Effect of the band structure on charge exchange during atom-surface collisions

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Within the framework of the time-dependent Anderson-Newns model, charge exchange between an atomic particle and a surface with arbitrary band spectrum during scattering is examined. The charge state of the scattered particle is shown to be, in general, an oscillating function of its energy. Such behavior is a consequence of interference effects arising from band finiteness and from the complex structure of electronic states, which develops when an atomic particle interacts with a surface. The possibility of a substantially nonexponential law of atomic-state decay is demonstrated. The results obtained are found to give the account for known experimental dependencies.

Charge exchange between an atomic particle and a solid surface is one of the most fundamental aspects of atom-surface interaction. Charge exchange controls nearly all dynamical processes that occur at surfaces. The probabilities for charge transfer were first calculated with use of the time-dependent Anderson-Newns model.[1-3]

However, most calculations of the charge-transfer reactions have been performed in the "wide-band" limit, since this approximation allows for analytical solution of this problem with minimal restrictions on the behavior of the hopping and the shift of the atomic level.[1,2] This approximation does not take into account the effect of band-structure features, especially of the finiteness of the bandwidth. Meanwhile, real bands are always restricted to some energy interval and can be described by a specific function $N(\varepsilon)$. What is more, the wide-band approach does not provide for even a qualitative description in the case when the valence-electronic-state energy of the scattered particle is close to the band edge. Thus, a wide range of experimental results cannot be described within this approximation.

In this paper we take into account the effect of the finiteness of the bandwidth and of the features of $N(\varepsilon)$ on charge exchange during atom-surface collisions.

The effects introduced by the finiteness of the bandwidth proved to be significant: band finiteness was found to lead to nonmonotonic dependence of the final charge state on kinetic energy. This nonmonotonic character is a consequence of interference effects related both to band finiteness and to the possible existence of short-living states similar to that in the wide-band limit. However, these states decay fast. Therefore, the interference effects related to band finiteness prevail and might be experimentally observable.

The most recent approach for the problem of electron exchange of an atomic particle with a solid surface uses the tunnel Anderson-Newns Hamiltonian:[3-5]

$$\hat{H}[R(t)]=\sum_{k,\sigma}\varepsilon(k)\hat{c}^{\dagger}_{k\sigma}\hat{c}_{k\sigma}+\varepsilon_a[R(t)]\sum_{\sigma}\hat{a}^{\dagger}_{\sigma}\hat{a}_{\sigma}+\frac{\lambda[R(t)]}{\sqrt{V}}\sum_{k,\sigma}(V^{*}_{k}\hat{a}^{\dagger}_{\sigma}\hat{c}_{k,\sigma}+\text{H.c.}), \quad (1)$$

where $\hat{c}^{\dagger}_{k\sigma},\hat{a}^{\dagger}_{\sigma}$ ($\hat{c}_{k\sigma},\hat{a}_{\sigma}$) are annihilation and creation operators of electrons with a spin σ in a Bloch state $|k\rangle$ and in the atomic state $|a\rangle$, respectively, $R(t)$ is the distance between the atom and the surface, $\varepsilon_a[R(t)]$ is the energy of the atomic level at the time t, and $\lambda[R(t)]V_k$ is the hopping-matrix element, normalized by the system volume V.

The problem is to find the value

$$n(+\infty)=\sum_{\sigma}\langle\hat{a}^{\dagger}_{\sigma}(+\infty)\hat{a}_{\sigma}(+\infty)\rangle, \quad (2)$$

representing the charge state of the atomic particle after scattering.

Usually the dependence $\lambda(t)$ is chosen in the form $\exp[-\gamma R(t)]$. Such a choice is justified by the fact that at large distances R the hopping-matrix element is exponentially dependent on R, while its behavior at small distances of approach is of minor importance when the velocity of approach is relatively small (i.e., when the deviation from adiabaticity is small). However, in many scattering experiments the energy of the valence level is close to either the upper or the lower band edge. In this case the entire pattern of the process is changed since, quite differently from the wide-band case, characteristic rates of electron transfer emerge from the nonexponential decay of the state in the vicinity of the band edge. In most of the scattering experiment the characteristic times of electron transfer are larger than those of the hybridization switching on and off, i.e., a strongly nonadiabatic process is realized. In this case the deciding role in the final-atom charge-state formation is played by the region of small values of R, where electron transition processes

are most intensive. Thus, the switching on and switching off are momentary in the system time scale. The most simple model dependence $\lambda(t)$, which describes this situation, is $\lambda(t)=\theta(t)\theta(\tau-t)$, where τ is the characteristic time of the establishment of the interaction, $\tau=2a/v_\perp$ where $v_\perp$ is the normal component of the scattered particle's velocity and a is of the order of the valence-shell radius. At this distance the hopping-matrix element is saturated and exhibits a weak power-law dependence on the distance, which allows us to consider it to be constant in this region.

Besides, it was supposed that ε_a could be shifted only as a result of the interaction with band states. Hence, $\varepsilon_a(t)=$const for the model in question. It is the suggested type of the $\lambda(t)$ dependence that allowed us to derive an analytical expression for $n(+\infty)$ without any restrictions upon the behavior of $N(\varepsilon)$ and $|V_{k(\varepsilon)}|$.

Within the accepted model of the interaction the occupation of the atomic state is constant in the time intervals $t<0$ and $t>\tau$. Hence, $n(-\infty)=n(0)$ and $n(+\infty)=n(\tau)$. Thus the charge-exchange process is restricted to the time interval $0<t<\tau$. Within the specified time interval the Hamiltonian (1) is time independent ($\lambda\equiv 1$), so equations for the $\hat{a}(t)$ and $\hat{c}_k(t)$ operators in Heisenberg representation may be written as

$$i\frac{\partial\hat{a}(t)}{\partial t}=\varepsilon_a\hat{a}(t)+\frac{1}{\sqrt{V}}\sum_k V_k^*\hat{c}_k(t)\ ,$$
$$i\frac{\partial\hat{c}_k(t)}{\partial t}=\varepsilon(k)\hat{c}_k(t)+\frac{1}{\sqrt{V}}V_k\hat{a}(t)\ . \tag{3}$$

The set (3) must be complemented with boundary conditions:

$$\hat{a}(t)|_{t=0}=\hat{a}(0)\ ,$$
$$\hat{c}_k(t)|_{t=0}=\hat{c}_k(0)\ . \tag{4}$$

Assuming that for $t<0$ the electronic system of the solid was in equilibrium with temperature T, the initial occupation of the atomic level being given by $n_\sigma(-\infty)$, the initial conditions are determined as follows:

$$\langle\hat{a}_\sigma^\dagger(0)\hat{a}_\sigma(0)\rangle=n_\sigma(0)=n_\sigma(-\infty)\ ,$$
$$\langle\hat{c}_{k,\sigma}^\dagger(0)\hat{c}_{k,\sigma}(0)\rangle=n_k=\frac{1}{e^{[\varepsilon(k)-\mu]/T}+1}\ ,$$
$$\langle\hat{c}_{k,\sigma}^\dagger(0)\hat{c}_{k',\sigma'}(0)\rangle=0,\quad k,\sigma\neq k',\sigma'\ ,$$
$$\langle\hat{c}_{k,\sigma}^\dagger(0)\hat{a}(0)\rangle=0\ , \tag{5}$$

where $n_\sigma(-\infty)$ and $n_\sigma(+\infty)$ ($\sigma=\pm 1$) are occupation numbers of the atomic states defined by (2). Resolving the set (3) as written and for the conjugated operators with use of the initial conditions, (5) yields the desired value of $n(+\infty)$:

$$n(+\infty)=n(\tau)=[n_\uparrow(-\infty)+n_\downarrow(-\infty)]\left|\int_{-\infty}^{+\infty}\frac{d\omega}{2\pi}e^{-i\omega\tau}G_{aa}^r(\omega)\right|^2$$
$$+\frac{2}{V}\sum_k|V_k|^2n_k\left|\int_{-\infty}^{+\infty}\frac{d\omega}{2\pi}e^{-i\omega\tau}G_{aa}^r(\omega)G_{kk}^{r(0)}(\omega)\right|^2\ , \tag{6}$$

where $G_{aa}^r(\omega)$ is the equilibrium retarded Green function,

$$G_{aa}^r(\omega)=\frac{1}{\omega-\varepsilon_a+i\delta-\frac{1}{V}\sum_k\frac{|V_k|^2}{\omega-\varepsilon(k)+i\delta}} \tag{7}$$

(δ is a positive infinitesimal), $G_{kk}^{r(0)}(\omega)$ is the unperturbed Green function of an ideal Fermi gas,

$$G_{kk}^{r(0)}(\omega)=\frac{1}{\omega-\varepsilon(k)+i\delta}\ . \tag{8}$$

To separate out the effects due to band finiteness, the cases of empty ($n_k=0$) and filled ($n_k=1$) bands will be considered first. For those cases expression (6) yield

$$n(+\infty)=n(-\infty)|G_{aa}^r(\tau)|^2,\quad n_k=0\ , \tag{9}$$
$$n(+\infty)=n(-\infty)|G_{aa}^r(\tau)|^2+2[1-|G_{aa}^r(\tau)|^2]\ ,$$
$$n_k=1\ . \tag{10}$$

Expressions (9) and (10) imply that the dependence of $n(+\infty)$ on the interaction time τ is regulated by the singularities of $G_{aa}^r(z)$ in the lower half of the complex Z plane. Therefore, the problem is reduced to the task of the determination of analytic continuation of $G_{aa}^r(\omega)$ into the complex plane with subsequent integration. The contour of integration must be passed so as to avoid possible singularities.

Now let us apply the technique of analytic continuation of $G_{aa}^r(z)$ requiring only slightly restrictions upon $N(\varepsilon)$ and $V_{k(\varepsilon)}$. Namely, the $N(\varepsilon)$ and $V_{k(\varepsilon)}$ functions will be assumed to be analytic in the upper half of the Z plane and bounded in infinity. Consider the mass operator

$$M(\omega)=\int_{E_1}^{E_2}\frac{N(\varepsilon)|V_{k(\varepsilon)}|^2d\varepsilon}{\omega-\varepsilon+i\delta}=\int_1^2\frac{N(\xi)|V_{k(\xi)}|^2d\xi}{\omega-\xi}\ , \tag{11}$$

where integration is along segment 12 (Fig. 1) ($[E_1-i\delta, E_2-i\delta]$). E_1 and E_2 are the bottom and the top of the band. Let us assume that $\omega \in \mathrm{Re}$. Then the integrand in (11) is analytic within the semi-infinite strip enclosed by line segment 12 and half-lines C_1 and C_2. Therefore, contour 12 can be transformed as shown in Fig. 1 ($12 \rightarrow 1342$). When segment 34 is moved down, its contribution becomes infinitesimal, so we have

$$M(z)=\left[\int_{C_1}+\int_{C_2}\right]\frac{N(\xi)|V_{k(\xi)}|^2 d\xi}{Z-\xi} . \tag{12}$$

Now values of z with a negative imaginary part, including the interiors of the C_1C_2 strip may be allowed. Therefore, (12) defines an analytic function in the entire lower half-plane (excluding half-lines C_1 and C_2, where the function is discontinuous).

Let us consider the following function $G^r_{aa}(z)$:

$$G^r_{aa}(z)=\frac{1}{\omega-\varepsilon_a+i\delta-M(z)} . \tag{13}$$

Since the mass operator $M(z)$ is discontinuous at the rays C_1 and C_2, the function $G^r_{aa}(z)$ is discontinuous there, too. Above that, $G^r_{aa}(z)$ has poles with coordinates given by the equation

$$Z-\varepsilon_a=M(z) . \tag{14}$$

As an example, let us consider the case when there is only one pole in the $12C_1C_2$ strip with a finite nonzero imaginary part, corresponding to a quasistationary atomic state with coordinates $z=\Omega-i\Gamma$ ($\Gamma>0$). There also might be two poles out of the $12C_1C_2$ strip with infinitesimal imaginary parts, corresponding to split-off levels near the band edges. For these poles, which correspond to levels located out of the band (γ_i), Eq. (14) arrives at the following:

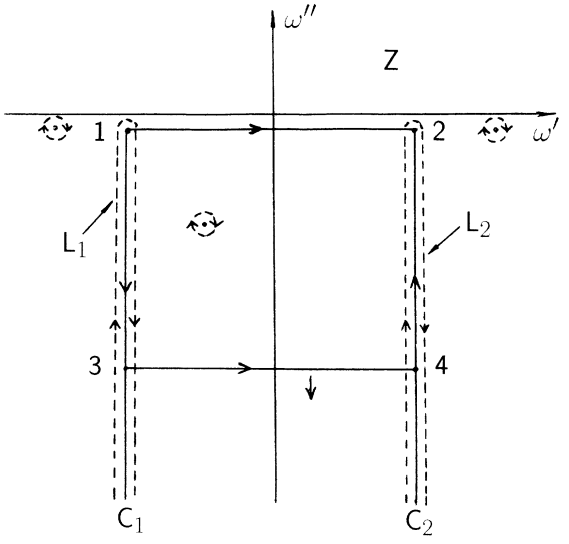

FIG. 1. The integration contour for the mass operator $M(z)$ (solid line) and the contour bypassing the singularities of $G^r_{aa}(z)$ (dashed line).

$$\gamma-\varepsilon_a=\int_{E_1}^{E_2}\frac{|V_{k(\varepsilon)}|^2 N(\varepsilon)d\varepsilon}{\gamma-\varepsilon} . \tag{15}$$

Note that level splitting of the band edge is a rare case with real-band spectra, occurring only if the electronic density of states has a finite nonzero value at the band edge.

Let us consider now the time dependence of G^r_{aa} on τ. The integration over ω is reduced to bypassing the poles and cuts in the lower half-plane (Fig. 1).

The result of the integration in case in question may be presented as

$$\begin{aligned}G^r_{aa}(\tau)=-i\{&\exp(-i\gamma_1\tau)A_1+\exp(-i\gamma_2\tau)A_2\\&+\exp(-i\Omega\tau)\exp(-\Gamma\tau)A_3\}\\&+\exp(-iE_1\tau)f_1(\tau)+\exp(-iE_2\tau)f_2(\tau) ,\end{aligned} \tag{16}$$

where A_1, A_2, A_3 are the residues in the poles of the $G^r_{aa}(z)$ function. The last two terms in (16) describe the contributions from the contours L_1 and L_2 designed to bypass the cuts C_1, C_2. Note that $f_1(\tau)$ and $f_2(\tau)$ decay slower than $e^{-\Gamma\tau}$ (nonexponential decay). For the three-dimensional spectrum, as an example, with the Van Hove peculiarities on the band edges being of square-root character, the above-mentioned behavior functions are like $1/\tau$ for large τ and are linearlike for small τ. Note that the last two terms in (16) may be interpreted as being related to effective states with energies equal to those of the band edges. The important point is that these states are long lived compared to the quasistationary states and thus may play a leading role in some processes, including the charge-exchange process. This always-present effect is the most dramatic among those arising from the finiteness of the bandwidth.

The final result of the interaction is the charge state of the atomic particle [as given by (9) and (10)] being found as interference of these states, with long-lived states predominating. As a result of this, the dependence of the atomic-state population on time or on reverse velocity will have a nonmonotonic oscillating shape. The frequencies of the constituent harmonics of this function will be given by the differences between the energies of the corresponding peculiarities.

The results obtained allow one to account for the variety of the experimental data, including the complicated data on ion scattering.[6] The authors of the latter have studied the changes of the charge state of N^+ ions scattered from the surface of NaCl crystals. The unpopulated $2p$ level of N^+ ($\varepsilon_a=14.7$ eV) falls within the filled $3p$ surface band of Cl near its lower edge E_1 ($E_1-\varepsilon_a\cong 1$ eV). The width of the band is $E_1-E_2\cong 7$ eV. An example of the dependence of the intensity of N^+ ions scattered elastically from Cl atoms on N^+ energy is given in Fig. 2.

The emergence of the oscillations in the N^+-ion yield, which are considerably different both in magnitude and frequency, may be explained as follows: The level Ω originating from the atomic level ε_a is pushed out of the band and becomes localized, that is, the $G^r_{aa}(z)$ function has no poles corresponding to states which fall within the band. In this case, splitting of a level off the upper band edge

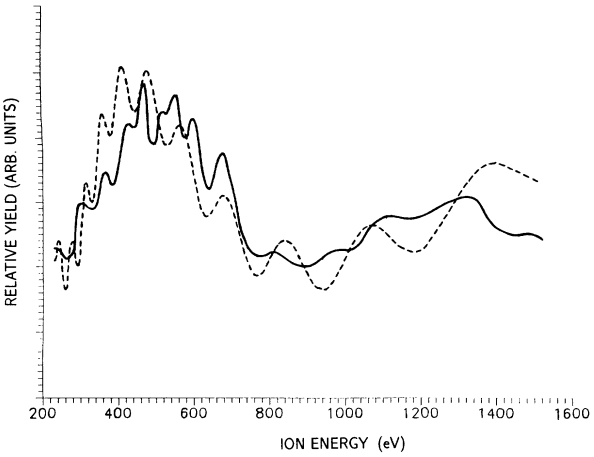

FIG. 2. The energy dependence of the relative yield of the N^+ ions elastically scattered from Cl atoms of an NaCl crystal. Solid line, experimental data. Dashed line, calculation using (17) with parameters $\Omega-E_1=1$ eV, $E_1-E_2=7$ eV.

($\gamma\cong E_2$) also occurs. Above those mentioned, the $G^r_{aa}(\tau)$ function will contain terms corresponding to effective states E_1 and E_2. Note that the weights of the γ and E_2 states in $G^r_{aa}(\tau)$ will be small in proportion to the value of $N(\varepsilon)|V_{k(\varepsilon)}|^2/(\varepsilon_a-E_2)$. The charge state of the atomic particle will result from the interference of the terms listed in (16). Consequently, the resulting dependence $n(\tau)$ will have oscillations with frequencies $\Omega-E_1$, $\Omega-E_2$, $\Omega-\gamma$, E_1-E_2, and $\gamma-E_2$. However, $\gamma\cong E_2$ and the amplitude of both these states is small, therefore these components will not be observable. The oscillations $\Omega-E_2$, $\Omega-\gamma$, and E_1-E_2 have high and nearly equal frequencies. Thus, for the probability W of the survival of the initial N^+-ion state we have

$$W=B_1(\tau)\cos[(\Omega-E_1)\tau+\varphi_1] +B_2(\tau)\cos[(E_1-E_2)\tau+\varphi_2] , \tag{17}$$

where $B_1>B_2$, $\Omega-E_1<E_1-E_2$. This is just the dependence that was observed in the experiments mentioned. The calculated function W [τ (being the kinetic energy)] is presented in Fig. 2 (dashed line).

Finally, let us deal with the case of the partially occupied band. To separate out the effects associated with partial occupation of the band, we will now set aside the effects resulting from band finiteness. Thus, we may use the wide-band approximation,

$$N(\varepsilon)=\text{const}=N_0, \quad |V_k|^2=\text{const}=V_0^2 . \tag{18}$$

And for the mass operator

$$M(\omega)=\frac{1}{V}\sum_k |V_k|^2\frac{1}{\omega-\varepsilon(k)+i\delta} , \tag{19}$$

we have $M(\omega)=-i\Gamma$, where $\Gamma=\pi V_0^2 N_0$.

Then for $G^r_{aa}(\omega)$ we have

$$G^r_{aa}(\omega)=\frac{1}{\omega-\varepsilon_a+i\Gamma} . \tag{20}$$

Substitution of (20) into expression (6) for $n(+\infty)$ yields

$$n(+\infty)=n(-\infty)\exp(-2\Gamma\tau)+\frac{2\Gamma}{\pi}\int_{-\infty}^{+\infty}\frac{d\varepsilon}{e^{\varepsilon/T}+1}\frac{1}{(\varepsilon-\varepsilon_a)^2+\Gamma^2} \times(1+\exp(-2\Gamma\tau)-\exp(-\Gamma\tau)\{\exp[i(\varepsilon-\varepsilon_a)\tau]+\exp[-i(\varepsilon-\varepsilon_a)\tau]\}) , \tag{21}$$

where energies are reckoned from the Fermi level.

In the $T\gg\Gamma$ case, (21) arrives at

$$n(+\infty)=n(-\infty)e^{-2\Gamma\tau} +2[\exp(\varepsilon_a/T)+1]^{-1}(1-e^{-2\Gamma\tau}) . \tag{22}$$

Note that (22) may be deduced from the classical rate equation.[7]

In the $T\ll\Gamma$ case, to make the analysis of (21) easier, let $T=0$. In the case $\varepsilon_a=0$ we have

$$n(+\infty)=n(-\infty)e^{-2\Gamma\tau}+(1-e^{-2\Gamma\tau}) . \tag{23}$$

In the case $\varepsilon_a\gg\Gamma>0$ we have

$$n(+\infty)=n(-\infty)e^{-2\Gamma\tau} +\frac{2\Gamma}{\pi\varepsilon_a}\left[1+e^{-2\Gamma\tau} -2e^{-\Gamma\tau}\varepsilon_a\tau\int_{\varepsilon_a\tau}^{+\infty}\frac{\cos(\xi)}{\xi}d\xi\right] . \tag{24}$$

From (24) it is seen that once the interaction time is sufficiently large ($\tau>\hbar/\varepsilon_a$), in the $n(+\infty)$ dependence on τ an oscillating term $e^{-\Gamma\tau}\sin(\varepsilon_a\tau)/\varepsilon_a\tau$ emerges. Similar results are realized in the case $\varepsilon_a<0$, $|\varepsilon_a|\gg\Gamma$. Note that the emergence of oscillations in $n(+\infty)$ dependence on τ is a manifestation of the effect of the quantum interference of the amplitudes. The presence of a sharp cutoff in the Fermi distribution and the difference between the energy ε_a and the Fermi energy lead to incomplete compensation of probability amplitudes, which leads to the resulting phase shift. That is, the resulting oscillations are of the same nature as those of the density-correlation function in the degenerate case or Friedel oscillations.[8]

In summary, the most dramatic effect among those due to the finiteness of the bandwidth is the occurrence of "effective states" with energies equal to those of band edges. The charge state of a scattered atomic particle is the result of the interference between these effective states and quasistationary and localized states, which arise from the interaction of the particle with the solid surface. It is

this interference that leads to oscillations in the dependence of the charge state of the scattered particle on its kinetic energy. The oscillations of the charge state due to the presence of a sharp cutoff in the electronic distribution at the Fermi level in the degenerate case (which are essentially similar to Friedel oscillations[8]) seem most unlikely to be observed experimentally, since they are a fast-decay function of the interaction time, in contrast to those mentioned above, which are due to band finiteness.

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