

Effect of band spectrum singularities on the charge transfer of atoms colliding with a surface

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We use the time-dependent Anderson–Newns model to consider the charge-transfer effect of atoms scattered by the surface of a solid. Our choice of a model time dependence of the hybridization matrix element of the band and atomic states makes it possible to analyze the case of an arbitrary shape of the band spectrum. We show that the charge state of a scattered atomic particle is a non-monotonic (generally speaking, oscillating) function of its energy. We use the results to explain known experimental results.

1. Recently the problem of the charge transfer from atoms and molecules scattered by the surface of a solid has been the subject of many experimental and theoretical studies (see, e.g., the detailed survey in Ref. 1). The interest is caused above all by the fact that scattering data contain valuable information both about the composition and the structure of the surface as well as about the electronic properties of the crystal itself which plays the role of the target. From a theoretical point of view the crux of the problem consists of the following.

We consider an atom A which is in some initial charge state. As a result of the scattering of this atom by the surface of the target T the charge state may be changed. If the atom approaches the surface sufficiently closely electrons may by virtue of the overlap of the atomic and crystal wave functions move from the solid to the atom and vice versa. We must determine the charge state of the atom after the scattering as a function of the energy of the incident particles. In other words, we are dealing with the calculation of the probability for charge transfer in processes such as $A^+ + M \rightarrow A + M^+$, or $A + M \rightarrow A^+ + M^-$.

The simplest model describing the process of charge transfer during elastic scattering of an atom by a surface is the time-dependent Anderson–Newns model.^{2,3} According to this model the atom A corresponds to a single-level system (one neglects excited states of the atom) interacting with the Bloch states of the crystal.

The Hamiltonian of the model has the form:

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

where $\hat{c}_{\mathbf{k}, \sigma}^+, \hat{a}_{\sigma}^+$ ($\hat{c}_{\mathbf{k}, \sigma}, \hat{a}_{\sigma}$) are the creation (annihilation) operators for electrons with spin σ in a Bloch state $|\mathbf{k}\rangle$ and in the nondegenerate atomic state $|a\rangle$, respectively, $R(t)$ is the distance between the atom and the surface at the time t (the motion of the atom is assumed to be classical), $\varepsilon(\mathbf{k})$

is the energy of the band electrons, $\varepsilon_a(R(t))$ is the position of the atomic energy level at time t , and $\lambda(R(t)) V_{\mathbf{k}}$ is the hybridization matrix element of the band and atomic states, normalized to the volume V of the system. We assume that we have $R = v_{\perp} |t|$, v_{\perp} is the velocity component perpendicular to the crystal surface, $\lambda(t)$ decreases exponentially as $R(t) \rightarrow \infty$, and $\varepsilon_a(\pm \infty) = -I$, where I is the ionization potential of an isolated atom. The charge state is simply determined by the average number of electrons in the state $|a\rangle$:

$$n(t) = \sum_{\sigma} \langle \hat{a}_{\sigma}^+(t) \hat{a}_{\sigma}(t) \rangle.$$

Blandin *et al.*⁴ using Keldysh's diagram technique⁵ and also Brako and Newns⁶ in the framework of the equations of motion for the Heisenberg operators have shown that this problem can be solved in the general form if one assumes that the density of states $N(\varepsilon)$ and the matrix element $V_{\mathbf{k}(\varepsilon)}$ are independent of the energy ε ($N(\varepsilon) = N_0 = \text{const}$, $V_{\mathbf{k}(\varepsilon)} = V_0 = \text{const}$) in the whole of the infinite energy range (broad band approximation).

This approximation is valid only when

a) the atomic level ε_a lands in the allowed part of the spectrum and the maximum width of the level $2\Gamma(t=0)$, which is connected with the finite lifetime of the electron in the state $|a\rangle$, is much smaller than the "distance" ΔE between ε_a and the edge of the allowed band;

b) the density of states $N(\varepsilon)$ and the matrix element $V_{\mathbf{k}(\varepsilon)}$ do not change appreciably on a scale Γ ;

c) the time scale δt for changes in the hybridization is large, i.e., $\delta t \Delta W \gg 1$, where ΔW is the width of the band.

In a number of cases (metals with a complicated density of states, narrow-band metals, narrow-gap semiconductors, high-velocity incident particles) these conditions are not satisfied. Moreover, the situation when the level ε_a lands in the forbidden band (this occurs, e.g., when He^+ ions are scattered from a Pb surface) is not even qualitatively described by this approximation.

There is therefore undoubtedly interest in an analysis of the general situation without any restrictions on the

shape of the spectrum or the position of the atomic level.

The aim of the present paper is such an analysis. In our considerations we shall, in contrast to the authors of Refs. 4 and 6, not start from definite functions $\varepsilon_a(t)$ and $\lambda(t)$ but assume that $\varepsilon_a(t) = \text{const} = \varepsilon_a$, and that $\lambda(t)$ is a step function

$$\lambda(t) = \theta(t)\theta(t-\tau), \quad \theta(t) = \begin{cases} 1, & t > 0, \\ 0, & t < 0, \end{cases} \quad (2)$$

where τ is the characteristic interaction time.

Just this model function $\lambda(t)$ makes it possible for us to carry out our considerations in a general form, i.e., to obtain an analytical expression for $n(\infty)$ without imposing any restrictions on the form of the density of states or the position of the atomic level. Moreover, the choice of such a dependence for the switching on (and switching off) the hybridization has a physical basis. Indeed, electronic tunneling processes become important only when the atom approaches the surface to a distance of the order of the size a_0 of the atomic orbitals. Just this region gives the main contribution to the charge transfer. Moreover, since in that region the hybridization matrix element depends only weakly on the time (saturation of the hybridization) we may assume the interaction to be adiabatic, which leads to the formation of quasistationary energy states of the atom-crystal system. The characteristic interaction time is thus $\tau = \alpha a_0 / v_1$, where α is a constant which plays the role of a fitting parameter. We shall neglect the tunneling time outside this time range. However, we consider in what follows also the effect of the exponential "tails" of switching on and off the hybridization.

2. We now turn to a determination of $n(\infty)$. The average number of electrons in the state $|a\rangle$ at time t is given by the following expression:

$$\langle \hat{n}(t) \rangle = \text{Sp}\{\hat{\rho}(t)\hat{n}\} = \text{Sp}\{\hat{\rho}(0)\hat{n}(t)\}, \quad (3)$$

where $\hat{\rho}(0)$ is the statistical operator at time $t=0$ and

$$\hat{n}(t) = \sum_{\sigma} \hat{a}_{\sigma}^{+}(t)\hat{a}_{\sigma}(t)$$

is the Heisenberg operator of the number of particles:

$$\hat{n}(t) = \hat{T} \exp\left[i \int_0^t \hat{H}(t') dt'\right] (\hat{n}_+ + \hat{n}_-) \hat{T} \\ \times \exp\left[-i \int_0^t \hat{H}(t') dt'\right]. \quad (4)$$

Here the \hat{n}_{\pm} correspond to opposite spin orientations, \hat{T} and \hat{T} are the chronological ordering and antiordeing operators, $\hat{H}(t)$ is the Hamiltonian (1), and we have put $\hat{n} \equiv 1$.

According to the assumed model for the interaction the number of electrons on the atom remains unchanged for times $t < 0$ and $t > \tau$. Therefore we have $n(-\infty) = n(0)$ and $n(\infty) = n(\tau)$. From the point of view of charge transfer we are thus only interested in the $0 < t < \tau$ time interval. Since in that interval the Hamiltonian is time-independent ($\lambda=1$) we can drop in Eq. (4) the chronological ordering operator and integrate over the time in the exponents. The

next step in the calculations consists of the following. Using the equation of motion for the Heisenberg operators $\hat{a}^{+}(t)$ and $\hat{a}(t)$ we can express them in terms of the operators \hat{a}^{+} , $\hat{c}_{\mathbf{k}}^{+}$ and \hat{a} , $\hat{c}_{\mathbf{k}}$ at time $t=0$. Then, substituting the expressions obtained into Eq. (3) and using the initial conditions:

$$\langle \hat{a}_{\sigma}^{+}(0)\hat{a}_{\sigma}(0) \rangle = n_{\sigma}(0) = n_{\sigma}(-\infty), \\ \langle \hat{c}_{\mathbf{k},\sigma}^{+}(0)\hat{c}_{\mathbf{k},\sigma}(0) \rangle = n_{\mathbf{k}} = \frac{1}{\exp\{\beta[\varepsilon(\mathbf{k}) - \mu]\} + 1}, \\ \langle \hat{c}_{\mathbf{k},\sigma}^{+}(0)\hat{c}_{\mathbf{k}',\sigma'}(0) \rangle = 0, \quad \mathbf{k}, \sigma \neq \mathbf{k}', \sigma', \\ \langle \hat{c}_{\mathbf{k},\sigma}^{+}(0)\hat{a}(0) \rangle = 0, \quad (5)$$

where $\beta = 1/T$ is the inverse temperature of the electron gas and μ is the chemical potential, we get the required quantity $\langle \hat{n}(t) \rangle$.

We illustrate what we have said by the example of the equation of motion for $\hat{a}(t)$. This equation has the form ($t > 0$)

$$i \frac{\partial \hat{a}(t)}{\partial t} = \varepsilon_a \hat{a}(t) + \frac{1}{\sqrt{V}} \sum_{\mathbf{k}} V_{\mathbf{k}}^{*} \hat{c}_{\mathbf{k}}(t). \quad (6)$$

In turn, we get for the operator $\hat{c}_{\mathbf{k}}(t)$

$$i \frac{\partial \hat{c}_{\mathbf{k}}(t)}{\partial t} = \varepsilon(\mathbf{k}) \hat{c}_{\mathbf{k}}(t) + \frac{1}{\sqrt{V}} V_{\mathbf{k}} \hat{a}(t). \quad (7)$$

We must add to the set of Eqs. (6) and (7) the boundary conditions

$$\hat{a}(t)|_{t=0} = \hat{a}(0), \quad \hat{c}_{\mathbf{k}}(t)|_{t=0} = \hat{c}_{\mathbf{k}}(0). \quad (8)$$

It is convenient to solve the set obtained in the Fourier representation. However, to do this we need define the operators $\hat{a}(t)$ and $\hat{c}_{\mathbf{k}}(t)$ on the whole of the time axis. We put $\hat{a}^{+}(t) \equiv 0$ and $\hat{c}_{\mathbf{k}}(t) \equiv 0$ for $t < 0$. To satisfy the boundary conditions (8) we must then add to the right-hand sides of Eqs. (6) and (7) the terms $i\hat{a}(0)\delta(t)$ and $i\hat{c}_{\mathbf{k}}(0)\delta(t)$, respectively. Changing to the Fourier representation we find

$$\hat{a}(\omega) = i \left[\hat{a}(0) + \frac{1}{\sqrt{V}} \sum_{\mathbf{k}} \frac{V_{\mathbf{k}}^{*} \hat{c}_{\mathbf{k}}(0)}{\omega - \varepsilon(\mathbf{k}) + i\delta} \right] \\ \times \left[\omega - \varepsilon_a + i\delta - \frac{1}{V} \sum_{\mathbf{k}} \frac{|V_{\mathbf{k}}|^2}{\omega - \varepsilon(\mathbf{k}) + i\delta} \right]^{-1}, \quad (9)$$

where $\delta > 0$ is an infinitesimally small quantity which has been added to guarantee the analyticity of $\hat{a}(\omega)$ in the upper ω half-plane (thus guaranteeing that the conditions $\hat{a}(t) \equiv 0$ and $\hat{c}_{\mathbf{k}}(t) \equiv 0$ are satisfied for $t < 0$).

One should note that $\hat{a}(\omega)$ can be expressed in terms of the equilibrium retarded Green function

$$G_{aa}^r(\omega) = \left[\omega - \varepsilon(\mathbf{k}) + i\delta - \frac{1}{V} \sum_{\mathbf{k}} \frac{|V_{\mathbf{k}}|^2}{\omega - \varepsilon(\mathbf{k}) + i\delta} \right]^{-1} \quad (10)$$

and the unperturbed Green function of an ideal Fermi gas:

$$G_{\mathbf{k}\mathbf{k}}^{r(0)}(\omega) = \frac{1}{\omega - \varepsilon(\mathbf{k}) + i\delta}. \quad (11)$$

One can similarly find the quantity $\hat{a}^+(\omega)$. Performing the inverse Fourier transformation and using (5) we get the required quantity:

$$\begin{aligned} n(\infty) &= n(\tau) \\ &= [n_1(-\infty) + n_1(-\infty)] \\ &\times \left| \int_{-\infty}^{\infty} \frac{d\omega}{2\pi} e^{-i\omega\tau} G_{aa}^r(\omega) \right|^2 + \frac{2}{V} \sum_{\mathbf{k}} |V_{\mathbf{k}}|^2 \\ &\times n_{\mathbf{k}} \left| \int_{-\infty}^{+\infty} \frac{d\omega}{2\pi} e^{-i\omega\tau} G_{aa}^r(\omega) G_{\mathbf{k}\mathbf{k}}^{r(0)}(\omega) \right|^2. \end{aligned} \quad (12)$$

One should note that the expression for $n(\infty)$ is obtained without any assumptions about the shape of the band spectrum and the position of the ε_a level. The terms in the right-hand side of (12) have a clear physical meaning. The first term describes the transition of the electrons from the electron state $|a\rangle$ to the free Bloch states $|\mathbf{k}\rangle$. The second term describes the inverse transition. We now turn to an analysis of Eq. (12) in the case of a specified shape of the band spectrum.

3. We start our considerations with the broad-band case. We must then, according to Refs. 4 and 6, assume that the density of states is $N(\varepsilon) = \text{const} = N_0$ and that $|V_{\mathbf{k}}|^2 = \text{const} = V_0^2$.

For the mass operator

$$M(\omega) = \frac{1}{V} \sum_{\mathbf{k}} |V_{\mathbf{k}}|^2 \frac{1}{\omega - \varepsilon(\mathbf{k}) + i\delta}; \quad (13)$$

we therefore have

$$M(\omega) = -i\Gamma, \quad (14)$$

where $\Gamma = \pi V_0^2 N_0$ is the halfwidth of the resonance level ε_a . As a result we get for the "atomic" Green function $G_{aa}^r(\omega)$

$$G_{aa}^r(\omega) = \frac{1}{\omega - \varepsilon_a + i\Gamma}. \quad (15)$$

Substituting (15) into Eq. (12) for $n(\infty)$ we find that:

$$\begin{aligned} n(\infty) &= [n_1(-\infty) + n_1(-\infty)] e^{-2\Gamma\tau} + \frac{2\Gamma}{\pi} \int_{-\infty}^{+\infty} d\varepsilon \\ &\times \frac{1 + e^{-2\Gamma\tau} - e^{-\Gamma\tau} [e^{i(\varepsilon - \varepsilon_a)\tau} + e^{-i(\varepsilon - \varepsilon_a)\tau}]}{(e^{\beta\varepsilon} + 1) [(\varepsilon - \varepsilon_a)^2 + \Gamma^2]}. \end{aligned} \quad (16)$$

The energy values are reckoned from the chemical potential of the system.

One checks easily from Eq. (16) that there are two characteristic temperature regions, $T \gg \Gamma$ and $T \ll \Gamma$ in which the behavior of $n(\infty)$ is essentially different.

We first consider the $T \gg \Gamma$ case. One can in this case take the fermion distribution function from under the integral sign, putting $\varepsilon = \varepsilon_a$ in it. One can easily get the remaining integral. As a result we get

$$\begin{aligned} n(\infty) &= [n_1(-\infty) + n_1(-\infty)] e^{-2\Gamma\tau} \\ &+ \frac{2(1 - e^{-2\Gamma\tau})}{e^{\beta\varepsilon_a} + 1}. \end{aligned} \quad (17)$$

We note that this result could have been obtained also from the classical kinetic equation.⁷

We now consider the opposite case, $T \ll \Gamma$. For simplicity we shall assume that $T = 0$. Only electrons with an energy $\varepsilon < 0$ will then contribute to the integral in Eq. (16). One can relatively easily give an analysis for three limiting cases: $\varepsilon_a = 0$; $\varepsilon_a > 0$ and $\varepsilon_a \gg \Gamma$; and $\varepsilon_a < 0$ and $|\varepsilon_a| \gg \Gamma$ (recall that the energy is reckoned from the Fermi level of the system). For instance, in the $\varepsilon_a = 0$ case one can easily evaluate the integral in (16) and get the following result:

$$n(\infty) = n(-\infty) e^{-2\Gamma\tau} + (1 - e^{-2\Gamma\tau}). \quad (18)$$

In the $\varepsilon_a \gg \Gamma > 0$ case we get:

$$\begin{aligned} n(\infty) &= n(-\infty) e^{-2\Gamma\tau} + \frac{2\Gamma}{\pi\varepsilon_a} \\ &\times \left(1 + e^{-2\Gamma\tau} - 2e^{-\Gamma\tau} \varepsilon_a \tau \int_{\varepsilon_a\tau}^{+\infty} \frac{\cos \xi}{\xi^2} d\xi \right). \end{aligned} \quad (19)$$

It is clear from (19) that if the interaction time τ is sufficiently long ($\tau > 1/\varepsilon_a$), $n(\infty)$ as function of τ becomes oscillatory: $e^{-\Gamma\tau} \sin(\varepsilon_a\tau)/\varepsilon_a\tau$. One obtains similar results for the $\varepsilon_a < 0$, $|\varepsilon_a| \gg \Gamma$ case.

We note that the appearance of an oscillatory behavior in $n(\infty)$ is a manifestation of the effect of the quantum interference of the amplitudes. The presence of a sharp Fermi boundary and a shift in the energy relative to the Fermi level leads to the probability amplitudes not completely canceling one another (the result is a phase shift). In that sense the picture obtained here is very reminiscent of a diffraction picture.

In conclusion we note that these results may be obtained from Ref. 6 for the case of a stepwise time-dependence of the hybridization.

4. We now consider the case of a finite band. It follows from Eq. (12) that $n(\infty)$ as a function of the interaction time τ is determined by the singularities of the function $G_{aa}^r(\omega)$ in the lower half-plane of the complex z plane. The problem reduces therefore to the analytical continuation of $G_{aa}^r(\omega)$ from the real axis into the lower z half-plane and the subsequent integration along a contour bypassing possible singularities.

For simplicity we shall consider the case of an empty ($n_{\mathbf{k}} = 0$) or a completely occupied ($n_{\mathbf{k}} = 1$) band. Using the commutation relation $\hat{a}^+(\tau)\hat{a}(\tau) + \hat{a}(\tau)\hat{a}^+(\tau) = 1$ we then get from (12):

$$\begin{aligned} n(+\infty) &= n(-\infty) \\ &\times \begin{cases} |G_{aa}^r(\tau)|^2, & n_{\mathbf{k}} = 0, \\ |G_{aa}^r(\tau)|^2 + 2(1 - |G_{aa}^r(\tau)|^2), & n_{\mathbf{k}} = 1. \end{cases} \end{aligned} \quad (20a)$$

$$(20b)$$

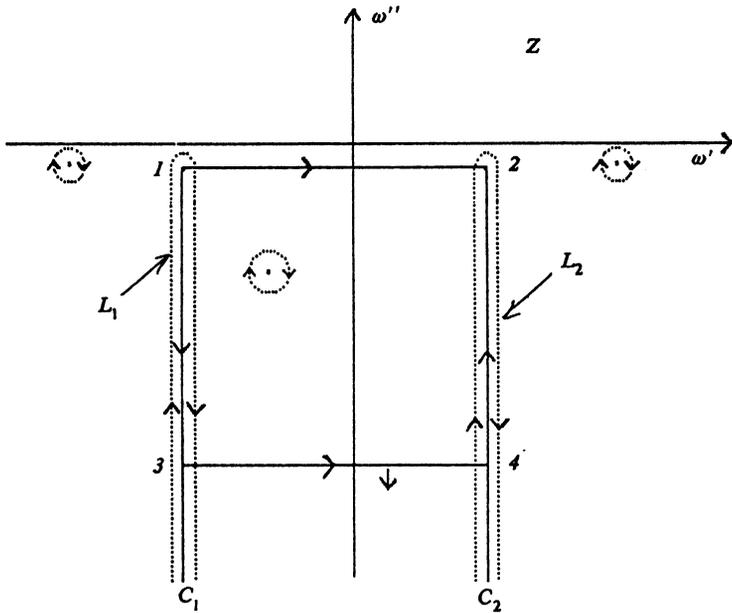


FIG. 1. Integration contour for the mass operator $M(z)$ (solid line) and the way to go round the singularities of the function $G'_{aa}(z)$ (dashed line).

The simplest way to carry out the analytical continuation consists in replacing ω by the complex $z = \omega' + i\omega''$ in the expression for $G'_{aa}(\omega)$. We then obtain a function $G'_{aa}(z)$ which is analytical in the whole of the z plane except for the section $[E_1 - i\delta, E_2 - i\delta]$ (E_1 and E_2 are here the energies of the band edges) and, possibly, for two poles with an infinitesimally small imaginary part $-i0$ and energies lying outside the allowed energy range. The condition for the appearance of such poles is determined by the presence of solutions of the equation:

$$E - \varepsilon_a = \text{V.P.} \int_{E_1}^{E_2} \frac{d\varepsilon |V_{k(\varepsilon)}|^2 N(\varepsilon)}{E - \varepsilon} \quad (21)$$

under the conditions that E lies outside the $[E_1, E_2]$ interval. The temporal behavior is thus determined by the residues from the poles and the integral over a contour enclosing the section $[E_1 - i\delta, E_2 - i\delta]$. The further analysis of the time dependence is thus reduced to calculating the contour integral by numerical methods. However, from the point of view of a qualitative analysis the nature of the temporal behavior of $G'_{aa}(\tau)$ remains unclear. In particular, there is no concept of a "resonance width" (or of a decay time of the state) in the approach considered here, so that the function $G'_{aa}(z)$ has no pole with a finite imaginary part in the lower z halfplane. All the information about the decay of the state is contained in the contour integral. The limitations of such an approach, from the point of view of a qualitative analysis, are particularly clear when we turn to the broad-band case ($E_1 \rightarrow -\infty, E_2 \rightarrow \infty$). In that limiting case there is a cut ($-\infty - i\delta, \infty - i\delta$) in the function $G'_{aa}(z)$ and it breaks, in fact, up into two analytical functions above and below the cut. Since the integration over ω is over the real axis, i.e., above the cut, the calculation of $G'_{aa}(\tau)$ again reduces to an integral over a contour enclosing the cut.

In the framework of the analytical continuation considered here we lose therefore clear ideas about the finite

life time of the quasi-particle state. We therefore consider another way to continue G'_{aa} which is applicable under rather general assumptions about the shape of the functions $N(\varepsilon)$ and $V_{k(\varepsilon)}$. It is convenient to demonstrate this method for the case of a rectangular spectrum which is of practical importance. Such a form of the spectrum corresponds to a situation where the atomic state ε_a interacts with a two-dimensional band of surface states (for the two-dimensional case the Van Hove singularities at the band edges have the form of steps).

We shall assume that $V_k = V_0 = \text{const}$ (we assume that the interaction $V(\mathbf{r})$ in coordinate space has a pointlike character). The density of states $N(\varepsilon)$ has the form:

$$N(\varepsilon) = \begin{cases} N_0, & E_1 < \varepsilon < E_2, \\ 0, & \varepsilon < E_1, \quad \varepsilon > E_2. \end{cases} \quad (22)$$

We consider the mass operator

$$M(z) = N_0 V_0^2 \int_1^2 \frac{d\tilde{z}}{z - \tilde{z}}, \quad (23)$$

where the integration is over the section 12 ($[E_1 - i\delta, E_2 - i\delta]$) (Fig. 1). We shall assume that z lies outside the band bounded by the segment 12 and the half-lines C_1 and C_2 . The integrand in (23) is then analytical inside this band. We can therefore deform the contour as shown in Fig. 1 (12 \rightarrow 1342). Lowering the section 34 to infinity and taking into account that the contribution from that section tends to zero we find that:

$$M(z) = N_0 V_0^2 \left(\int_{C_1} + \int_{C_2} \right) \frac{d\tilde{z}}{z - \tilde{z}}. \quad (24)$$

We can now postulate that the value of z can lie inside the band, i.e., we can continue the function $M(z)$ inside the region 12 C_1C_2 . Expression (24) thus defines an ana-

lytical function in the whole of the Z plane except the half-lines C_1 and C_2 (on which it has a discontinuity). Evaluating the integrals over the contours C_1 and C_2 we obtained:

$$M(z) = g \ln \left(\frac{z - E_1 + i\delta}{z - E_2 + i\delta} \right), \quad (25)$$

where $g = N_0 V_0^2$.

Let us consider the function $G_{aa}^r(z)$. Since the mass operator $M(z)$ has discontinuities on the contours C_1 and C_2 , it follows that $G_{aa}^r(z)$ must also have discontinuities. Moreover, for the function $G_{aa}^r(z)$ there occurs a pole in the lower half-plane with a finite imaginary part and an energy in the interval $[E_1, E_2]$ (provided the bare energy ε_a lies inside that range). The coordinates of the pole are determined by the roots of the equation $z - \varepsilon_a = M(z)$. We put $z = \Omega - i\Gamma$ with $\Gamma > 0$. The equations for the coordinates of the pole then take the form:

$$\begin{aligned} \Omega - \varepsilon_a &= \frac{g}{2} \ln \frac{(\Omega - E_1)^2 + \Gamma^2}{(\Omega - E_2)^2 + \Gamma^2}, \\ \Gamma &= g \left[\text{sign}(\Omega - E_1) \left(\frac{\pi}{2} + \text{arctg} \frac{\Gamma}{|\Omega - E_1|} \right) \right. \\ &\quad \left. - \text{sign}(\Omega - E_2) \left(\frac{\pi}{2} + \text{arctg} \frac{\Gamma}{|\Omega - E_2|} \right) \right]. \end{aligned} \quad (26)$$

It follows from an analysis of Eqs. (26) that there is not always a solution of this set; the level ε_a must lie sufficiently far from the band edges:

$$|E_{1,2} - \varepsilon_a| \gg \frac{g}{2} \ln \frac{(E_1 - E_2)^2 + \pi^2 g^2}{\pi^2 g^2}.$$

In the broad-band limit ($E_1 \rightarrow -\infty, E_2 \rightarrow \infty$) the coordinates of the pole become $\Omega = \varepsilon_a, \Gamma = \pi g$, i.e., they are the same as those found above [see (14) and (15)].

The set of Eqs. (26) refers to the case when the real part of Ω lies inside the allowed part of the spectrum. For poles outside this range the equations for the coordinates have the form:

$$\Omega - \varepsilon_a = g \ln \left| \frac{\Omega - E_1}{\Omega - E_2} \right|, \quad \Gamma = +0. \quad (27)$$

We note that condition (27) is the same as (21). This is not surprising since a deformation of the contour 12 does not change the values of the function $M(z)$ [and hence also of $G_{aa}^r(z)$] outside the band $12C_1C_2$. We should stress that conditions (27) [and in the general case condition (21)] determine the coordinates of the pole only outside the limits of the continuous spectrum. In other words, if there are solutions of Eq. (21) with Ω lying inside the range $[E_1, E_2]$ they do not correspond to any singularities of the function $G_{aa}^r(z)$. It follows from (27) that in the case of a rectangular spectrum there always exist two poles with zero damping (localized states). This fact that for any however

weak interaction of the atomic level with the band, levels are split off from the band edges is a manifestation of the special features of a two-dimensional (or one-dimensional) spectrum when however close we get to the limit of the spectrum there is still a finite density of states.

We now consider the dependence of G_{aa}^r on the interaction time τ . Integration over ω reduces to going around the poles and the cuts C_1 and C_2 in the lower Z half-plane. We can write the result of the integration in the form:

$$\begin{aligned} G_{aa}^r(\tau) &= -i(A_1 e^{-i\Omega_1 \tau} + A_2 e^{-i\Omega_2 \tau} + A_3 e^{-i\Omega_3 \tau} e^{-\Gamma \tau}) \\ &\quad + f_1(\tau) e^{-iE_1 \tau} + f_2(\tau) e^{-iE_2 \tau}. \end{aligned} \quad (28)$$

Here the $A_{1,2,3}$ are the residues from the poles of $G_{aa}^r(z)$:

$$A_{1,2} = \left[1 + g \frac{\Delta W}{(\Omega_{1,2} - E_1)(\Omega_{1,2} - E_2)} \right]^{-1}, \quad (29)$$

where we have $\Delta W = E_1 - E_2$, the $\Omega_{1,2}$ are the roots of Eq. (27), and

$$A_3 = \left[1 + g \frac{\Delta W}{(\Omega_3 - i\Gamma - E_1)(\Omega_3 - i\Gamma - E_2)} \right]^{-1}, \quad (30)$$

where Ω_3 and Γ are the roots of Eqs. (26).

The last two terms in Eq. (28) describe the contribution from the integrals over the contours L_1 and L_2 (see Fig. 1),

$$\begin{aligned} f_{1,2}(\tau) &= \mp \int_0^{+\infty} d\xi e^{-\xi \tau} \left\{ \left[-i\xi - (\varepsilon_a - E_{1,2}) \right. \right. \\ &\quad \left. \mp \frac{g}{2} \ln \frac{\xi^2}{\xi^2 + \Delta W^2} + ig \left(\frac{\pi}{2} + \text{arctg} \frac{|\xi|}{\Delta W} \right) \right\}^2 \\ &\quad \left. + \pi^2 g^2 \right\}^{-1}. \end{aligned} \quad (31)$$

In the case of a weak interaction of the atomic level ε_a with the continuous spectrum ($g/|\varepsilon_a - E_{1,2}| \ll 1$) the term $A_3 e^{-i\Omega_3 \tau} e^{-\Gamma \tau}$ is the leading one and, hence, the decay of the state is basically exponential. In the case of intermediate coupling constants ($g \sim (\varepsilon_a - E_{1,2})$) all terms (28) are quantities of the same order of magnitude. Moreover, since the functions $f_{1,2}(\tau)$ decrease for large times more slowly, generally speaking, than the exponential, the contribution from the singularities at the limits of the spectrum are for $\tau \gg 1/\Gamma$ larger than the corresponding contribution from the pole singularity. For interaction times when $\tau \gg 1/\Gamma$ ($\Gamma \sim g$) we have thus

$$\begin{aligned} G_{aa}^r(\tau) &= -i(A_1 e^{-i\Omega_1 \tau} + A_2 e^{-i\Omega_2 \tau}) + f_1(\tau) e^{-iE_1 \tau} \\ &\quad + f_2(\tau) e^{-iE_2 \tau}. \end{aligned} \quad (32)$$

One easily obtains the asymptotic behavior of $f_1(\tau)$ and $f_2(\tau)$ for times $\tau \gg 1/g, 1/(\varepsilon_a - E_{1,2}), 1/\Delta W$. Indeed, carrying out a change in variables, $y = \xi \tau$, in the integral (31) and splitting off the leading terms we get

$$f_{1,2}(\tau) = \begin{cases} \frac{1}{g\tau(\ln \Delta W \tau)}, & \tau \gg \frac{1}{g}, \frac{1}{\varepsilon_a - E_{1,2}}, \frac{1}{\Delta W} \text{ and } g \sim |\varepsilon_a - E_{1,2}|, \\ \frac{g}{(\varepsilon_a - E_{1,2})^2 \tau}, & \frac{1}{g}, \frac{1}{\varepsilon_a - E_{1,2}}, \frac{1}{\Delta W} \ll \tau \ll \frac{1}{\Delta W} e^{|\varepsilon_a - E_{1,2}|/g} \text{ and } g \ll |\varepsilon_a - E_{1,2}|, \\ \frac{1}{g\tau(\ln \Delta W \tau)^2}, & \tau \gg \frac{1}{\Delta W} e^{|\varepsilon_a - E_{1,2}|/g} \text{ and } g \ll |\varepsilon_a - E_{1,2}|. \end{cases} \quad (33)$$

The boundedness of the spectrum thus leads to a relatively slow (power-law) decay of the atomic state.

The required quantity $n(\infty)$ can be calculated from (20a,b). One sees easily that besides a monotonic behavior of the kind of those considered above there appear oscillations at frequencies $\Omega_1 - \Omega_2$, $\Omega_1 - \Omega_3$, $\Omega_1 - E_1$, and so on. One can therefore reach the following conclusion about the behavior of the atomic level-bounded spectrum system. As the result of the level-band interaction the atomic state becomes quasi-stationary. The relaxation of the state has an exponential character only in the case of small coupling constants and for sufficiently short interaction times. Besides, this interaction leads to the appearance of new effective energy levels (E_1, E_2) and also to true levels (Ω_1, Ω_2) which interfere with one another and with the state $\Omega_3 - i\Gamma$, which genetically follows from the atomic state, and as a result give an oscillatory behavior of $n(\tau)$.

5. The case of a more complex shape of the density of states $N(\varepsilon)$ can be considered in the framework of the approach proposed above. One needs only continue the function $N(\varepsilon)$ (and also the function $|V_{\mathbf{k}(\varepsilon)}|^2$, if its energy dependence is important) from the section $[E_1, E_2]$ of the real axis to the band $12C_1C_2$ in such a way that in that band it has as far as possible fewer singularities and that it moreover is bounded at infinity. One must then deform the contour 12 as shown in Fig. 1, enclosing possible singularities of $N(z)|V(z)|^2$. As a result we get for the mass operator

$$M(z) = \sum_i \frac{A_i}{z - z_i} + \left(\int_{C_1} + \int_{C_2} \right) \frac{|V(\tilde{z})|^2 N(\tilde{z}) d\tilde{z}}{z - \tilde{z}} + \sum_n \int_{C_n} \frac{|V(\tilde{z})|^2 N(\tilde{z}) d\tilde{z}}{z - \tilde{z}}, \quad (34)$$

where the z_i are the points in which the function $|V(z)|^2 N(z)$ has pole singularities in the band $12C_1C_2$ and the C_n are contours bypassing possible cuts of the function $|V(z)|^2 N(z)$.

One can then find from the equation $z - \varepsilon_a = M(z)$ the poles of the Green function $G_{aa}^r(z)$. One should note that as a rule the analytical form of the spectrum is unknown. One can therefore approximate separate parts of it or the spectrum as a whole by simple functions such that the resulting $N(\varepsilon)$ function is close to the known one, obtained, for instance, from numerical calculations.

We note that in contrast to the previous considerations the function $G_{aa}^r(z)$ may have several poles in the band $12C_1C_2$. Moreover, as $|V_{\mathbf{k}}|^2 \rightarrow 0$ there must remain a single

pole $z = \varepsilon_a + i(-0)$. We must thus assume that for small $|V_{\mathbf{k}(\varepsilon)}|^2 N(\varepsilon)$ there is only one pole inside the band, $z = \varepsilon'_a - i\Gamma'$, corresponding to a quasistationary atomic state. As regards the poles lying outside the limits of the allowed spectrum, their position is determined by the roots of Eq. (21). In that sense condition (21) is a universal one. We emphasize again that one cannot use (21) to look for poles in the region of the continuous spectrum.

We also note the fact that since the Van Hove singularities at the band edges have for a three-dimensional spectrum a square-root character, the mass operator $M(\omega)$ remains a finite quantity in the points $\omega = E_1, E_2$. Therefore there are not always levels which are split off, but only when the bare level ε_a is close enough to the band edge.

The fact that $M(\omega)$ is finite at the boundary points causes also the contribution from the contour integrals around the cuts C_1 and C_2 to behave always like $1/\tau$ for large times τ .

Just as the case considered above, the quantity $n(\infty)$ will oscillate at frequencies corresponding to the differences between the characteristic frequencies of the system.

6. When the band is partially filled one can more conveniently carry out the analysis by using the expression

$$n(\infty) = n(\tau) = n(-\infty) + \frac{1}{V} \sum_{\mathbf{k}} |V_{\mathbf{k}}|^2 [2n_{\mathbf{k}} - n(-\infty)] \times \left| \int_{-\infty}^{\infty} \frac{d\omega}{2\pi} e^{-i\omega\tau} G_{aa}^r(\omega) \cdot G_{\mathbf{k}\mathbf{k}}^{r(0)}(\omega) \right|^2, \quad (35)$$

which can be obtained from the general Eq. (12). In that case there may appear additional oscillations connected with the presence of a sharp boundary of the Fermi distribution.

7. Our main result is therefore that the charge state of an atom after the scattering process is a nonmonotonic (in general, oscillating) function of the characteristic interaction time τ (or the energy of the incident particles). One should in this connection note Ref. 8 in which was studied the change in the charge state of N^+ ions scattered by the surface of NaCl crystals. The unfilled $2p$ level of N^+ ($\varepsilon_a = 14.7$ eV) lies opposite the filled $3p$ surface band of Cl, close to its edge: E_1 ($E_1 - \varepsilon_a \approx 1$ eV). The band width is $E_1 - E_2 \approx 7$ eV. We show in Fig. 2 the characteristic behavior of the yield of N^+ ions as function of the energy of the incident particles. To explain the observed behavior the authors of Ref. 8 used essentially a model similar to the one considered by us. However, their whole discussion was

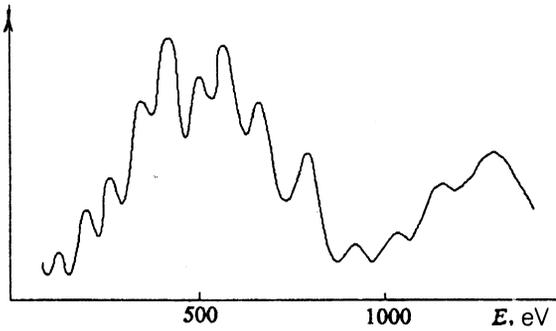


FIG. 2. Energy dependence of the relative yield of N^+ ions.⁸

based only on an analysis of an equation similar to Eq. (21) which, as we indicated above, is not valid. The appearance in the yield of N^+ ions of oscillations which are significantly different both in frequency and in amplitude (where a lower amplitude corresponds to the high-frequency oscillations) can be explained from our point of view as follows. Apparently, because the level ε_a is situated near the lower band edge, the function $G'_{aa}(z)$ does not have any poles on the continuous-spectrum section (the level is expelled beyond the band limits). Moreover, a localized state is split off from the nearest band edge with an energy $\varepsilon_1 \sim \varepsilon_a, E_1$ which is "genetically" connected with the initial ε_a state. Incidentally, the amplitude with which the localized state occurs in $G'_{aa}(\tau)$ will therefore be of the order of unity. Besides this term the function $G'_{aa}(\tau)$ will also contain terms corresponding to the effective states E_1, E_2 (band limits) and also a term describing the contribution from a state split-off from the far band edge with energy $\varepsilon_2 \approx E_2$. We note that the amplitude with which the states ε_2 and E_2 occur in $G'_{aa}(\tau)$ will be small to the extent that the quantity $N(\varepsilon) |V_{k(\varepsilon)}|^2 / (\varepsilon_a - E_2)$ is small. The charge state of the atom will be determined by the interference of these various contributions. In the resulting function $n(\tau)$ there will thus appear oscillations at frequencies $\varepsilon_1 - E_1, \varepsilon_1 - E_2, \varepsilon_1 - \varepsilon_2$, and $E_1 - E_2$, where the high-frequency oscillations ($\varepsilon_1 - E_2, \varepsilon_1 - \varepsilon_2$, and $E_1 - E_2$) will have practically the same frequency. We have thus the following function $n(\tau)$:

$$n(\tau) = A'_1 \cos((\varepsilon_1 - E_1)\tau + \varphi_1) + A'_2 \cos((E_1 - E_2)\tau + \varphi_2), \quad (36)$$

where $A'_1 > A'_2, \varepsilon_1 - E_1 < E_1 - E_2$. This picture is just the one observed in the above-mentioned experiments (Fig. 2).

In similar vein we can explain the results of Ref. 9 where oscillations were observed in the energy spectrum of excited Si^{+*} ions. In that case the electron exchange took place between an isolated level and an unfilled surface band with a width of ≈ 2 eV.

8. We discuss briefly the role of the exponential "tails" on-and-off switching of the hybridization. We assumed that the tunnelling processes are instantaneously switched

on (off). However, the actual time dependence of the hybridization has besides a flat section also exponentially increasing and decreasing sections. We can estimate the contribution from the exponential "tails" using the results obtained by Rosen and Zener¹⁰ who considered the charge transfer effect for a two-level system for an arbitrary resonance defect $\Delta = \varepsilon_1 - \varepsilon_2$. The authors of Ref. 10 obtained a formula which can satisfactorily be applied in a wide range of hybridization time-dependences $V(t)$:

$$P = \left| \frac{\sin(\int_{-\infty}^{\infty} V(t) dt)}{\int_{-\infty}^{\infty} V(t) dt} \int_{-\infty}^{\infty} V(t) e^{i\Delta t} dt \right|^2, \quad (37)$$

where P is the charge transfer probability.

One can, in particular, obtain from this expression the well known Demkov formula:¹¹

$$P = \text{sech}^2(\pi\gamma\Delta) \sin^2 \int_{-\infty}^{+\infty} V(t) dt, \quad (38)$$

where γ is a characteristic time for the exponential decrease, which is valid in the case of a small resonance defect Δ [$\Delta \ll V(0)$, where $V(0)$ is the maximum value of the hybridization reached in the flat section].

An analysis of Eq. (37) shows that if the flat section of the function $V(t)$ extends further than or of the order of the characteristic time for the interaction switching-off, taking the exponential "tails" into account makes only a small contribution to the amplitude of the oscillations and does not introduce new frequency dependences.

9. The main result of the work done here is the analysis of the most general case occurring when a single-level system interacts with a bounded band of allowed states. In the case of an empty or completely filled band the analysis then reduces to considering the retarded Green function $G'_{aa}(\tau)$, the most general structure of which is given by Eq. (28).

An interesting fact, caused by the finiteness of the band, is the appearance in the function $G'_{aa}(\tau)$ of terms describing effective states with energies coinciding in position with the band edges which interfere with the formed quasistationary and localized states and lead to $n(\infty)$ being an oscillating function of the interaction time (reciprocal of the velocity). It is important that the presence of such effective states can lead to a non-exponential decay of the atomic state.

We obtained Eq. (35) which enabled us to carry out an analysis in the case of a partially filled band. Using the "broad band" example we showed that in that case, apart from $n(\infty)$ oscillations due to terms occurring additively in $G'_{aa}(\tau)$, oscillations connected with the presence of a sharp boundary of the Fermi distribution are also possible.

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