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Electronic excitations produced by deep-level promotion during atomic collisions in solids

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Expressions have been derived for electron-energy distributions of electrons excited in solids by one-electron core-level promotion processes during low-energy ion bombardment. Excitation occurs either due to the well-known autoionization of a promoted level or due to the excitation of electrons from occupied conduction-band states by a process indirectly mediated by core-level promotion. These expressions have been applied to evaluate electron-energy spectra of bombarded Al metal. As an example, two Al atoms in Al metal that collide with a kinetic energy of 1000 eV give rise to a one-electron energy spectrum which extends beyond the $2p$ Auger peak energy ($\epsilon \approx 54$ eV) and which can be described approximately by an exponential dependence $\exp(-\epsilon/10)$.

INTRODUCTION

The interaction of localized electronic levels with a continuum of levels plays a crucial role in a variety of physical processes, which include the interaction of adsorbed atoms with solid surfaces,[1] the scattering of ions from surfaces,[2] and the autoionization of molecules.[3,4] The theoretical description of a localized level-continuum interaction has been discussed in the literature from various points of view, particularly in connection with the solution of the dynamic Anderson-Newns Hamiltonian[5] for resonant neutralization and ionization of atoms at metal surfaces, where for specific cases analytical solutions of the Hamiltonian have been found.

In this paper we wish to discuss the application of the theory to the problem of electronic excitation produced by deep-level promotion during atomic collisions in solids. It is well established that this excitation can be described in terms of electronic transitions in the quasimolecule formed transiently during the collision. The electronic states of the quasimolecule can be reasonably well approximated by one-electron molecular orbitals (MO's). Some of these orbitals can be promoted to higher energies due to the competing effect of the increased nuclear charge in the quasimolecule with decreasing internuclear distance and of the increase in kinetic energy of the electron caused by its increased localization. The promoted localized molecular orbitals interact with the continuum of the conduction-band electrons and with the continuum states in vacuum. Due to the dynamics of the interaction between the promoted MO (which plays the role of the localized level) and the continuum of levels, the excitation of electrons takes place with possible subsequent electron emission [one-electron kinetic electron emission (KEE) induced by the level promotion]. Moreover, the promoted MO's may create a hole in the core levels of one of the colliding atoms. The hole can then be neutralized by a conventional two-electron Auger process or by processes involving more electrons. All these one-, two-, and multiple-electron excitations contribute to the energy distribution of emitted electrons, and it is difficult to disentangle individual contributions experimentally. One of the aims of this paper is to provide a theoretical description of the electron-energy distributions in KEE, which are due to one-electron promotion processes only. Part of the analysis has been already carried out before in a simplified version.[6,7] In this paper we first formulate the problem of the localized level-continuum interaction quite generally, pointing out in detail various approximations leading to analytical formulas. The resulting expressions for the energy distributions due to one-electron excitation will then be applied to a specific problem, namely, to the energy distribution of electrons excited in binary collisions of Al atoms in Al metal due to $2p$-$2s$ Al core-level promotion.

THEORETICAL DESCRIPTION

We will describe a system consisting of a continuum of states and a set of localized levels, which interact time dependently with the states of the continuum. The system is described by the time-dependent Hamiltonian $H(t)$ having the general characteristic that $H(-\infty)=H(+\infty)$. We assume that the total time-dependent wave function $\phi(t)$ can be expressed as a linear combination of a suitably truncated set of continuum wave functions ψ_k and by a set of localized wave functions ψ_l

$$\phi(t)=\sum_k a_k(t)\psi_k(t)+\sum_l a_l(t)\psi_l(t) . \tag{1}$$

We further assume that the self-energies ϵ_k of the states in the continuum are time independent and that $\psi_k(t)$ and $\psi_l(t)$ are orthogonal at any time, i.e.,

$$\langle \psi_k(t)|H(t)|\psi_k(t)\rangle = \epsilon_k \,, \tag{2}$$

$$\langle \psi_k(t)|\psi_{k'}(t)\rangle = \delta_{kk'} \,, \tag{3}$$

$$\langle \psi_l(t)|\psi_k(t)\rangle = 0 \,, \tag{4}$$

$\psi_l(t)$ are obtained by diagonalizing the Hamiltonian $H(t)$ at any time t within the basis formed only of localized functions. Therefore,

$$\langle \psi_l(t)|\psi_{l'}(t)\rangle = \langle \psi_l(t)|H(t)|\psi_{l'}(t)\rangle = 0 \,, \tag{5}$$

where $l \neq l'$.

The self-energy coresponding to $\psi_l(t)$ is time dependent, thus

$$\langle \psi_l(t)|H(t)|\psi_l(t)\rangle = \epsilon_l(t) \,. \tag{6}$$

The total time-dependent wave function $\phi(t)$ must satisfy the Schrödinger equation (in a.u.)

$$i\frac{\partial \phi(t)}{\partial t} = H(t)\phi(t) \,. \tag{7}$$

As usual we substitute (1) into (7), and, using relations (2)–(6), we obtain the following set of equations for $a_l(t)$ and $a_k(t)$ [we drop the explicit notation of the time dependence of $\psi_k(t)$, $\psi_l(t)$, and $H(t)$]:

$$\begin{aligned} i\frac{\partial a_k(t)}{\partial t} - \epsilon_k a_k(t) &= \sum_{k'} \left[\langle \psi_k|H|\psi_{k'}\rangle - i\left\langle \psi_k \middle| \frac{\partial \psi_{k'}}{\partial t} \right\rangle \right] a_{k'}(t) \\ &\quad + \sum_{l} \left[\langle \psi_k|H|\psi_l\rangle - i\left\langle \psi_k \middle| \frac{\partial \psi_l}{\partial t} \right\rangle \right] a_l(t) \,, \end{aligned} \tag{8}$$

$$i\frac{\partial a_l(t)}{\partial t} - \epsilon_l(t) a_l(t) = \sum_{k} \left[\langle \psi_l|H|\psi_k\rangle - i\left\langle \psi_l \middle| \frac{\partial \psi_k}{\partial t} \right\rangle \right] a_k(t) \,. \tag{9}$$

Because of the orthogonality relations (3) and (4) it can be easily shown that the matrix elements in square brackets in (8) and (9) are Hermitian. To simplify the notation we will denote the elements in the square brackets as follows:

$$\langle \psi_k|H|\psi_{k'}\rangle - i\left\langle \psi_k \middle| \frac{\partial \psi_{k'}}{\partial t} \right\rangle = V_{kk'}(t) \,, \tag{10}$$

$$\langle \psi_k|H|\psi_l\rangle - i\left\langle \psi_k \middle| \frac{\partial \psi_l}{\partial t} \right\rangle = V_{kl}(t) \,. \tag{11}$$

Equations (8) and (9) can then be rewritten as

$$\begin{aligned} i\frac{\partial a_k(t)}{\partial t} - \epsilon_k a_k(t) &= \sum_{k'} V_{kk'}(t) a_{k'}(t) \\ &\quad + \sum_{l} V_{kl}(t) a_l(t) \,, \end{aligned} \tag{12}$$

$$i\frac{\partial a_l(t)}{\partial t} - \epsilon_l(t) a_l(t) = \sum_{k} V_{lk}(t) a_k(t) \,. \tag{13}$$

It should be stressed that except for ϵ_k all quantities in (12) and (13) are time dependent. Equations (12) and (13) can be further simplified using the following substitution

$$a_u(t) = c_u(t) \exp\left[-i \int_{-\infty}^{t} \epsilon_u(\tau) d\tau \right] \tag{14}$$

or, when ϵ_u is time independent,

$$a_u(t) = c_u(t) \exp(-i\epsilon_u t) \,. \tag{15}$$

After substituting (14) and (15) into (12) and (13) we get

$$i\frac{\partial c_k(t)}{\partial t} = \sum_{k'} V_{kk'}(t) \exp[i(\epsilon_k - \epsilon_{k'})t] c_{k'}(t) + \sum_{l} V_{kl}(t) \exp\left[i\left[\epsilon_k t - \int_{-\infty}^{t} \epsilon_l(\tau) d\tau \right] \right] c_l(t) \,, \tag{16}$$

$$i\frac{\partial c_l(t)}{\partial t} = \sum_{k} V_{lk}(t) \exp\left[-i\left[\epsilon_k t - \int_{-\infty}^{t} \epsilon_l(\tau) d\tau \right] \right] c_k(t) \,. \tag{17}$$

If we neglect the existence of the localized levels (ψ_l), the system of equations (16) and (17) reduces to

$$i\frac{\partial c_{k'}}{\partial t} = \sum_{k'} V_{kk'}(t) \exp[i(\epsilon_k - \epsilon_{k'})t] c_{k'}(t) \,. \tag{18}$$

These are the equations for excitations in the continuum of levels, that are mostly responsible for electronic energy losses of moving particles in solids. When the "slowness" approximation is introduced, we obtain

$$c_k(t) = c_k(-\infty) + \frac{1}{i} \sum_{k'} \int_{-\infty}^{t} d\tau \exp[i(\epsilon_k - \epsilon_{k'})\tau] T_{kk'}(\tau) c_{k'}(-\infty) \,, \tag{19}$$

where $T_{kk'}$ is the T matrix for the valence electron $k-k'$ scattering caused by the perturbing potential V. In the first Born approximation the matrix $T_{kk'}$ becomes equal to $V_{kk'}$. Physical consequences of this scattering process are discussed in Ref. 8.

In the next step we neglect direct $k-k'$ interaction [thus we put $V_{kk'}(t)=0$ in (16)] and assume, for simplicity, that only one localized level l is relevant in the excitation process. Thus,

$$\frac{\partial c_k(t)}{\partial t} = -iV_{kl}(t)\exp\left[i\left[\epsilon_k t - \int_{-\infty}^{t}\epsilon_l(\tau)d\tau\right]\right]c_l(t) , \tag{20}$$

$$\frac{\partial c_l(t)}{\partial t} = -i\sum_k V_{lk}(t)\exp\left[-i\left[\epsilon_k t - \int_{-\infty}^{t}\epsilon_l(\tau)d\tau\right]\right]c_k(t) . \tag{21}$$

From (20) we obtain

$$c_k(t) = -i\int_{-\infty}^{t}d\tau\, V_{kl}(\tau)\exp\left[i\left[\epsilon_k\tau - \int_{-\infty}^{\tau}\epsilon_l(\tau')d\tau'\right]\right]c_l(\tau) + c_k(-\infty) . \tag{22}$$

When (22) is substituted in (21) we get

$$\begin{aligned}\frac{\partial c_l(t)}{\partial t} = {}& -\sum_k V_{lk}(t)\int_{-\infty}^{t}d\tau\, V_{kl}(\tau)\exp\left[i\left[\epsilon_k(\tau - t) - \int_{t}^{\tau}\epsilon_l(\tau')d\tau'\right]\right]c_l(\tau) \\ & -i\sum_k V_{lk}(t)\exp\left[-i\left[\epsilon_k t - \int_{-\infty}^{t}\epsilon_l(\tau)d\tau\right]\right]c_k(-\infty) .\end{aligned} \tag{23}$$

The matrix elements $V_{lk}(t)$ depend upon the wave vector k. To take this dependence into account would, however, complicate the calculation and does not seem to yield physically new results. Thus in the next section we will neglect the k dependence, and we will replace $V_{lk}(t)$ by an averaged value $V_l(t)$. Then instead of summing we integrate over the continuum, i.e.,

$$\sum_k = \int \rho(\epsilon_k)d\epsilon_k . \tag{24}$$

Consequently (23) can be rewritten as

$$\begin{aligned}\frac{\partial c_l}{\partial t} = {}& -V_l(t)\int_{-\infty}^{t}d\tau\, V_l^*(\tau)\int d\epsilon_k \rho(\epsilon_k)\exp\left[i\epsilon_k(\tau - t) - i\int_{t}^{\tau}\epsilon_l(\tau')d\tau'\right]c_l(\tau) \\ & -iV_l(t)\int d\epsilon_k\rho(\epsilon_k)\exp\left[-i\epsilon_k t + i\int_{-\infty}^{t}\epsilon_l(\tau)d\tau\right]c_k(-\infty) .\end{aligned} \tag{25}$$

In the first term on the right-hand side of (25) we can integrate over ϵ_k. The integral over ϵ_k is the Fourier transform of the density of states

$$\int d\epsilon_k\rho(\epsilon_k)\exp[-i\epsilon_k(t-\tau)] = F(t-\tau) . \tag{26}$$

The first term can then be written as

$$-V_l(t)\int_{-\infty}^{t}d\tau\, V_l^*(\tau)F(t-\tau)\exp\left[-\int_{t}^{\tau}\epsilon_l(\tau')d\tau'\right]c_l(\tau) . \tag{27}$$

The value of $F(t-\tau)$ is essentially zero when $t-\tau$ is greater than the inverse of the electronic bandwidth ΔE (bandwidth of the continuum) of the solid, i.e., if $|t-\tau| > 1/\Delta E$. As we assume that both $V_l(t)$ and $\epsilon_l(t)$ do not change much within the time $1/\Delta E$, we can use the "slowness" approximation[9] and in (27) introduce the following approximate relations:

$$\begin{aligned}& V_l(\tau) = V_l(t) , \\ & \exp\left[-\int_{t}^{\tau}\epsilon_l(\tau')d\tau'\right] = \exp[-i\epsilon_l(\tau)(\tau - t)] , \\ & c_l(\tau) = c_l(t) .\end{aligned} \tag{28}$$

Thus, (27) can be rewritten as a product of $c_l(t)$ and of

$$-|V_l(t)|^2\int_{-\infty}^{t}d\tau\, F(t-\tau)\exp[i\epsilon_l(\tau)(t-\tau)] = -|V_l(t)|^2 K(t) , \tag{29}$$

where we have introduced the notation

$$K(t) = \int_{-\infty}^{t}d\tau\, F(t-\tau)\exp[i\epsilon_l(\tau)(t-\tau)] . \tag{30}$$

Equation (29) is the generalization of the formula for the virtual linewidth often used in solid-adsorbate studies. In those studies the adsorbate is characterized by the energy $\epsilon_l(t)$ of the adsorbate virtual level, which lies always within the electronic band of the solid and the band is assumed to be very wide. The electronic density of states $\rho(\epsilon_k)$ can then be well approximated by a constant value at $\epsilon = \epsilon_l$ denoted by $\rho(\epsilon_l)$ and (26) yields

$$F(t-\tau)=2\pi\rho(\epsilon_l)\delta(t-\tau)\ . \tag{31}$$

When (31) is substituted into (30) we obtain

$$K(t)=\pi\rho(\epsilon_l)\ , \tag{32}$$

and (29) simplifies to

$$\pi|V_l(t)|^2\rho(\epsilon_l)=\Delta(\epsilon_l,t)\ , \tag{33}$$

where $2\Delta(\epsilon_l,t)$ is the linewidth of the virtual level described by ψ_l.

To obtain the general solution for $c_l(t)$ we will keep (29) in its general form and resort to the approximate expression (33) for semiqualitative studies. We now substitute (29) in the first term on the right-hand side of (25). Further, we will assume that the initial conditions are such that only one $c_k(-\infty)$ is equal to 1; the other $c_k(-\infty)$ are equal to zero. Then (25) can be written as

$$\frac{\partial c_l(t)}{\partial t}=-|V_l(t)|^2K(t)c_l(t)-iV_l(t)\exp\left[-i\epsilon_k t+i\int_{-\infty}^{t}\epsilon_l(\tau)d\tau\right]c_k(-\infty)\ . \tag{34}$$

This is a standard first-order differential equation, which can be solved in a closed form. The solution is

$$\begin{aligned}c_l(t)=&-i\exp\left[i\int_{-\infty}^{t}\epsilon_l(\tau')d\tau'\right]\int_{-\infty}^{t}d\tau\, V_l(\tau)\exp\left[\int_{t}^{\tau}|V_l(\tau')|^2K(\tau')d\tau'-i\epsilon_k\tau+i\int_{t}^{\tau}\epsilon_l(\tau')d\tau'\right]c_k(-\infty)\\&+c_l(-\infty)\exp\left[-\int_{-\infty}^{t}|V_l(\tau)|^2K(\tau)d\tau\right]\ .\end{aligned} \tag{35}$$

It is important to realize that (35) together with (22) give all the information on $c_l(t)$ and $c_k(t)$ that are needed. The results depend only upon the initial conditions. If we are interested, for example, in the probability that the localized level, originally situated below the Fermi level, is occupied by a hole at the end of the process (i.e., at $t=\infty$) we should interpret $|c_n(t)|^2$ as the probability that the state ψ_n is occupied by a hole. The initial conditions in (35) are now such that $c_l(-\infty)=0$ (i.e., the localized level is originally occupied by an electron, thus the hole occupation probability of the state ψ_l at $t=-\infty$ is zero). Only the states ψ_k above the Fermi energy are occupied by holes, i.e., $c_k(-\infty)=1$ for one of those levels. The total probability P_l of the hole occupancy of the state ψ_l at $t=+\infty$ is obtained by squaring (35) and summing over all unoccupied states, i.e.,

$$\begin{aligned}P_l=&\sum_{|k|>|k_F|}|c_l(\infty)|^2\\=&\int_{\epsilon_F}^{\infty}\rho(\epsilon_k)\left|\int_{-\infty}^{+\infty}d\tau\, V_l(\tau)\exp\left[\int_{\infty}^{\tau}|V_l(\tau')|^2K(\tau')d\tau'-i\epsilon_k\tau+i\int_{\infty}^{\tau}\epsilon_l(\tau')d\tau'\right]\right|^2\ .\end{aligned} \tag{36}$$

If we are interested in the probability that a state ψ_k above the Fermi energy is occupied by an electron at $t=+\infty$, we must use (22) and substitute for $c_l(\tau)$ from (35). Because the state ψ_k is originally (at $t=-\infty$) unoccupied by an electron, $c_k(-\infty)$ in (22) must be equal to zero. By substituting (35) into (22) we have thus only two contributions. The first contribution is due to direct electron excitation from the localized level, provided it is occupied by an electron at $t=-\infty[c_l(-\infty)=1]$. Then the probability that an electron will be excited from ψ_l into the unoccupied ψ_k by this process is

$$|c_k(\infty)|^2=\left|\int_{-\infty}^{+\infty}d\tau\, V_l^*(\tau)\exp\left[i\left[\epsilon_k\tau-\int_{-\infty}^{\tau}\epsilon_l(\tau')d\tau'\right]\right]\exp\left[-\int_{-\infty}^{\tau}|V_l(\tau')|^2K(\tau')d\tau'\right]\right|^2|c_l(-\infty)|^2\ . \tag{37}$$

Naturally (37) and (36) are closely related. It should also be noted that (37) is essentially equivalent to the formula describing the autoionization of quasimolecules in atomic collision physics.[3] The introduction of $K(\tau)$ enables us to describe the continuum boundary (the bottom of the conduction band is normally neglected in atomic quasimolecular studies).

The second contribution results from electrons that are transferred from occupied states $\psi_{k'}$ below the Fermi level to the originally unoccupied state ψ_k above the Fermi level via the interaction with the localized state ψ_l. Since the process is entirely analogous to the process of a direct excitation (19) from $\psi_{k'}$ into ψ_k due to the matrix $V_{kk'}$ it must be possible using the slowness approximation to cast the final formulation of this process into a similar form by the use of a T matrix.

This can be shown if we substitute (35) [with $c_l(-\infty)=0$] into (22). We should keep in mind that $c_k(-\infty)$ in (35) corresponds to an occupied state $\psi_{k'}$ below the Fermi level and thus is equal to one. We obtain

$$\begin{aligned}c_k(\infty)=&-\int_{-\infty}^{+\infty}d\tau\, V_l^*(\tau)\exp[i(\epsilon_k\tau)]\\&\times\int_{-\infty}^{\tau}d\tau''V_l(\tau'')\exp\left[\int_{\tau}^{\tau''}|V_l(\tau''')|^2K(\tau''')d\tau'''-i\epsilon_{k'}\tau''+i\int_{\tau}^{\tau''}\epsilon_l(\tau''')d\tau'''\right]c_{k'}(-\infty)\ .\end{aligned} \tag{38}$$

This complex expression for the transfer of an electron from $\psi_{k'}$ into ψ_k can be considerably simplified if we assume that the localized level always lies within the conduction band and that the virtual linewidth $\Delta(t)$ of the level is always such that $\epsilon_l(t)$ and $V_l(t)$ do not change much within the time $1/\Delta(t)$. These are the essential conditions for application of the slowness approximation as discussed in connection with Eqs. (27)–(29). The only difference in this case is that the limiting time is given by the inverse of the virtual linewidth rather than by the inverse bandwidth.

First, we introduce the virtual linewidth $\Delta(t)$ of ψ_l by using (32) for $K(t)$ in (38). Secondly, in the spirit of the slowness approximation [see (28)], we replace $V_l(\tau'')$ in (38) by $V_l(\tau)$ and the integral $\int_\tau^{\tau''}\epsilon_l(\tau''')d\tau'''$ by $\epsilon_l(\tau)(\tau''-\tau)$. Then we can integrate in (38) the integral over τ'' and obtain

$$c_k(\infty)=-\int_{-\infty}^{+\infty}d\tau|V_l(\tau)|^2\frac{\exp[i(\epsilon_k-\epsilon_{k'})\tau]}{\Delta(\epsilon_l,\tau)-i\epsilon_{k'}+i\epsilon_l(\tau)}c_{k'}(-\infty)\ . \tag{39}$$

When we compare (39) and (19) we can immediately identify the T matrix for the process of excitation from $\psi_{k'}$ into ψ_k via ψ_l, namely,[9,6]

$$T_{kk'}(\tau)=\frac{|V_l(\epsilon_l,\tau)|^2}{i\Delta(\epsilon_l,\tau)+\epsilon_{k'}-\epsilon_l(\tau)}\ . \tag{40}$$

The probability of excitation from occupied orbitals $|k'\rangle$ into the empty orbital $|k\rangle$ is then equal to

$$|c_k(\infty)|^2=\int_{-\infty}^{\epsilon_F}d\epsilon_{k'}\rho(\epsilon_{k'})\left|\int_{-\infty}^{+\infty}d\tau\frac{|V_l(\epsilon_l,\tau)|^2}{i\Delta(\epsilon_l,\tau)+\epsilon_{k'}-\epsilon_l(\tau)}\exp[i(\epsilon_k-\epsilon_{k'})\tau]\right|^2\ . \tag{41}$$

In summary, we can say that there are basically four different processes that lead to excitation of electrons due to a time-dependent perturbing potential $V(t)$. The first is described by (19) and requires nonzero matrix elements of $V(t)$ between the delocalized states ψ_k, i.e., $V_{kk'}(t)\neq 0$. This process is essentially equivalent to the classical particle-electron collision mechanism. The second process, described by (37), is due to a direct electron transfer from the uppermost quasimolecule level into the empty states and is known as a quasimolecular ionization (or autoionization). The matrix element of V between the quasimolecular state ψ_l and the ψ_k states must be nonzero, i.e., $V_{lk}(t)\neq 0$. The third process, described by (41), again requires nonzero V_{lk} matrix elements. An electron is transferred in this process from an occupied $\psi_{k'}$ state into the empty but previously occupied ψ_l state and subsequently from ψ_l into an empty ψ_k state. Though it is of second order in V_{lk}, the contribution of this mechanism to the electron excitation is considerable, particularly at high electron kinetic energies. Finally the fourth process, which was not described in this paper, would require both V_{lk} and $V_{kk'}$ to be nonzero and would depend on the cross product $V_{lk}V_{kk'}$. The analysis of this mechanism has not yet been carried out.

Except for the first process, which is equivalent to a particle-electron collisional excitation, the three remaining processes depend critically upon the promotion of the antibonding quasimolecular orbital. The energy of this level, which we have previously denoted by ϵ_l, and the energies of other quasimolecular levels are plotted as a function of the interatomic distance R in correlation diagrams. A typical p-level promotion in a symmetrical collision is illustrated in the correlation diagram of Fig. 1. The maximum energy (OE) to which a promoted level is shifted depends on the impact energy (IE), which in turn determines the distance of closest approach, i.e., $R_3<R_2<R_1$, for corresponding energies $IE_3>IE_2>IE_1$, as shown in Fig. 1.

Core-level binding energies are a function of the specific atomic configuration and can vary over a large range of energies. Some metal atoms in solids for example have localized $2p$ and $3p$ orbitals, where the $2p$ binding energy may be hundreds of eV, while the $3p$ energy may be only tens of eV. Here it may be possible to collisionally promote the $3p$ level to a fairly high molecular orbital (in, say, a 5-keV collision), which can ionize and produce kinetic secondary electrons with energies of perhaps hundreds of eV. In such cases it may be unlikely

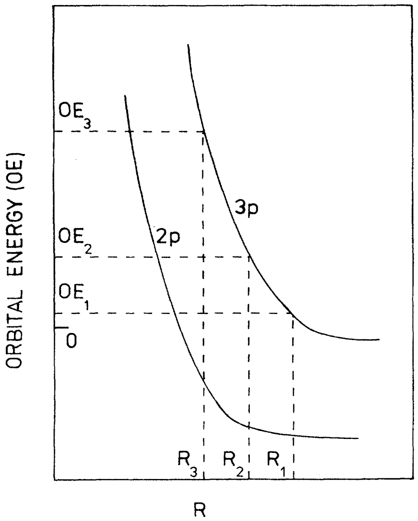

FIG. 1. The part of the correlation diagram that shows the promotion of p levels in an atomic binary collision. R denotes the interatomic distance; R_n denotes the distance of closest approach for a given impact energy. The vacuum level is indicated by 0 and the highest orbital energy for a given R_n by OE_n.

that the $2p$ level also will be excited (in a 5-keV collision) to such high energies. We illustrate such a two-level ($2p,3p$) case in Fig. 1, where at R_3 (the distance of closest approach for a given impact energy) only the $3p$ level can be excited into the continuum. Therefore the consideration of invoking only one localized level as used here in our theoretical analysis is usually justified. In the next section we will illustrate the conclusions reached in this chapter by analyzing collisional excitations in Al metal as an example. Al atoms have only one deep level ($2p$), which can be promoted, and thus the quasimolecular orbital scheme is rather simple.

APPLICATION TO ALUMINUM

We apply the analysis of the preceding section to the problem of one-electron excitation in aluminum metal during violent binary collisions of Al atoms. The role of the localized level is, as discussed above, in this case played by the highest antibonding orbital formed by the core levels of the transient Al-Al quasimolecule. As in the preceding section, the energy of the level is denoted by ϵ_l and the interaction matrix element between the localized level and a level $|k\rangle$ in the continuum is denoted by V_l, which is the value of V_{kl} averaged over k.

A similar problem has been treated previously using the numerical solution of the dynamical problem in which an incomplete set of localized functions (i.e., the $1s$ level has been neglected) was used.[7] The inclusion of this $1s$ level in the analysis does significantly influence the "fastness" of the promotion process and thus the dynamics of the excitation process at higher collision energies.

The Hamiltonian $H(t)$, which describes the collision, depends upon the electron coordinate r and upon the interatomic separation $D(t)$ of the two colliding atoms, i.e., we can write $H(t)=H(r,D(t))$. As in Ref. 7, the Hamiltonian $H(r,D(t))$ has been chosen as follows: We adopt the picture of the free-electron model for the states in the conduction band of the solid (metal), so that ψ_k are the free-electron wave functions. The two colliding atoms in the solid are represented by properly screened atomic potentials. Specifically we have used for ion cores the independent-particle-model (IPM) potential of Green, Sellin, and Zachor[10] screened by free electrons. The formation of adiabatic quasimolecular levels for various interatomic distances has been described by the variable-screening model of Eichler and Wille.[11] The effective single-electron potential is, in this model, obtained by smoothly interpolating the screening parameters of the IPM potentials between the separate and united-atom limits. This model allows us to calculate, with reasonable precision, the wave functions and energies of deep levels, in our case ψ_l and ϵ_l of the highest antibonding level.

The IPM potential (in a.u.) of an ion is assumed to have the same form as in Ref. 7, i.e.,

$$V_i(r)=[(N-1)\Gamma-Z]/r \ , \tag{42}$$

where

$$\Gamma=1-\Omega(r) \tag{43}$$

with

$$\Omega(r)=\{(\eta/\xi)[\exp(\xi r)-1]+1\}^{-1} \ , \tag{44}$$

where N is the total number of electrons in the atom (or ion) plus one electron, which is calculated; Z is the nuclear charge. The parameters η and ξ are found for the given Z and N in Refs. 10. To the potential (42) one must add the potential of the $(Z-N+1)$ conduction electrons. When the conduction electrons are homogeneously distributed within a sphere of the radius R_a this additional potential is equal to

$$\begin{aligned} &\frac{3(Z-N+1)}{2R_a}\left[1-\frac{1}{3}\left[\frac{r}{R_a}\right]^2\right] \quad \text{for } r<R_a \ , \\ &\frac{Z-N+1}{r} \quad \text{for } r>R_a \ . \end{aligned} \tag{45}$$

The total potential is then

$$\begin{aligned} &V(r)=\frac{Z}{r}\left\{\frac{(N-1)\Gamma-Z}{Z}+\frac{3r(Z-N+1)}{2R_aZ}\left[1-\frac{1}{3}\left[\frac{r}{R_a}\right]^2\right]\right\} \quad \text{for } r<R_a \ , \\ &V(r)=0 \quad \text{for } r>R_a \ , \end{aligned} \tag{46}$$

which can be also written as

$$V(r)=-\frac{Z}{r}\phi(r,\xi,\eta,R_a,Z,N) \ , \tag{47}$$

where $\phi(r,\xi,\eta,R_a,Z,N)$ is the parametrical screening function.

The radius R_a can be calculated from the condition that the electron density should be equal to the conduction-electron density in the metal. To improve the accuracy of the potential (46) we use R_a as an additional fitting parameter such that (46) satisfies the Friedel sum rule. It should be noted that the fitted potential (46) gives the transport cross sections σ_t in close agreement with the σ_t calculated using the best density-functional potentials.

For the purpose of calculating molecular correlation diagrams and wave functions, the variable screening model[11] can be very useful. This model is based on the idea that the mutual screening of the atoms making up the quasimolecule can be properly approximated by a spherical, but variable (as a function of the internuclear distance D) screening function. The electronic states of the separated and the united atom may be generated to a good approximation by phenomenological single-electron potentials $V(r)=(-Z/r)\phi(r,\alpha)$, which depend on sets of parameters collectively described by α^{sa} and α^{ua}, respectively. If we adopt the interpolation scheme[11]

$$\alpha_i^{\text{eff}}=\frac{\alpha^{sa}\lambda^2+\alpha^{ua}\rho_i^2}{\lambda^2+\rho_i^2}\ , \tag{48}$$

where $\lambda^2=3$ and $\rho_i=2r_i/D$, we can expect that

$$V^{\text{eff}}(r_1,r_2,D)=-\frac{Z}{r_1}\phi(r_1,\alpha_1^{\text{eff}})-\frac{Z}{r_2}\phi(r_2,\alpha_2^{\text{eff}}) \tag{49}$$

will be a good approximation to the molecular single-electron potential, where r_1 and r_2 are the distances of the electron from the nuclei.

For two colliding aluminum atoms, that in the united-atom limit form an Fe atom the parameters are the following[10]

$$\begin{aligned}
&\eta^{sa}=3.544\ ,\\
&\xi^{sa}=2.496\ ,\\
&R_a^{sa}=3.5\ ,\\
&Z^{sa}=13\ ,\\
&N^{sa}=11\ ,\\
&\eta^{ua}=4.18\ ,\\
&\xi^{ua}=1.596\ ,\\
&R_a^{ua}=2.2\ ,\\
&Z^{ua}=26\ ,\\
&N^{ua}=24\ .
\end{aligned} \tag{50}$$

For a given interatomic separation D, we can calculate the energy levels $\epsilon_l(D)$ and the wave function $\psi_l(D)$ by solving the Schrödinger equation

$$[-\tfrac{1}{2}\nabla^2+V^{\text{eff}}(r_1,r_2,D)]\psi_l=\epsilon_l\psi_l\ . \tag{51}$$

In order to solve (51) for the relevant energy levels (i.e., levels originating from $2s$, $2p$, and $1s$ deep levels), we expand the wave function ψ_l in terms of six basis functions $\psi_{2p\sigma}(r_1)$, $\psi_{2p\sigma}(r_2)$, $\psi_{2s}(r_1)$, $\psi_{2s}(r_2)$, $\psi_{1s}(r_1)$, and $\psi_{1s}(r_2)$ and use simple orbitals (with distances in a.u.), which, together with the potential (46), give the correct atomic energies:

$$\begin{aligned}
&\psi_{2p\sigma}=25.14z\exp(-6.5r)+8.296z\exp(-3.5r)\ ,\\
&\psi_{2s}=6.4\exp(-6.8r)-32r\exp(-5.2r)\ ,\\
&\psi_{1s}=23.72\exp(-12r)\ .
\end{aligned} \tag{52}$$

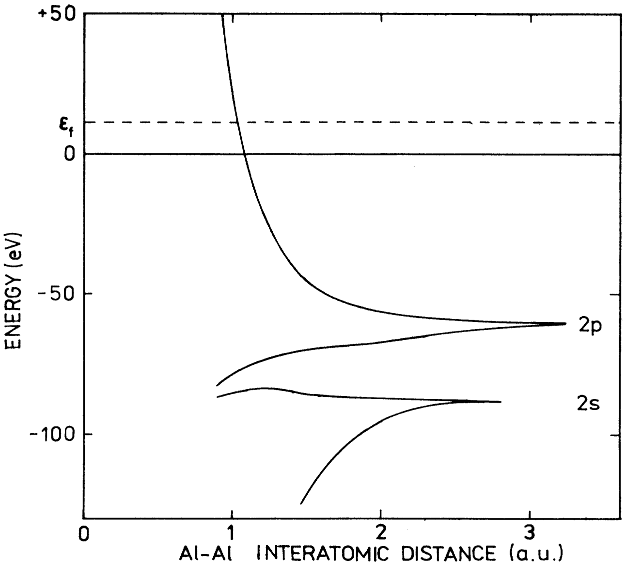

FIG. 2. The energies of $2p$-$2s$ levels of an Al-Al quasimolecule embedded in Al metal as a function of the interatomic distance D. The energies are in electronvolts. The bottom of the conduction band of Al is at $\epsilon=0$ and the Fermi energy at $\epsilon=\epsilon_F=11$ eV. The energies of the quasimolecule have been calculated with the use of the variable screening model (Ref. 11) with potentials appropriate to Al atoms embedded in Al metal.

The diagonalization of (51) yields energies of the Al-Al quasimolecule. Of interest is the energy ϵ_l at various interatomic distances D. The calculated ϵ_l as a function of D are shown in Fig. 2. The inclusion of $1s$ orbitals in the calculation causes the energy of the highest orbital to increase monotonically with decreasing D and is important for modeling high-energy excitations. The dependence of $\epsilon_l(D)$ on D can be converted into a time-dependent $\epsilon_l(t)$ once the time dependence of D is known. We have calculated $D(t)$ for head-on collisions at various center-of-mass kinetic energies using the Molière interatomic potential. The resulting ϵ_l for Al-Al collisions at different center-of-mass energies are shown in Fig. 3. Also shown in the figure by a dotted line is the analytical approximation of $\epsilon_l(t)$ for 1000-eV impact, namely,

$$\epsilon_l(t)=\frac{40}{\cosh(4.7t)}(\text{eV})\ . \tag{53}$$

This expression has been used here to numerically calculate the excitations. In Fig. 2, in (53) and in all numerical calculations we use electronvolts (eV) as the unit of energy and, correspondingly, for time we use $(\text{eV})^{-1}$ with $\hbar=1$.

According to the analysis described in the previous chapter, there are two contributions to the one-electron excitations that are due to level promotion. One contribution is given by (37) and represents a direct transfer of one electron from the localized level into empty states$|k\rangle$. The second contribution is described by (38) or by its simplified version (39). The probability of excitation into empty states $|k\rangle$ due to (39) is given by (41) and represents the probability of excitation, which is indirectly mediated by the dynamics of the promoted level.

To estimate the energy distributions from (37) and from (41) one needs to know the value of $V_l(t)$, $\rho(\epsilon)$, and $\Delta(\epsilon_l,t)$. We have calculated V_{lk} for various interatomic distances D. The values of V_{lk} vary from small values for small k near the bottom of the band to large values (> 10 eV) for smaller D, the averaged value of V_l being larger for smaller D. In expression (33) both V_l and ρ depend on ϵ_l and therefore on time. To include all these variations would involve a complicated numerical integration and would not yield much new information. Thus we choose to neglect the dependence of ρ on ϵ and express (37) and (41) only in terms of $\Delta(\epsilon_l(t))$ and $\epsilon_l(t)$, where $\epsilon_l(t)$ is calculated from (51) and the function $\Delta(\epsilon)$ is an adjustable function of ϵ.

Within this approximation the relation (37) would give the number $n(\epsilon_k)$ of electrons excited in the energy interval between ϵ_k and $\epsilon_k + d\epsilon_k$ as

$$n_1(\epsilon_k) = \frac{1}{\pi} \left| \int_{-\infty}^{+\infty} d\tau [\Delta(\tau)]^{1/2} \exp\left[i\epsilon_k \tau - i \int_{-\infty}^{\tau} \epsilon_l(\tau')d\tau' \right] \exp\left[-\frac{1}{\pi} \int_{-\infty}^{\tau} \Delta(\tau')d\tau' \right] \right|^2 . \tag{54}$$

Similarly one can simplify (41). The number $n_2(\epsilon_k)$ of electrons excited between ϵ_k and $\epsilon_k + d\epsilon_k$ due to this second process is then

$$n_2(\epsilon_k) = \frac{1}{\pi^2} \int_{-\infty}^{\epsilon_F} d\epsilon_{k'} \left| \int_{-\infty}^{+\infty} d\tau \frac{\Delta(\epsilon_l, \tau)}{i\Delta(\epsilon_l, \tau) + \epsilon_{k'} - \epsilon_l(\tau)} \exp[i(\epsilon_k - \epsilon_{k'})\tau] \right|^2 . \tag{55}$$

The expression (55) can be still further simplified if we assume that the virtual width 2Δ is time independent during the excitation process and that $\epsilon_l(\tau)$ can be approximated by a linear time dependence $\epsilon_l(\tau) = b\tau + c$, where b and c are constants. Evaluation of the integrals in (55) can be carried out analytically[6] in this case, yielding

$$n_{2'}(\epsilon_k) = \frac{2\Delta}{b} \exp\left[-\frac{2\Delta}{b}(\epsilon_k - \epsilon_F) \right] . \tag{56}$$

To estimate the contributions of (54), (55), and (56), quantitatively we take for $\epsilon_l(t)$ the expression (53) and for $\Delta(t)$ the same functional dependence on t [assuming essentially that $\Delta(t)$ is proportional to $\epsilon_l(t)$], i.e.,

$$\Delta(t) = \frac{\Delta_0}{\cos(4.7t)} . \tag{57}$$

The value of $\Delta(t)$ at $t = 0$ is an adjustable constant Δ_0,

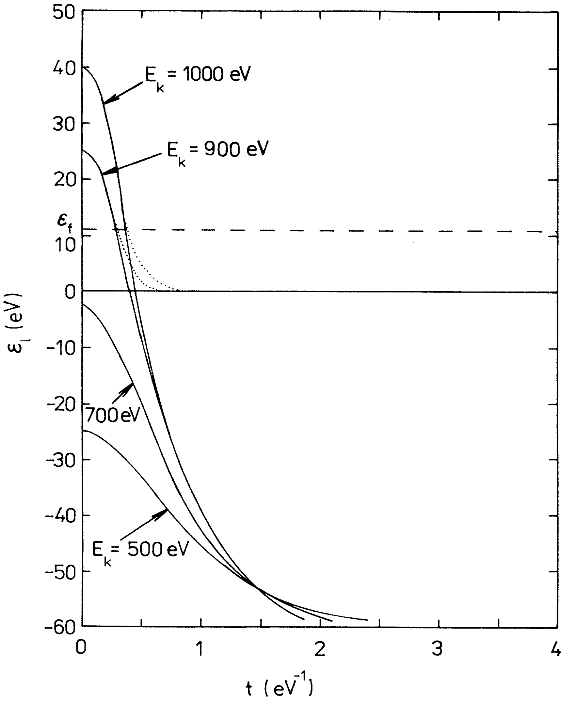

FIG. 3. The highest energy ϵ_l of the Al-Al quasimolecule from Fig. 2 is plotted as a function of time for head-on collisions with different center-of-mass kinetic energies (500, 700, 900, and 1000 eV). The distance dependence in Fig. 1 has been converted into a time dependence using the Molière potential. The unit of time is eV^{-1} ($\hbar = 1$) and $t = 0$ corresponds to the distance of closest approach. The analytical function (53) is indicated by a dotted line, which approximately describes $\epsilon_l(t)$ in the interaction region responsible for excitation and which is used in the numerical calculation.

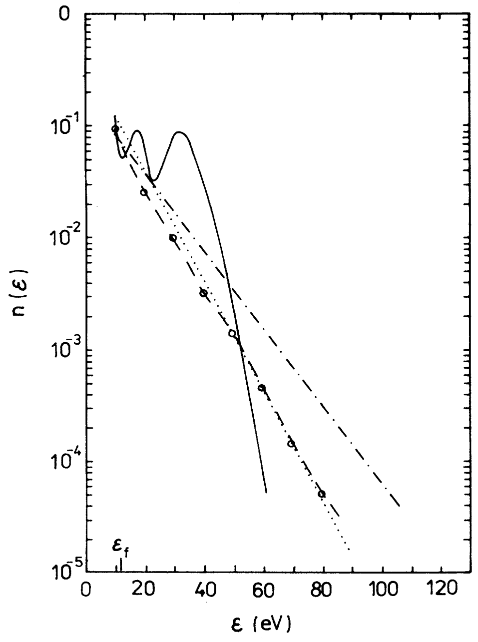

FIG. 4. Distributions (in units of the number of excited electrons per eV) of one-electron excitations obtained for 1000-eV Al-Al collisions. The distributions were calculated from (54) (full line), from (55) (dashed line), from (56) with $b = 56$ (dotted line), and from (56) with $b = 103$ (dashed dotted line). The dashed line interpolates between the values (circles) calculated numerically from (55).

which we take equal to 10 eV in the actual numerical calculation. The constant Δ in (56) can be obtained by substituting in (57) for t the time when $\epsilon_l(t)$ crosses the Fermi energy. The constant b can be obtained from the derivative of (53) at t when $\epsilon_l(t)$ crosses the Fermi energy. This procedure yields $b=56$ eV^2 and $\Delta=3$ eV. The value of b can also be determined directly from the calculated $\epsilon_l(t)$ in Fig. 3, and such a procedure gives $b=103$ eV^2.

The resulting $n_1(\epsilon_k)$, $n_2(\epsilon_k)$, and $n_{2'}(\epsilon_k)$ for a collision energy of 1000 eV are shown in Fig. 4. $n_1(\epsilon_k)$ shows characteristic oscillations due to interference effects.[3] Typically, $n_1(\epsilon_k)$ decreases rapidly at energies ϵ_k higher than the maximum value of ϵ_l achieved during the collision, whereas the distribution $n_2(\epsilon_k)$ spreads monotonically to higher values of ϵ_k.

As seen from Fig. 4, the simple analytical expression (56) gives results practically equivalent to those obtained numerically from (55) provided the same descriptions of $\epsilon_l(t)$ and $\Delta_l(t)$ are used. In view of the uncertainties in determining the constant b, the actual values of $n_{2'}(\epsilon_k)$ can lie between the dotted and dashed-dotted lines in Fig. 4.

CONCLUSION

Expressions for electron excitation caused by the promotion of electronic levels in bombarded solids have been derived using a method developed for studying localized level-continuum interactions. The necessary approximations have been discussed in detail. Two excitation processes have been found to be important, i.e., the direct electron transfer from the promoted level into empty states (autoionization of the quasimolecule) and the excitation from occupied levels into empty states mediated by level promotion. The expressions for these processes have been applied to estimate quantitatively electron excitation and emission during binary atomic collisions in Al metal. For this purpose the electronic levels of an Al_2 quasimolecule embedded in Al metal have been calculated with a method described previously,[7] but now using a larger set of localized wave functions. The calculated dependence of the promoted level on the interatomic distance was the basis for evaluating the excitation probabilities. For a center-of-mass kinetic energy of 1000 eV, it was found that the tail of the calculated electron-energy distribution extends beyond the energies of the $2p$ Auger lines and can be described by $\exp(-\epsilon_k/w)$, where w is around 10 eV. In aluminum the intensity and energy distributions of the calculated one-electron excitation process depend strongly upon the impact energy. The intensity would be very small and the energy distribution very narrow for center-of-mass kinetic energies below 700 eV.

The one-electron excitation formulas (54), (55), and (56) appear to describe characteristic features of recently measured kinetic electron emission spectra from bombarded Ge and Ga.[12] They fail, however, to explain the extended, very slowly decaying energy-distribution tails reported in Ref. 13, which are presumably caused by many-electron processes.

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