H(\infty)$. In particular we have

$$\mathcal{E}_i=\mathcal{E}_0+E_i\ ,$$

where $\mathcal{E}_0$ is the ground-state energy and E_i the excitation energy already encountered in the boson approximation.

Let us consider the adiabatic state $|\Psi_{0,1/2}\rangle$ which is the ground state of $H(t_{1/2})$ when the variation of the parameters is half their total variation $[E_1(t_{1/2})=E_{\mathrm{at}}/2;\ \beta_1(t_{1/2})=\beta/2]$. We have verified that if we build another basis by using the condition

$$|\langle\psi_{0,1/2}|\Psi_{fi}\rangle|>0.05 \tag{36}$$

instead of condition (35) we do not add any new determinants in basis 1. Our basis is therefore able to well describe the adiabatic state at intermediate times. This is an important feature since we expect that at any time the projection of the actual state $|\Psi(t)\rangle$ on the instantaneous adiabatic state is large.

By projecting the Schrödinger equation (34) on the basis we obtain a system of differential equations where all the $\langle\Psi_{fi}|H(t)|\Psi_{fj}\rangle$ terms have to be calculated. Special attention must be paid to the sign of this matrix element. For example, when $|\Psi_{fi}\rangle$ and $|\Psi_{fj}\rangle$ differ by only one one-electron ket, say $|\phi_i\rangle$ for $|\Psi_{fi}\rangle$ and $|\phi_j\rangle$ for $|\Psi_{fj}\rangle$ $[|\phi\rangle_i$ and $|\phi_j\rangle$ are two of the sixty one-electron eigenfunctions of $H(\infty)]$, we have

$$\langle\Psi_{fi}|H(t)|\Psi_{fj}\rangle=(-1)^{n_{ij}}\left\langle\phi_i\left|\left\{E_1(t)|1\rangle\langle1|+\sum_{j\ \mathrm{neigh1}}\beta_1(t)(|1\rangle\langle j|+|j\rangle\langle1|)\right\}\right|\phi_j\right\rangle\ , \tag{37}$$

where n_{ij} is the number of permutations necessary for obtaining $|\phi\rangle_i$ and $|\phi_j\rangle$ and the same place in the two determinants $|\Psi_{fi}\rangle$ and $|\Psi_{fj}\rangle$.

The solution of the system of differential equations has been made numerically with an optimized precision. A control of the results can be achieved by verifying that, at any time, $|\Psi(t)\rangle$ remains normalized:

$$\sum_i|\langle\Psi(t)|\Psi_{fi}\rangle|^2\sim1\ .$$

This condition is fulfilled with a precision better than 10^{-7} in all our calculations. Some of the $n_1(t)$ variations are given in Fig. 2 for various η values. The comparison between the results obtained with basis 1 and basis 2 is given in Table I. The similarity of the two sets of results leads us to think that the use of basis 1 gives a sufficient accuracy. Our values of $P^+(E_c)$ deduced from $n_1(\infty)$ at

various energies E_c are given in Fig. 1. We observe that as $E_c\rightarrow0$, $n_1(\infty)\rightarrow1$ and $P^+(E_c)\rightarrow0$, which means that, as expected, at low velocities the system tends to adopt at large times the adiabatic behavior.

Let us compare the exact results to the bosonization approximation results (Fig. 1). The general behavior is the same. In the approximation P^+ is proportional to $v_\perp^2$ up to large energies $50<E_c<10^4$ eV, at higher energies P^+ tends towards its maximum sudden limit value. In the exact calculation one may roughly distinguish three ranges. The curve exhibits a variation proportional to $v_\perp$ for $50<v_\perp<10^4$ eV. Then it increases as $v_\perp^{2.4}$ for $5\times10^2<v_\perp<10^4$ eV. Of course at higher energies the two curves tend to the same sudden limit.

The difference between the two approaches is larger at low E_c energies. We may try to understand this point. In both treatments we follow the evolution with time of a state which is projected on a limited basis containing an
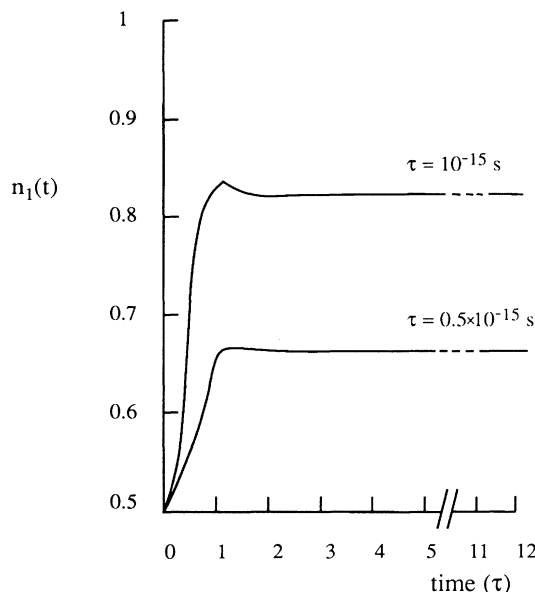
FIG. 2. Variation with time of the population $n_1(t)$ on atom 1 for two η values. The upper curve is for $\eta = 2.4 \times 10^{15}$ s^{-1} ($E_c = 1.44 \times 10^4$ eV), the lower curve is for $\eta = 4.8 \times 10^{15}$ s^{-1} ($E_c = 5.76 \times 10^4$ eV). The unit of time on the abscissa axis is, respectively, $\tau = 10^{-15}$ s and $\tau = 0.5 \times 10^{-15}$ s.

$i = 0$ ground state and various $i \neq 0$ excited states. In the boson method the only coupling is between the $i = 0$ and the $i \neq 0$ states while in the fermion "exact" treatment direct $\langle \Psi_{fi} | H(t) | \Psi_{fi} \rangle$ terms with i and $j \neq 0$ are present.

By examining the order of magnitude of these terms we see that they are always smaller (in absolute value) than $\langle \Psi_{fi} | H(t) | \Psi_{f0} \rangle$ terms. From this feature one may expect that the i and $j \neq 0$ terms will be active in the calculation only when the decoupling process occurs slowly, i.e., for low E_c values.

To conclude, we may say that the previous discussion shows the importance of introducing a possible excitation of the electrons during the decoupling process. In our calculation such excitations are present. They are not due to a thermal effect but to nonadiabatic screening effects. In Table I we give the excited states which have the largest weights in $|\Psi(t)\rangle$ at three different times. As expected, we see that, while state $i = 0$ (final ground state) has the largest weight, the excited states take also a large part in the process.

One may try to understand how such excitations act on the $P^+(v_\perp)$ dependence. A qualitative explanation may be found. If the target electronic structure is in its ground state, the atomic level which resonates with it can only lose its excitation. On the contrary, when excitations are created in the target electronic structure they can be transferred to the atomic level and exchanges occur in both directions from the atom to the target and from the target to the atom. A first consequence is that the effective distance where most of the exchanges occur is further from the surface (for example, in thermal models $z^* \sim 5-10$ Å). The other consequence is that the $P^+(v_\perp)$ law is not of an exponential time-of-life law but of a power-law type.

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