Charge state formation mechanism for an atomic particle departing from a solid surface

D. V. Klushin, M. Yu. Gusev, and I. F. Urazgil'din

M. V. Lomonosov State University, 119899 Moscow, Russia
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Charge exchange between a solid surface and an atomic particle departing from the surface is treated within the framework of the nonstationary Anderson-Newns model. A justification is given for treating initial conditions as equilibrium in the sense of the total "hybridized atom + surface" system. An analytical solution for the final charge state of the atomic particle is obtained, and the existence of two charge exchange channels, dynamic and memory-related, is demonstrated. Situations in which one of the channels dominates are analyzed, as is the case of the quantum interference of the channels. The effect of temperature on electron exchange is treated in detail. A method for determining the degree of the local heating of the electron subsystem of the solid in the region of interaction with the beam is suggested. Charge exchange in secondary ion emission from a metal, both in the low- and high-temperature regimes, is considered. The solution obtained demonstrates the existence of two mechanisms, tunneling and thermalization, for formation of the charge state of an ion.

1. INTRODUCTION

This paper presents a theoretical discussion of the electron exchange processes involved in the scattering (or emission) of atomic particles from the surface of a solid.

The problem requires a multi-particle approach and is generally treated on the basis of the Anderson–Newns model.[1,2] Within this model, the charge exchange problem was first treated by using the Keldysh formalism[3] and subsequently discussed based on the method of equations of motion.[4,5]

In these studies, the final results are obtained in the "wide-band" approximation and under the assumption that the "memory" effects in the system may be neglected.

In a more general form (in particular, with a touch on the memory effects), the problem is treated in Ref. 6. Subsequently, in the review article of Brako and Newns[7] it is pointed out that very often the memory regime may also dominate, in the scattering of atomic particles from a nonmetal surface, in the case of a resonant electron exchange with a surface state band; it is noted, however, that there is no consensus on the subject.

The basic difficulty one faces is the simultaneous inclusion of different factors of importance, particularly for low velocities of the atomic particle (weakly nonadiabatic motion).

Accordingly, in the present work the authors have deliberately addressed a situation where the influence of a bounded band spectrum on the charge state of an atomic particle may be neglected (this problem was treated by the authors in more detail elsewhere[8]), and concentrated on the problems of resonance tunneling in the case of a weakly nonadiabatic motion (the atomic particle energy below a few hundred electron volts). The problem then reduces to describing the departure from an initial state which is equilibrium in the sense of the total, "hybridized atom + surface," system.

The present work treats the effect of such initial conditions on the final charge state. An additional resonance charge exchange channel associated with the system memory is investigated and it is shown that its existence simultaneously with the "dynamic" charge exchange channel, may lead to a quantum interference of the two.

A detailed discussion of the effect of temperature on the electron exchange process is given, and a method for estimating the local heating of the solid's electron subsystem in the solid-beam interaction region is proposed.

By considering the shift of atomic levels due to the image potential, a description of the charge exchange in the secondary ion emission from a metal is given. At present there exist two basic models describing the electron exchange in secondary ion emission, the electron tunneling model[9] and the semi-phenomenological model due to Šroubek.[10] Both employ the kinetic equation but, due to different approaches used, are in effect independent. Although the basic features of secondary ion emission are qualitatively described by either model, a great deal of experimental data exist which can be adequately described by only one of them. In the present work we have been able to obtain, within the quantum mechanical description, an analytical solution for the ionization probability of the secondary particle. Analysis of the solution shows that there are generally two ion charge state formation mechanisms, tunneling and thermalization, corresponding in their essence to the above mentioned models. Under certain conditions, one of these prevails.

2. PROBLEM FORMULATION

The Anderson–Newns model Hamiltonian is

$$H=\sum_k E_k C_k^+ C_k + E_a(t) C_a^+ C_a + \sum_k \{V_{ak}(t) C_a^+ C_k + \text{h.c.}\}, \tag{1}$$

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where C_k^+ and C_a^+ are the creation operators for the electron in a band state $|k\rangle$ and in the orbital state $|a\rangle$ of the moving atom. Because of the independence of the two spin subspaces the spin index is dropped. The parameters of the Hamiltonian (1) are time-dependent owing to the motion of the atom. The energies E_k and $E_a(t)$ are measured from the Fermi level.

It is assumed that the dependences on k and t in the hybridization matrix element $V_{ak}(t)$ separate:

$$V_{ak}(t)=V_{ak}U(t). \tag{2}$$

We will assume that the level E_a is always opposite the band of the solid and lies far enough from the band edges; that the characteristic time T for switching hybridization on and off is large [i.e., $T(E_a-E_1)\gg 1$, $T(E_2-E_a)\gg 1$, where E_1 and E_2 are the lower and upper band edges respectively ($\hbar=1$)]; and that the density of k states is a sufficiently smooth function of the energy E_k in the vicinity of E_a. These requirements are, in particular, quite justifiable for wide-band materials under the above mentioned conditions on the motion and on the position of E_a. Therefore in the following we assume that the band size is infinite, that the Fermi level is taken to be the origin, and that it is adequate to apply the wide-band approximation for the resonance level width Δ

$$\Delta(\omega)=\pi\sum_k |V_{ak}|^2\delta(\omega-E_k)=\Delta, \tag{3}$$

independent of ω.

The time dependence $E_a(t)$ is defined as $E_a[z(t)]$, where $z(t)$ is the trajectory of the atomic motion. By the shift in the electron level $E_a(z)$ is meant a shift due to the presence of the image potential. The introduction of the $E_a(t)$ dependence in this way is only justified in the case when all the characteristic times of the process, including the charge exchange time ($\sim 1/\Delta$), turn out to be much greater than Maxwell's relaxation time t_M for the nonequilibrium charge density. For normal metals, due to high conductivity we have $t_M\approx 10^{17}$ s, and the above requirement is fulfilled. For lower conductivity materials t_M may prove comparable to the charge exchange time and so introducing $E_a(t)$ manually is not entirely correct (to account for the effect of the image in this case one needs, as a minimum, to employ information about the dynamic dielectric permittivity of the system). In some cases ($t_M\gg 1/\Delta$, $t_M\gg T$) the shift in level E_a due to the image is negligible ($E_a\approx$const.).

The characteristic dependence of the (hybridization) matrix element V_{ak} on time is shown in Fig. 1:

$$T=\frac{a}{v_\perp} \tag{4}$$

is the switching (off) time, a is the characteristic decay length of the wave function outside the sample and $v_\perp$ is the surface-normal component of the velocity v of the departing atom.

The presence of a gentle portion in the $U(t)$ dependence is due to the existence of the saturation region for the hybridization V_{ak} and also to the existence of the turning

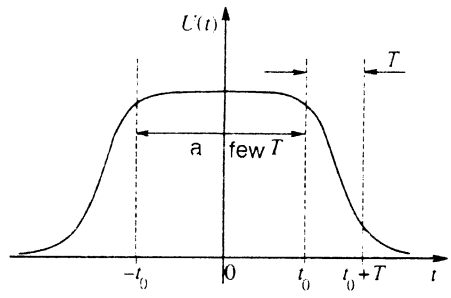

FIG. 1. The characteristic dependence of the hybridization matrix element $V_{ak}(t)=V_{ak}U(t)$ on time.

region for the scattered atom. Without going into details, we note that both the regions begin at the distances to the surface of the order of the interatomic distance in the solid.

It should also be noted that the $U(t)$ dependence is not generally symmetric about the point $t=0$. This relates to the fact that the scattering of an atomic particle from a solid surface is an inelastic process, that is, part of the particle's energy is lost in the scattering act. A consequence is that the characteristic time for switching hybridization on turns out to be less than that for switching off. In the case when the atomic particle loses an insignificant part of its energy, the difference between the characteristic times is small. Moreover, as will be made clear below, we will be primarily interested in the departure process (i.e., $t>t_0$). Therefore, in what follows, by T we mean the characteristic time for switching hybridization off.

Apart from the atom approach conditions already introduced, in what follows we will only treat a weakly nonadiabatic motion. We will consider the non-adiabaticity parameter $T\Delta$ to be sufficient that the time the atom stays in the region where the hybridization V_{ak} is more or less constant, is of the order of ten or more characteristic charge exchange times $1/\Delta$ (for an atomic weight in excess of 10, this requirement is fulfilled up to particle kinetic energies of order a few keV). Then within the framework of the Anderson–Newns model one finds that, by the time instant t_0 (see Fig. 1) the entire system "atom + surface" will, to good accuracy, attain the equilibrium populations. But, since the above model contains no information about any dissipation processes, we will assume that the time over which hybridization is more or less constant is sufficient for the electron subsystem to attain equilibrium, with a certain temperature θ, in the region of its interaction with the scattered beam. And, generally speaking, θ need not be equal to the ion temperature in this region.

Thus, measuring time from t_0 (see Fig. 1), we arrive at the following departure model problem:

$$H=\sum_k E_kC_k^+C_k+E_a(t)C_a^+C_a+U(t)\sum_k\{V_{ak}C_a^+C_a + \text{h.c.}\}, \tag{5}$$

where $U(t)$ is a certain switching-off function, with a char-

acteristic time T [cf. Eq. (4)]. At $t=0$, the entire system "atom + surface" is in equilibrium at temperature θ.

3. A STUDY OF THE NONSTATIONARY ANDERSON-NEWNS MODEL WITH EQUILIBRIUM INITIAL CONDITIONS FOR THE WIDE BAND

3.1. Method of equations of motion

We change to the Heisenberg representation and use the system of units in which $\hbar=1$. Using the equations of motion for operators it is not difficult to obtain the equation of motion for the average $n_a(t)=\langle C_a^+(t)C_a(t)\rangle$:

$$\frac{\partial n_a(t)}{\partial t}=iU(t)\sum_k\{V_{ak}\langle C_a^+(t)C_k(t)\rangle-\text{c.c.}\}. \tag{6}$$

Using in (6) the solution of the equation of motion for $C_k(t)$, i.e.,

$$C_k(t)=C_k(0)\exp[-iE_kt]-iV_{ak}\int_0^t dt'U(t')C_a(t')\times\exp[-iE_k(t-t')], \tag{7}$$

and its conjugate for $C_k(t)$, it is found that, for the wide-band approximation (3),

$$\frac{\partial n_a(t)}{\partial t}==2\Delta(t)-iU9t)\sum_k\{V_{ak}\langle C_a^+(t)C_k(0)\times\exp[-iE_kt]-\text{c.c.}\}, \tag{8}$$

where

$$\Delta(t)=\Delta[U(t)]^2. \tag{9}$$

The solution to the equation of motion for the correlation function $\langle C_a^+(t)C_k(0)\rangle$, after substituting the expression for $C_{k'}^+(t)$ and using Eq. (3) has the form

$$\begin{aligned}\langle C_a^+(t)C_k(0)\rangle=&\sum_k V_{ak}\langle C_a^+(0)C_k(0)\rangle\\&\times\exp\left[\int_0^t(iE_a(t')-\Delta(t'))dt'\right]\\&+\sum_{k'}V_{k'a}\langle C_{k'}^+(0)C_k(0)\rangle\int_0^t dt'U(t')\\&\times\exp\left[iE_{k'}t'\right.\\&\left.+\int_{t'}^t(iE_a(t'')-\Delta(t''))dt''\right].\end{aligned} \tag{10}$$

Substituting Eq. (10) and its conjugate into Eq. (8), after a little manipulation we obtain

$$\begin{aligned}n_a(t)=&n_a(0)\exp\left[-2\int_0^t\Delta(t')dt'\right]\\&+\exp\left[-\int_0^t\Delta(t'')dt''\right]\int_0^t dt'U(t')\\&\times\exp[-\int_{t'}^t\Delta(t'')dt'']2\text{Im}\left\{\sum_k V_{ak}\right.\\&\times\langle C_a^+(0)C_k(0)\rangle\exp\left[-iE_kt'\right.\\&\left.\left.+\int_0^{t'}iE_a(t'')dt''\right]\right\}+\sum_k\sum_{k'}V_{ka}V_{ak'}\\&\times\langle C_k^+(0)C_{k'}(0)\rangle\int_0^t dt'U(t')\\&\times\exp\left[iE_kt'-\int_0^{t'}iE_a(t''')dt'''\right.\\&\left.-\int_{t'}^t\Delta(t''')dt'''\right]\int_0^t dt''U(t'')\exp\left[-iE_{k'}t'\right.\\&\left.+\int_0^{t''}iE_a(t''')dt'''-\int_{t''}^t\Delta(t''')dt'''.\right.\end{aligned} \tag{11}$$

Note that expression (11) involves arbitrary initial conditions. If one takes initial conditions to be nonequilibrium (in the sense of the entire system with nonzero hybridization),

$$\langle C_k^+(0)C_{k'}(0)\rangle=\frac{\delta_{kk'}}{\exp[E_k/\theta]+1,}\quad\langle C_a^+(0)C_k(0)\rangle=0,$$

then Eq. (11) transforms into the form

$$\begin{aligned}n_a(t)=&n_a(0)\exp\left[-2\int_0^t\Delta(t')dt'\right]\\&+\frac{\Delta}{\pi}\int_{-\infty}^{+\infty}\frac{d\omega}{\exp[\omega/\theta]+1}\left|\int_0^t dt'U(t')\exp\left[i\omega t'\right.\right.\\&\left.\left.+\int_{t'}^t(iE_a(t'')-\Delta(t''))dt''\right]\right|^2,\end{aligned}$$

i.e., into the Brako–Newns result.[5] In what follows we will employ equilibrium initial conditions.

3.2. Determination of equilibrium initial conditions

Equilibrium initial conditions for $\langle C_a^+(0)C_a(0)\rangle$, $\langle C_a^+(0)C_k(0)\rangle$, and $\langle C_k^+(0)C_{k'}(0)\rangle$ have been determined using the temperature Green's functions (for more of the details of the two- time formalism, see, e.g., Ref. 11). The corresponding system of algebraic equations for the temperature Green's functions $\langle\langle C_a|C_a^+\rangle\rangle_\varepsilon$ and $\langle\langle C_k|C_a^+\rangle\rangle_\varepsilon$ turns out to be closed and is solved straightforwardly. Also, in finding $\langle\langle C_k^+(0)C_{k'}(0)\rangle\rangle$ use has been made of the following statement which is readily proved from the spectral density properties of the temperature Green's functions:

$$\langle\langle B|A\rangle\rangle_\varepsilon=\eta\langle\langle A|B\rangle\rangle_{-\varepsilon},$$

where B, A are certain operators; the coefficient $\eta=\pm1$ and its choice is a matter of convenience for determination of $\ll B|A\gg_\varepsilon$ line (in the following $\eta=-1$ throughout).

Finally, using the wide-band approximation (3) the equilibrium initial conditions are as follows:

$$\langle C_a^+(0)C_a(0)\rangle = n_a(0)$$
$$= \frac{\Delta}{\pi}\int_{-\infty}^{+\infty}\frac{d\omega}{\exp[\omega/\theta]+1}\frac{1}{[\omega-E_a(0)]^2+\Delta^2}, \quad (12)$$

$$\langle C_a^+(0)C_k(0)\rangle = -\frac{V_{ka}}{2\pi i}\int_{-\infty}^{+\infty}\frac{d\omega}{\exp[\omega\theta]+1}\{G_a^{(r)}G_k^{0(r)} - G_a^{(a)}G_k^{0(a)}\}, \quad (13)$$

$$\langle C_k^+(0)C_{k'}(0)\rangle = \frac{\delta_{kk'}}{\exp[E_k/\theta]+1} - \frac{V_{ak}V_{k'a}}{2\pi i}\int_{-\infty}^{+\infty}\frac{d\omega}{\exp[\omega/\theta+1]} \times\{G_a^{(r)}G_k^{0(r)}G_{k'}^{0(r)} - G_a^{(a)}G_a^{(a)}G_{k'}^{0(a)}\}, \quad (14)$$

where, for brevity, we have introduced the notation

$$G_a^{\{r\}}(\omega) = \frac{1}{\omega-E_a(0)\pm i\Delta}, \quad G_k^{0\{r\}}(\omega) = \frac{1}{\omega-E_k\pm i0}.$$

3.3. Final theoretical result

Using Eqs. (12), (13), and (14) it proves possible to reduce Eq. (11) to a more compact form:

$$n_a(t) = \frac{\Delta}{\pi}\int_{-\infty}^{+\infty}\frac{d\omega}{\exp[\omega/\theta]+1}\left|i\frac{\exp\left[-\int_0^t\Delta(t')dt'\right]}{\omega-E_a(0)+i\Delta} + \int_0^t dt'U(t')\exp\left[-i\omega t' + \int_0^{t'} iE_a(t'')dt'' - \int_{t'}^t\Delta(t'')dt''\right]\right|^2. \quad (15)$$

From Eq. (15), it is easily shown that the expression for the ionization probability of the departing particle, $R^+(t) = 1 - n_a(t)$, can be written in the form

$$R^+(t) = \frac{\Delta}{\pi}\int_{-\infty}^{+\infty}d\omega\frac{\exp[\omega/\theta]}{\exp[\omega/\theta]+1}\left|i\frac{\exp\left[-\int_0^t\Delta(t')dt'\right]}{\omega-E_a(0)+i\Delta} + \int_0^t dt'U(t')\exp\left[-i\omega t' + \int_0^{t'} iE_a(t'')dt'' - \int_{t'}^t\Delta(t'')dt''\right]\right|^2. \quad (16)$$

In the following two limiting cases are discussed, of either weak or strong variation of $E_a(z)$ with distance.

4. ANALYSIS OF THE CASE E_a=const

In this section we will assume that $U(T) = \exp[-t/T]$, where T is the switching -offtime (4), and that $E_a(T) = E_a$=const. To be specific, we take $E_a < 0$ and perform the entire analysis for $R^+(\infty)$, hence forth simply R^+. [In the case $E_a > 0$, we note that due to the electron -hole symmetry, all the results below should be referred to $N_a(\infty)$]. It will also be assumed for simplicity that $|E_a|T > 1$.

4.1. Zero temperature. The formation of two charge exchange channels

Integrating over t in (16), and after some algebra (see Appendix A), we obtain for the ionization probability of the departing atom the following expression:

$$R^+ = \frac{2}{\pi}\exp\left[-\frac{\pi|E_a|T}{2} + \frac{\exp[-T\Delta]}{(T\Delta)^2}\frac{1}{2}\left[\frac{1}{2} - \frac{1}{\pi}\arctan|\varepsilon| - \frac{|\varepsilon|}{\pi(1+|\varepsilon|^2)}\right] + \frac{\exp\left[-\frac{1}{2}\left(\Delta+\frac{\pi}{2}\left|E_a\right|\right)T\right]}{(T\Delta)^{3/2}}B\cos\left(\frac{T}{2}\left|E_a\right|(1 - \ln|\varepsilon|) + \varphi\right)\right], \quad (17)$$

where

$$\varepsilon = \frac{E_a}{\Delta}, \quad B = \frac{4}{\sqrt{\pi}(1+|\varepsilon|^2)\sqrt{\frac{\pi^2}{4}+(\ln|\varepsilon|)^2}},$$

$$\varphi = -arg\left\{\frac{1}{\frac{\pi}{2}-i\ln|\varepsilon|}\right\} - \arg\left\{\frac{1+i|\varepsilon|}{(1-il|\varepsilon|)^3}\right\}.$$

The first two terms in (17) give a monotonic dependence on the inverse velocity (T), whereas the third represents oscillations on its background. Clearly the oscillations will only be noticeable if their amplitude is comparable to that of the carrier dependence.

Analysis of the ionization probability (17) in the case $T\Delta \sim 10$ yields (see also Fig. 2):

a) if $|E_a| < 0.6\Delta$ (in particular, $|E_a| \ll \Delta$), then to good accuracy

$$R^+ = \frac{2}{\pi}\exp\left[-\frac{\pi|E_a|T}{2}\right].$$

It should be noted that this result has been obtained by other methods (see, for example, Refs. 3 and 5).

b) when $|E_a| > 1.5\Delta$ we obtain

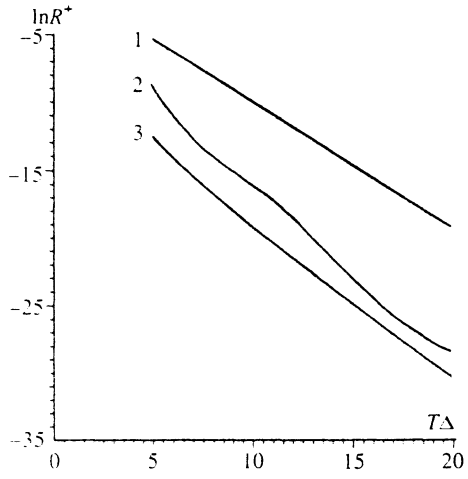

FIG. 2. The dependence of the ionization probability of the level $E_a(E_a<0)$ of the departing particle on the parameter $T\Delta=a\Delta/v_\perp$ (inverse of the velocity). Curves: *1*—$|E_a|\sim 0.6\Delta$; *2*—$|E_a|\sim 1.1\Delta$; *3*—$|E_a|\sim 1.8\Delta$.

$$R^+=\exp[-T\Delta]\left\{\frac{1}{(T\Delta)^2}\frac{1}{2}\left[\frac{1}{2}-\frac{1}{\pi}\arctan|\varepsilon|-\frac{|\varepsilon|}{\pi(1+|\varepsilon|^2)}\right]+\frac{1}{(T\Delta)^3}\frac{1}{4}\left[3\left(\frac{1}{2}-\frac{1}{\pi}\arctan|\varepsilon|\right)-\frac{|\varepsilon|(3|\varepsilon|^4+8|\varepsilon|^2+13)}{\pi(1+|\varepsilon|^2)^3}\right]+\cdots\right\}.$$

$$(R^+(t=0)=\frac{1}{2}-\frac{1}{\pi}\arctan|\varepsilon|).$$

In particular, if one assumes that $|E_a|\gg\Delta(|\varepsilon|\gg 1)$ then

$$R^+=\frac{1}{3}\frac{\Delta}{\pi|E_a|}\frac{\exp[-T\Delta]}{(|E_a|T)^2},\quad\left(R^+(t=0)=\frac{\Delta}{\pi|E_a|}\quad\text{for}\quad|E_a|\approx\Delta\right);$$

c) in the case $|E_a|\sim(0.8\text{–}1.3)\Delta$, expression (17) represents a weakly modulated oscillatory dependence on the inverse velocity T (the oscillation amplitude being 10–15% of the carrier dependence amplitude, see Fig. 2). Note that as a function of the parameter $T/2$ [which is just the effective decay time of the width $\Delta(t)$ of the tunneling transition probability], R^+ oscillates at a frequency $\sim|E_a|$.

All of this can readily be understood physically. When the velocity of the departing atom is infinitesimal ($T\to\infty$), then $R^+\to 0$ (since $E_a<0$), that is, the level E_a possesses an electron. As the velocity is increased, there arises the possibility of ionization of the level E_a. This can proceed via two channels.

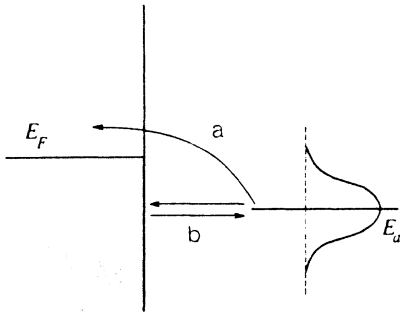

FIG. 3. Formation of two charge exchange channels in a weakly nonadiabatic departure of an atomic particle from a surface. (a) Channel involving the electron transfer into an excited state above E_F due to the finite value of the characteristic interaction switching-off time; (b) Channel associated with the memory of the system (in the sense that the conditions as of t_0, see Fig. 1, have an influence on the final charge state).

The first channel-corresponding to case a)—is due to the fact that the effective staying time of the atom in the region of interaction with the surface is finite and hence there is a nonzero probability for the electron to transfer to a vacant place above E_F, see Fig. 3. The initial state does not play a major role because, for a slow departure, the population probability of the level E_a is close to unity; what is important is the degree of nonadiabaticity of the departure, so in the following we will call this channel *dynamic*.

The second channel-corresponding to case b)—has to do with system memory effects. The effect of hybridization is that the electrons are in some sense *collectivized*, that is, to some extent they belong to the sample and to some, to the level E_a ($\langle C_a^+C_k\rangle\neq 0$). There is a continuous exchange of electrons between the level and the band, most actively involved being the electrons with energies around E_a. On switching hybridization off, the electrons are distributed between the sample and the level E_a (we can speak of an atom electron and of a sample electron). The probability of ionization of the atom in such a process is determined by the integrated contribution from the difference between the charge flows from the atom into the zone and vice versa, thus being proportional to $\exp[-\int_0^\infty\Delta(t)dt]$. Clearly, this probability depends both on the initial state and on the manner in which hybridization is switched off.

In the case where the contributions to the charge exchange from the two channels are comparable, the channels interfere, which leads to an oscillatory dependence of the ionization probability on the inverse velocity.

To end this subsection let us point out that the above approach to the case $E_a=\text{const}$, $\theta=0$ K differs from previous ones and makes it possible to account consistently for the system memory terms. If we make use of the saddle point method in the standard way (i.e., by first integrating over energy and then over time, in analogy with Refs. 5 and 7), certain difficulties will arise. If the initial instant of time is taken to be $t=-\infty$, the major difficulty will be in accounting for the actual dependence $U(t)$ (see Fig. 1). If we take the initial moment to be t_0 and the dependence $U(t)$ to be exponential, the main difficulty is that the in-

tegrand is irregular in the vicinity of the initial point, and in order to take into account the contribution from the end portion of the integration contour, a means to combat this difficulty will have to be devised. In either case it proves difficult to obtain a solution accounting for memory effects (in the sense that the conditions as of t_0, see Fig. 1, affect the final charge state), and this is apparently the reason for the lack of such solutions in Refs. 5 and 7.

4.2. Finite temperatures

We first note that in the adiabatic limit $T\to\infty$ we obtain from Eq. (15) a physically obvious result that

$$n_a(\infty)=\frac{1}{\exp[E_a/\theta]+1}.$$

In the study of the weakly nonadiabatic situation, we will assume - quite justifiably - that $\theta\ll\Delta$ and $\theta\ll|E_a|$ since both $|\Delta|$ and E_a are of the order of electron volts (1 eV = 11600 K).

We consider two limiting cases: $\theta\ll 1/T$ (low-temperature regime) and $\theta\gg 1/T$ (high-temperature regime).

a) $\theta\ll\frac{1}{T}$.

Clearly, in this case temperature effects will introduce a small correction irrespective of whether the dynamic or memory channel is dominant.

Using the standard method for the approximate evaluation of Fermi distribution integrals, we obtain from Eq. (16) the expressions for the dynamic charge exchange channel,

$$R^+ + \frac{2}{\pi}\exp\left[-\frac{\pi|E_a|T}{2}\right]\left(1+\left(\frac{\pi T\theta}{2}\right)^2\right), \tag{18}$$

and for the memory-related channel,

$$R^+=\frac{\exp[-T\Delta]}{(T\Delta)^2}\,\frac{1}{\pi}\times\sum_{n\geqslant 2}\frac{F_n(\infty)-F_n(|\varepsilon|)-\frac{\pi}{3}\left(\frac{\theta}{\Delta}\right)^2\frac{\partial^2}{\partial\xi^2}F_n(\xi)|\xi=|\varepsilon|}{(T\Delta)^{n-2}}, \tag{19}$$

where

$$F_n(\xi)=\int f_n(\xi)d\xi,\quad \sum_n\frac{f_n(x)}{(T\Delta)^2}=|f(x)|$$

and the definition of $f(x)$ is given in Appendix A.

Thus we see that if $\theta T\ll 1$ and $\theta\ll\Delta$, the temperature correction is small and cannot alter substantially the dependence on T of the ionization probability of the departing particle.

b) $\theta\gg\frac{1}{T}$.

A different situation obtains in the high-temperature regime. In this case, temperature effects begin to dominate and it is therefore to be expected that $R^+\sim\exp[-|E_a|/\theta]$, which corresponds to the ionization probability of the level E_a for hybridization being switched off adiabatically ($t\to\infty,\theta\ll|E_a|$).

In fact, using Eq. (16) we obtain

$$R^+\approx\int_{-\infty}^{+\infty}\exp\left[\frac{\Delta}{\theta}\left(x+\frac{E_a}{\Delta}\right)\right]\frac{T\Delta}{2\cosh\left(\frac{\pi T\Delta}{2}x\right)}dx$$

$$=\exp\left[-\frac{|E_a|}{\theta}\right]\cos^{-1}\left(\frac{1}{\theta T}\right).$$

Noting that $\theta T\gg 1$, the final result is

$$R^+=\exp\left[-\frac{|E_a|}{\theta}\right]\left(1+\frac{1}{2(\theta T)^2}\right). \tag{20}$$

Note that in this case R^+ depends linearly on the kinetic energy $E_a^{\rm kin}$ of the departing particle because $1/T^2\sim E_a^{\rm kin}$.

It should be noted that the characteristic dependence of the ionization probability on θ in the high-temperature regime $\theta T\gg 1$, just obtained for $E_a=$const, may remain in the case of E_a dependent on distance (see the next section for further detail):

$$R^+\sim\exp\left[-\frac{|E_a(z^*)|}{\theta}\right],\quad z^*=\frac{a}{2}\ln\Delta T. \tag{21}$$

We remind that by θ we mean the temperature of the electron subsystem in the region of interaction with the incident beam, the value of the temperature not necessarily being equal to the ion temperature there (hereafter θ_0). From the shape of the dependence $R^+(\theta)$ in the high-temperature regime, it is not difficult to establish whether the electron subsystem is warmed-up in the interaction region - and to what extent.

Suppose we have measured the ionization probability of the atomic particles emitted from the surface as a function of the temperature θ_0 for the high-temperature case ($\theta_0 T\gg 1$). If the electron temperature in the interaction region, θ, and the ion temperature, θ_0, are equal, then the dependence of R^+ on θ_0 will approximately correspond to the curve 1 in Fig. 4, i.e., R^+ will grow rapidly with the temperature. A local heating of the electron subsystem will give rise to a gentle portion in the curve (see curve *2* in Fig. 4), because in this case the temperature is sustained more by an external heat-inducing agent (an incident beam, for example) than by the ion framework, even though this latter may be the main heat removal channel in the system. From the extension of the gentle portion one can assess the degree of the local heating of the electrons (see Fig. 4).

5. INCLUSION OF THE SHIFT OF THE LEVEL $E_a(z)$; DESCRIPTION OF THE ELECTRON EXCHANGE IN SECONDARY ION EMISSION

In the preceding section the case $E_a=$const has been treated; in Sec. 5 we analyze the effect of the shift in the level $E_a(z)$ on the final charge state of the atom. If the level $E_a(z)$ varies strongly enough with the distance to the surface (so that it can intersect the Fermi level, for example),

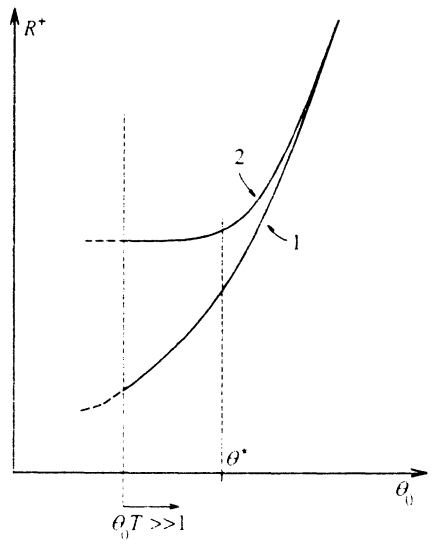

FIG. 4. The characteristic dependence of the ionization probability R^+ on the local ion temperature θ_0 in the bombardment region for the high-temperature regime $\theta_0 T \gg 1$ in the absence (curve *1*) and in the presence (curve *2*) of local heating of the electron subsystem in this region; θ^* is the electron temperature in the heating region.

then the initial state ceases to be of any importance, that is, the memory effects may be neglected. As an example, the electron exchange in secondary ion emission in both the low- ($\theta T \ll 1$) and high-temperature ($\theta T \gg 1$) regimes is considered. As before, it is assumed that the width of the atomic level decreases exponentially with distance, i.e., $\Delta(z) = \Delta \exp[-2z/a]$.

5.1. Low-temperature regime ($\theta T \ll 1$)

Using Eq. (16) and neglecting the memory terms (as justified by the final result which is much greater than $\exp[-2\int_\infty \Delta(t')dt']$), we obtain an expression for the secondary ion ionization probability:

$$R^+ = \frac{1}{\pi v} \Big| \int_{\gamma'} ds' \int_{\gamma''} ds'' \frac{\sqrt{\Delta(s')\Delta(s'')}}{s'-s''} \times \exp\left[\frac{1}{v_\perp} G(s')\right] \exp\left[\frac{1}{v_\perp} G^*(s'')\right],$$

$$\mathrm{Im}(s'-s'') > 0, \quad G(s) = \Big| \int_s^\infty d\xi [\Delta(\xi) - iE_a(\xi)]. \tag{22}$$

The contour $\gamma'(\gamma')$ is obtained by deforming the real axis onto the upper (lower) part of the complex plane. It is assumed that $\Delta(s)$ and $E_a(s)$ are regular in the vicinity of the contours γ' and γ''; that in preparing γ' and γ'' the nonanalyticity points and branch points of $\Delta(s)$ and $E_a(s)$ were not passed through; and that the contour $\gamma'(\gamma'')$ passes through the saddle point $s_0(s_0^*)$, which is a simple saddle point, i.e.,

$$G'(s_0) = \Delta(s_0) - iE_a(s_0) = 0,$$

$$G''(s_0) = \Delta'(s_0) - iE_a'(s_0) \neq 0,$$

$$G'(s) = \frac{\partial}{\partial s} G(s), \quad G'(s) = \frac{\partial}{\partial s} G'(s),$$

$$\Delta'(s) = \frac{\partial}{\partial s} \Delta(s),$$

$$E_a'(s) = \frac{\partial}{\partial s} E_a(s).$$

By application of the saddle point method, for the integrals in Eq. (22) we obtain (for more details see Refs. 5 and 7)

$$R^+ = \frac{1}{\mathrm{Im} s_0} \left| \frac{\Delta(s_0)}{\Delta'(s_0) - iE_a(s_0)} \right| \exp\left[-i \frac{1}{v_\perp} \int_{s_0}^{s_0} E_a(s) ds - \frac{2}{v_\perp} \mathrm{Re} \int_{s_0}^\infty \Delta(s) ds \right]. \tag{23}$$

Thus the entire problem is reduced to that of finding the saddle point, i.e., to the solution of the equation $G'(s_0) = 0$.

Let us consider secondary ion emission from a metal. Its feature is that $E_a(z)$, due to the image potential, varies rather strongly with the distance to the surface: E_a crosses the Fermi level (which we recall is taken as energy zero) at a certain point z_0, i.e., $E_a(z) > 0$ for $z < z_0$ and $E_a(z) < 0$ for $z > z_0$; $E_a(\infty) = (\varphi - I) < 0$, where I is the ionization potential of the isolated metal atom, and φ is the work function of the metal. Note that, typically, $z \sim a$, and the condition $|\Delta'(z_0)| \ll |E_a'(z_0)|$ is fulfilled.

For the power-law decrease of $E_a(z)$ characteristic of the image- induced shift in the level E_a, the condition $|\Delta'(z_0)| \ll |E_a'(z_0)|$ in fact implies

$$z_0 \Delta(z_0)/a |E_a(\infty)| \ll 1,$$

In this case it is a simple matter to obtain the saddle point:

$$s_0 \approx z_0 - i\Delta(z_0)/E_a'(z_0),$$

Substituting the above saddle point into Eq. (23) and noting that $|\Delta'(z_0)| \ll |E_a'(z_0)|$ yield the following result for the ionization probability of a secondary ion:

$$R^+ = \exp\left[-\frac{2}{v_\perp} \int_{z_0}^{+\infty} \Delta(z) dz \right] = \exp[-T\Delta(z_0)]. \tag{24}$$

5.2. High-temperature regime ($\theta T \gg 1$)

We begin by noting that the energy distribution of secondary ions emitted from a metal or a semiconductor has a pronounced maximum in the energy range of 5–15 eV. If one estimates the temperature parameter θT for this energy range, it turns out that for Cu, for example, the situation is close to the high-temperature regime for $\theta > 500$ K. The question of the electron temperature in the bombardment region is an open one. At least, there are reasons to believe that this temperature differs from the ion tempera-

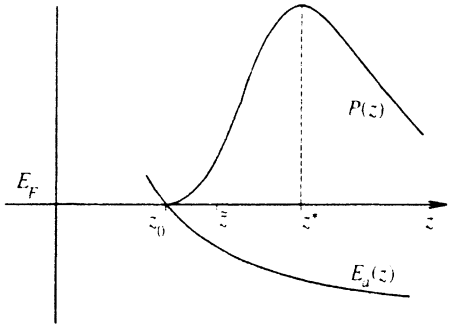

FIG. 5. The energy of the atomic level E_a and the function $P(z)$ [see Eq. (25)] versus the distance to the surface; z_0 the effective neutralization distance, z^* the effective thermalization distance.

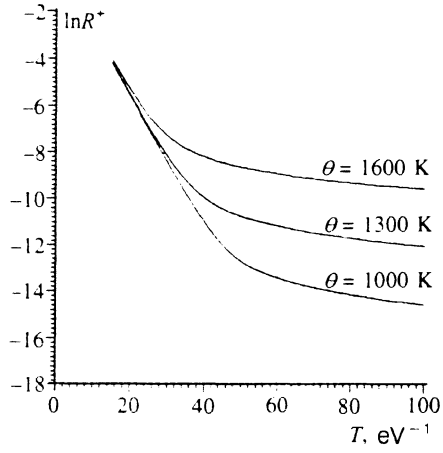

FIG. 6. The characteristic dependence of the ionization probability R^+ in secondary ion emission on the inverse velocity T for various temperatures. The parameters are chosen as follows: $\Delta = 1.5$ eV; $E_a = -2$ eV $[E_a(z) = E_a - E_a z_0/z]$; $a = 3$ Å, $z_0 = 2.5$ Å. The range of the parameter T from 15 to 80 eV corresponds (for Al, for example) to a secondary ion energy range of 100 to 5 eV.

ture in this region and may be strongly nonequilibrium (according to some estimates,[12] θ may reach several thousand K).

Integration over ω in Eq. (15) yields

$$n_a(\infty) = -i\frac{\theta T}{2a}\int_{-\infty}^{+\infty} \times dzP(z)\int_{-\infty}^{+\infty} d\tau \frac{\exp\left[-\frac{1}{v_\perp}\int_{z-\tau}^{z} iE_a(x)dx\right]}{\sinh\left(\pi\theta T\frac{\tau}{a} - i0\right)}, \tag{25}$$

where

$$P(z) = \frac{\partial}{\partial z}\left\{\exp\left[-\frac{2}{v_\perp}\int_z^{+\infty}\Delta(z')dz'\right]\right\}.$$

$P(z)$ represents an asymmetric bell with a maximum at $z^* = a/2\ln T\Delta$ and a width of order a. In writing Eq. (25) it has been taken into account that $\Delta(z)$ varies weakly on the scale $a/\pi\theta T$ and that $\Delta(z^*) = 1/T \ll \theta$.

Now let $E_a(z)$ cross the Fermi level at point z_0 (typically $z_0 \sim a$ in metals). Also, in the high-temperature regime we normally have $z^* > z_0$ (see Fig. 5). Then after some manipulation (see Appendix B) Eq. (25) reduces to

$$R^+ = \exp[-T\Delta(z_0)] + \Gamma\left(\frac{|E_a'(z^*)|a}{2\theta} + 1\right) \times \exp\left[-\frac{|E_a(z^*)|}{\theta}\right] \tag{26}$$

(Γ being the Gamma function).

The first term in the expression for the ionization probability R^+ equals the value of R^+ for the low-temperature regime and is due primarily to the kinetic effects associated with the relatively rapid change in the energy of the level $E_a(z)$ at the point z_0 of its intersection with the Fermi level. The quantity z_0 is the effective neutralization distance, that is, starting from $z > z_0$ there is a high probability for the electron to tunnel to an atomic level. The second term relates to the "atomic level thermalization" (that is, to the attainment of the atomic level population corresponding to the local electron temperature; z^* is the effective thermalization distance).

In general, then, in secondary ion emission one can distinguish among two mechanisms of charge state formation, the tunneling mechanism (the term "tunneling" is somewhat vague in character, its application here being associated with the well accepted term "electron tunneling model" introduced[9] for a similar mechanism) and the thermalization mechanism. Which of the two predominates in the formation of secondary ions with high-temperature-regime energies, depends on the particular situation being studied. For semiconductors, the thermalization mechanism seems to prevail. For metals, the situation is more complex in that either the tunneling or the thermalization mechanism may dominate. This depends upon a variety of factors (behavior of the level $E_a(z)$, of the distance z_0, level width Δ, local electronic temperature *etc.*) and requires that each case be treated separately. Nevertheless, in the general case it proves possible to predict the characteristic behavior of R^+ as a function of the inverse velocity T (see Fig. 6). For small T (large velocities), the situation corresponds to the low-temperature regime and the only ion formation mechanism is by tunneling. With increasing T (decreasing velocity), a high-temperature regime is realized. However, even for the high-temperature regime, the tunneling mechanism may prove dominant until certain T values. As T is increased still further, temperature effects begin to show up and very soon the thermalization mechanism becomes predominant in the formation of the ion charge state (changeover to saturation in the curve $\ln R^+$ of Fig. 6).

6. CONCLUSION

The main results of the present work may be summarized as follows:

1. It is shown that for a weakly nonadiabatic motion of the particle the problem of the resonant charge exchange with a solid surface reduces to the description of the particle departure. A justification for the use of equilibrium initial conditions is given ("equilibrium" in the sense of the total "hybridized atom + surface" system).

2. An analytical solution of the charge exchange problem is obtained within the framework of the Anderson-Newns model with equilibrium initial conditions for the wide band.

3. A new technique for calculating the case $E_a=\text{const}$ in the low-temperature regime is suggested, which enables one to consistently take into account the terms associated with the memory of the system. Based on this approach, it proved possible to demonstrate that two charge exchange channels exist: a dynamic channel (the transfer of an electron to an excited state above E_F due to the finite characteristic time for the interaction switching-off process) and a channel associated with the memory of the system (in the sense of the influence of the conditions as of t_0, see Fig. 1, on the final charge state). Situations in which one of the channels is dominant are treated, and the case when the channels interfere is considered.

4. A method is proposed for determining the degree of the local heating of the electron subsystem in the region of its interaction with the scattered beam.

5. The charge exchange process in secondary ion emission from a metal, with account for the shift in the level $E_a(z)$ due to the image potential, is considered. Analysis of the solution shows that in the formation of the ion charge state, two basic mechanisms participate. The tunneling mechanism involves resonant neutralization that occurs when the atomic particle level crosses the Fermi level. The thermalization mechanism is via the attainment of the atomic level population corresponding to the local electronic temperature of the metal in the bombardment region. Depending on the particular situation and the particular metal, either the tunnel or thermalization mechanism may predominate.

APPENDIX A

Integrate in (16) over t introducing the notation

$$A=\frac{T\Delta}{2},\quad x=\frac{\omega}{\Delta}-\varepsilon,\quad \varepsilon=\frac{E_a}{\Delta},\quad \alpha=\frac{1}{2}+iAx.$$

Then (16) transforms to

$$R^+=\frac{1}{\pi}\int_{|\varepsilon|}^{+\infty} dx\,|e^{-A}f(x)+AA^{-\alpha}\Gamma(\alpha)|^2,$$

where

$$f(x)=\frac{1}{1-ix}-AA^{-\alpha}\theta^A\Gamma(\alpha,A),$$

$\Gamma(\alpha)$ is the Gamma function and $\Gamma(\alpha, A)$ is the incomplete complementary Gamma function.

Note that in the adiabatic limit $T\to\infty$ $(A\to\infty)$ we obtain the obvious result $R^+\to 0$.

Next, put R^+ in the form $R^+=I_1+I_2+\mathrm{Re}I_3$, where the integrals I_1, I_2, and I_3 arise after the removal of the modulus sign from the expression for R^+:

$$I_1=\int_{|\varepsilon|}^{+\infty} dx\,\frac{A}{\cosh(\pi Ax)}$$

$$=\frac{2}{\pi}\arctan\left\{\exp\left[-\frac{\pi|E_a|T}{2}\right]\right\}$$

$$\approx\exp\left[-\frac{\pi|E_a|T}{2}\right],$$

$$I_2=\frac{\exp[-T\Delta]}{\pi}\int_{|\varepsilon|}^{+\infty} dx\,|f(x)|^2,$$

$$I_3=e^{-A}2^{3/2}A^{1/2}\pi^{-1/2}\int_{|\varepsilon|}^{+\infty} dx\,f(x)\exp\left[A\left(-\frac{\pi}{2}x\right.\right.$$

$$\left.\left.+ix(\ln(x)-)\right)\right].$$

In writing I_3 we have used the asymptotic form of the Gamma function:

$$\Gamma(cz+d)\approx(2\pi)^{1/2}\theta^{-cz}(cz)^{cz+d-1/2}, c>0 \text{ (Ref. 13)}.$$

The integral I_3 is easily estimated by using the saddle point method (see Ref. 14); it can be shown that the leading asymptotic behavior is given by the end portion of the integration contour (i.e., $x=|\varepsilon|$). Then we have

$$I_3=2^{3/2}(\pi A)^{-1/2}f(|\varepsilon|)$$

$$\times\frac{\exp\left[-A\left(1+\frac{\pi|\varepsilon|}{2}+i\left|\varepsilon\right|(1-\ln|\varepsilon|)\right)\right]}{\frac{\pi}{2}-i\ln|\varepsilon|}.$$

Making use of the representation of $\Gamma(\alpha, A)$ in a continued fraction form[13] we can expand $f(x)$ in powers of $1/A$ giving

$$f(x)=\frac{1}{2A}\frac{1+ix}{(1-ix)^3}-\frac{1}{8A^2}\frac{4+7ix-x^2}{(1-ix)^5}+\cdots.$$

In the general expression $R^+=I_1+I_2+\mathrm{Re}I_3$, noting the approximate calculation of I_3, it makes sense to retain only the first term in the expansion of $f(x)$ [in the analysis of various charge exchange channels, also the second term in the expansion of $f(x)$ will be considered in I_2].

APPENDIX B

Let us break the integration over z in Eq. (25) in two regions, from $-\infty$ to $\tilde{z}$, and from $\tilde{z}$ to $+\infty$. The point $\tilde{z}$ lies between z_0 and z^*, the only condition being that $\tilde{z}-z_0\gg a/\pi\theta T$. Specifically let us assume that $\tilde{z}-z_0\sim a/2$ (see Fig. 5). The point $\tilde{z}$ plays an auxiliary role and, as is shown below, the result will be independent of its choice. For us here its is important that for $z>\tilde{z}$, $|E_a(z)|\gg|E_a'(z)|a/\pi\theta T$ $[E_a'(z)=(\partial/\partial z)E_a(z)]$. For $z<\tilde{z}$, noting the dominant role of the vicinity of z_0, let us

approximate the behavior of the level by $E_a(z)=E_a'(z_0)\times(z-z_0)$. Then Eq. (25) transforms into the form

$$n_a(\infty)=-i\frac{\theta T}{2a}\int_{-\infty}^{+\infty}dz\,P(z)\int_{-\infty}^{+\infty}d\tau\times\frac{\exp\left[-i\frac{E_a'(z_0)\tau}{v_\perp}(z-z_0)+i\frac{E_a'(z_0)\tau^2}{2v_\perp}\right]}{\sinh\left(\pi\theta T\frac{\tau}{a}-i0\right)}$$

$$+i\frac{\theta T}{2a}\int_{\tilde z}^{+\infty}dz\,P(z)\int_{-\infty}^{+\infty}d\tau\times\frac{\exp\left[-i\frac{E_a'(z_0)\tau}{v_\perp}(z-z_0)+i\frac{E_a'(z_0)\tau^2}{2v_\perp}\right]}{\sinh\left(\pi\theta T\frac{\tau}{a}-i0\right)}$$

$$+\int_{\tilde z}^{+\infty}dz\,P(z)F_F(E_a(z),\theta).$$

Recall that $P(z)$ is defined in Eq. (25) and that $F_F(E_a(z),\theta)$ is the Fermi distribution.

Let us take up the second term in the expression for $n_a(\infty)$. Note that the integration over τ is dominated by the region $|\tau|<a/\pi\theta T$. Then in the argument of the exponential we can neglect the term $iE_a'(z_0)\tau^2/2v_\perp$ compared to $iE_a'(z_0)\tau(z-z_0)/v_\perp$ since $z-z_0\gg a/\pi\theta T$ ($z>z_0$; $\tilde z-z_0\sim a/2$). As a result,

$$n_a(\infty)=-i\frac{\theta T}{2a}\int_{-\infty}^{+\infty}dz\,P(z)\int_{-\infty}^{+\infty}d\tau\times\frac{\exp\left[-i\frac{E_a'(z_0)\tau}{v_\perp}(z-z_0)+i\frac{E_a'(z_0)\tau^2}{2v_\perp}\right]}{\sinh\left(\pi\theta T\frac{\tau}{a}-i0\right)}$$

$$+\int_{\tilde z}^{+\infty}dz\,P(z)[F_F(E_a(z),\theta)-F_F(E_a'(z_0)(z-z_0),\theta)]=I_1+I_2.$$

Now let us treat I_1 separately. Performing integration by parts on z, and after a little manipulation in order to remove the imaginary unit from the denominator using the Sokhotsky formula

$$\frac{1}{x-i0}=\frac{1}{x}+i\pi\delta(x)\left(\sinh\left(\pi\theta T\frac{\tau}{a}-i0\right)\right.$$

$$\left.\approx\cosh\left(\pi\theta T\frac{\tau}{a}-i0\right)\left[\mathrm{th}\left(\pi\theta T\frac{\tau}{a}\right)-i0\right],\right.$$

we obtain

$$I_1=1+\frac{\theta T}{2a}\int_{-\infty}^{+\infty}d\tau\frac{E_a'(z_0)\tau}{v_\perp\sinh\left(\pi\theta T\frac{\tau}{a}\right)}\exp\left[i\frac{E_a'(z_0)\tau^2}{2v_\perp}\right]Q(\tau),$$

where

$$Q(\tau)=\int_{-\infty}^{+\infty}dy\exp\left[-i\frac{E_a'(z_0)\tau}{v_\parallel}y-\frac{2}{v_\parallel}\int_{z_0}^{+\infty}\Delta(x)dx\right](y=z-z_0),$$

$|Q(\tau)|$ is a narrow peak of width $2v_\perp/\pi|E_a'(z_0)|a$ at point $\tau=0$ [for $\Delta(z)=\Delta\exp[-2z/a]$ we indeed obtain $Q(\tau)\sim\Gamma(-iE_a'(z_0)a\tau/2v_\perp)$; $|\Gamma(i\eta)|^2=\pi/\eta\sinh(\pi\eta)$, Γ is the Gamma function].

Also, we generally have $|A_a'(z_0)|a/2\gg\theta$, i.e., the dominant contribution is given by a somewhat narrower vicinity of $\tau=0$ than $a/\pi\theta T$, which allows one to write

$$I_1=1+\frac{E_a'(z_0)}{2\pi v_\parallel}\int_{-\infty}^{+\infty}d\tau\exp\left[i\frac{E_a'(z_0)\tau^2}{2v_\parallel}\right]Q(\tau).$$

By performing the integration over τ we obtain

$$I_1=1-\int_{-\infty}^{+\infty}dy\times\exp\left[-\frac{2}{v_\parallel}\int_{z_0+y}^{+\infty}\Delta(x)dx\right]\frac{1}{2}(i\,2|E_a'(z_0)|\pi v_\parallel)^{1/2}\times\exp\left[-i\frac{|E_a'(z_0)|y^2}{2v_\parallel}\right].$$

The last integral is easily evaluated by the saddle point method (the saddle point is $y=0$):

$$I_1=1-\exp\left[-\frac{2}{v_\perp}\int_{z_0}^{+\infty}\Delta(z)dz\right]=1-\exp[-T\Delta(z_0)].$$

Now consider the integral I_2. Noting that, for $z>\tilde z$, $|E_a(z)|\gg\theta$ and $|E_a'(z_0)(z-z_0)|\gg\theta$, it is found that

$$I_2=-\int_{\tilde z}^{+\infty}dz\,P(z)\left(\exp\left[\frac{E_a(z)}{\theta}\right]-\exp\left[\frac{E_a'(z_0)(z-z_0)}{\theta}\right]\right)$$

$$\approx-\int_{\tilde z}^{+\infty}dz\,P(z)\exp\left[\frac{E_a(z)}{\theta}\right.$$

We have neglected $\exp[E_a'(z_0)(z-z_0)/\theta]$ in comparison with $\exp[E_a(z)/\theta]$ because $|E_a(z)|<|E_a'(z_0)(z-z_0)|$ for $z>\tilde z$ (see Fig. 5).

It remains to show that I_2 depends weakly on $\tilde z$. Let us employ the approximation $E_a(z)=E_a(z^*)+E_a'(z^*)\times(z-z^*)$ [recall $z^*=a/2\ln T\Delta$ is the position of the maximum of $P(z)$]. Then

$$I_2 = -\gamma[\xi, T\Delta(\tilde{z})]\exp\left[-\frac{|E_a(z^*)|}{\theta}\right.$$

$$\approx -\Gamma(\xi)\exp\left[-\frac{|E_a(z^*)|}{\theta}\right.,$$

$$\xi = \frac{|E_a'(z^*)|a}{2\theta} + 1, \quad \gamma(\xi, T\Delta(\tilde{z}))$$

$$= \Gamma(\xi) - \Gamma[\xi, T\Delta(\tilde{z})],$$

where $\gamma[\xi, T\Delta(\tilde{z})]$ is the incomplete Gamma function, $\Gamma(\xi)$ is the Gamma function, and $\Gamma[\xi, T\Delta(\tilde{z})]$ is the incomplete complementary Gamma function. It is taken into account that $\Gamma(\xi) \gtrsim 1$, $\Gamma[\xi, T\Delta(\tilde{z})] \sim \exp[-T\Delta(\tilde{z})]$ and $T\Delta(\tilde{z}) > 1$.

The final result is

$$n_a(\infty) = 1 - \exp[-T\Delta(z_0)] - \Gamma\left(\frac{|E_a'(z^*)|a}{2\theta} + 1\right)\exp\left[-\frac{|E_a(z^*)|}{\theta}\right].$$

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