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## Contribution to the theory of charge exchange at surfaces

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**Résumé.** — La fraction ionique  $P$  de particules pulvérisées ou diffusées est calculée dans un schéma d'électrons indépendants pour des variations exponentielles des éléments matriciels de couplage avec une constante de temps  $\mu^{-1}$  le long de la trajectoire émergente et, dans le cas de la diffusion,  $\lambda^{-1}$  le long de la trajectoire incidente, sans hypothèse particulière sur la structure électronique du substrat. Si la formation d'un ion résulte de transitions réparties dans le temps,  $P$  se comporte à  $\mu$  petit comme  $\exp(-C_1/\mu)$  dans la plupart des cas.  $C_1$  est une certaine intégrale de la fonction  $\varphi(\varepsilon) = -\arg \sigma(\varepsilon)$  où  $\sigma(\varepsilon)$  est la self-énergie de l'atome couplé (statiquement) au substrat. Interviennent ici aussi bien les processus résonants proches (c'est-à-dire quasi isoénergétiques) que lointains (impliquant un saut d'énergie). Si les transitions sont provoquées par la discontinuité de la dérivée par rapport au temps des éléments matriciels de couplage à  $t=0$ , due aux conditions de raccordement imposées, on obtient  $P \propto (\mu + \lambda)^2 \exp(-C_2/\mu)$  ou des expressions plus compliquées, avec  $C_2 = 0$  pour un système à niveaux discrets. Le domaine de validité des différentes expressions est précisé. Afin d'illustrer et de corroborer les résultats généraux et d'examiner d'autres dépendances en temps du couplage, trois cas particuliers sont étudiés : le cas où une méthode d'équation maîtresse s'applique, le modèle à bande large et le modèle à deux niveaux de caractère atomique.

**Abstract.** — The ion fraction  $P$  of sputtered or scattered particles is calculated in an independent-electron scheme for exponential variations of atom-substrate coupling matrix elements with a time constant  $\mu^{-1}$  along the outward trajectory and, in the scattering case,  $\lambda^{-1}$  along the inward trajectory, without specific assumptions about the electronic structure of the substrate. If ion formation results from transitions continuous in time,  $P$  behaves at small  $\mu$  as  $\exp(-C_1/\mu)$  in most cases.  $C_1$  is a certain integral of the function  $\varphi(\varepsilon) = -\arg \sigma(\varepsilon)$  where  $\sigma(\varepsilon)$  is the self-energy for the (static) coupled atom-substrate system. The contributing processes are near-resonant (i.e. quasi isoenergetic) as well as far-resonant (implying an energy jump) processes. If transitions are provoked by the discontinuity of the time derivative of coupling matrix elements at  $t=0$ , due to assumed matching conditions, one obtains  $P \propto (\mu + \lambda)^2 \exp(-C_2/\mu)$  or more complicated expressions, with  $C_2 = 0$  for a discrete-level system. The range of validity of the various expressions is delimited. In order to illustrate and corroborate the general results and examine other time dependences of the coupling, three special cases are studied : the case where a rate equation approach is applicable, the wide-band model and the atomic-like two-level model.

## 1. Introduction.

The problem of the charge state of an atomic particle leaving a surface is met chiefly in two situations: scattering, where the particle originates from outside the substrate, and sputtering, where it is extracted from it through a series of collisions initiated by a fast projectile [1]. In both cases, an essential factor governing the charge state is the emergence velocity, which will be assumed sufficiently low, as it usually is, for the most probable charge state to be the equilibrium one, i.e. the charge state the particle would acquire by being driven adiabatically away from the surface.

Theoretically this assumption leads both to a complication and a simplification. The complication is that perturbation methods, as used in collision theory, are inapplicable or insufficient. The simplification is that non-adiabatic processes occur through few channels and presumably at minimal energy cost, justifying a number of approximations in the description of the system. For instance, if the atomic level involved in charge exchange, called the  $a$ -level in the sequel, remains far from band edges or any other sharp structure in the substrate density of states during the decisive step for ion formation, a uniform density of states can be assumed (wide-band limit). At other times, the  $a$ -level crosses band edges, couples with discrete levels, is involved in multi-electron configurations and a more sophisticated description is necessary. The presence of adsorbates, displacements of substrate atoms under impact of a fast projectile, alter the electronic structure and may complicate the description or, sometimes, simplify it if they open channels which tend to dominate charge exchange.

If the probability of charge transfer at some time can be regarded, according to a classical picture, as depending only on the charge state of the particle and configuration of the system at that time, the dynamic problem reduces to the resolution of a rate (or master) equation. Widely used in neutralization theories for scattered ions [2, 3], this approach allows an equal treatment of one- and two-electron processes (resonant and Auger processes in this context), but implies weak interaction with delocalized substrate electrons only. If the collision which expels the atom from the surface plays an important role in charge exchange, it may be treated separately in an atomic model [4], but such a decomposition of the charge exchange process is rather rough.

The first full quantum calculations for a many-electron system were performed with a simplified version (wide-band limit,  $U = 0$ ) of the Newns-Anderson Hamiltonian [5-8], which has the advantage of being exactly solvable, but is applicable to a limited number of situations, essentially those where charge exchange occurs at some distance from the surface. Addition of a deep-lying level at the outgoing and substrate atoms, coupled with the upper level through a one [9] or two-body [10] interaction, gave an explanation of the oscillatory behaviour of the ionization probability of noble gas ions scattered from some surfaces as a function of the inverse velocity. Another extension of the model was to include the effect of a high velocity parallel to the surface [11, 12]. An alternative to the wide-band model is the tight-binding semi-infinite chain [13], in which both the charge state and energy loss were studied [14]. Inclusion of the Coulomb interaction  $U$  between opposite spins poses a difficult problem, not completely solved. If spin symmetry is initially broken, Hartree-Fock or similar approximations can be used, at least tentatively [15, 16]. More reliable treatments seem possible with approximate many-electron wave functions [17, 18].

Quantum calculations have also been made with clusters. Though convergence with the cluster size may be very slow [19], the method offers a means to explore effects such as movements of substrate atoms [20], the role of the Coulomb interaction  $U$  [21] and complex electronic structures [22, 23].

The present study focusses on the problem of the substrate electronic structure. The

purpose is to express a dynamic quantity, the ion fraction, in terms of static properties of the coupled atom-substrate system. The formalism is an independent-electron one, as expounded in chapter 2. The few assumptions, stated in chapter 3, essentially concern the time dependence of the atom-substrate coupling. For pedagogic reasons, three special cases are considered first, the case where the rate equation approach is applicable (chap. 4), the wide-band model (chap. 5) and the two-level model which is a prototype for cluster models and makes contact with atomic collision theory (chap. 6). The general case is treated in chap. 7, where the solution of the dynamic problem is obtained in terms of infinite series. These series can easily be calculated numerically, but more convenient and transparent expressions are their asymptotic (i.e. low velocity) form, usually a good approximation. The latter are derived for the sputtering and scattering cases in chapters 8 and 9 respectively, which contain the main results of this work.

A preliminary account of the essential results of chapters 7 and 8 appeared in two papers [24, 25]. In the first one they were applied to two model cases, the detachment of the end atom from a semi-infinite chain and the knocking-off of an atom  $a$  by an atom  $b$  itself coupled to a wide-band substrate. In the second paper, a model for secondary  $\text{Cu}^+$  emission was proposed and solved both by computing the series of chapter 7 and using the asymptotic form of chapter 8, with a good agreement between the two evaluations at velocities of physical interest. No new application will be presented here, efforts being directed towards embracing a variety of possible situations. Some of the material contained in chapters 5 and 7 was summarized in a review paper [26] or is borrowed from a thesis work [27].

For language simplicity, phrases like « ion formation » are used to mean formation of a non-equilibrium charge state, this being often (but not always) the ionic one. Units of  $\hbar = 1$  are employed throughout.

## 2. Formalism.

For a system of independent electrons submitted to a time-dependent potential, the expectation value of any physical quantity can be obtained by the following Green function method.

First consider a single electron governed by the time-dependent Hamiltonian  $H(t)$  of matrix elements  $H_{qq'}(t)$ 's in some fixed basis set  $\{q\}$ . The components  $c_q(t)$ 's of the wavevector in the same basis set obey :

$$i \frac{\partial c_q(t)}{\partial t} = \sum_{q'} H_{qq'}(t) c_{q'}(t) \quad (2.1)$$

which can formally be solved as :

$$c_q(t) = \sum_{q'} i G_{qq'}(t, t_0) c_{q'}(t_0) \quad (2.2)$$

$t_0$  being some initial time. The  $G_{qq'}$ 's are the matrix elements of the retarded Green operator  $G$  which obeys Schrödinger's equation :

$$i \frac{\partial G(t, t')}{\partial t} = H(t) G(t, t') \quad (2.3)$$

for  $t > t'$  with boundary condition  $G(t, t) = -i \mathbb{1}$ . If  $H(t)$  is decomposed into a time-independent part  $H_0$  whose Green operator  $G_0$  is known and a time-dependent part

$H_1(t)$ ,  $G$  appears as the solution of the (Dyson) integral equation :

$$G(t, t') = G_0(t - t') + \int d\tau G_0(t - \tau) H_1(\tau) G(\tau, t') \quad (2.4a)$$

or, in reverse form :

$$G(t, t') = G_0(t - t') + \int d\tau G(t, \tau) H_1(\tau) G_0(\tau - t'). \quad (2.4b)$$

For the sake of later calculations, we also introduce the adiabatic Green operator  $G^{\text{ad}}(t - t'; T)$  calculated with  $H = H(T)$  fixed. The latter is more conveniently represented by its Fourier-Laplace transform  $g^{\text{ad}}$ , defined by :

$$g^{\text{ad}}(z; T) = \int_0^\infty d\tau G^{\text{ad}}(\tau; T) e^{iz\tau} = [z - H(T)]^{-1} \quad (2.5)$$

for  $\text{Im } z > 0$  and by the analytic continuation of (2.5) for  $\text{Im } z \leq 0$ . In accordance with (2.4a),  $g^{\text{ad}}$  is the solution of the matrix equation :

$$g^{\text{ad}}(z; T) = g_0(z) + g_0(z) H_1(T) g^{\text{ad}}(z; T). \quad (2.6)$$

Now consider a system of independent electrons, each governed by  $H(t)$ . The second-quantized Hamiltonian of the system reads :

$$\mathcal{H}(t) = \sum_{q, q'} H_{qq'}(t) \hat{c}_q^+ \hat{c}_{q'}.$$

The equation of motion for the Fermi operator  $\hat{c}_q(t)$  in the Heisenberg picture is identical with (2.1) and has the same solution (2.2) with  $\hat{c}$  instead of  $c$ . Take  $t_0$  such that, for  $t < t_0$ ,  $H(t)$  is independent of time (a special case being  $t_0 \rightarrow -\infty$ ). The expectation value of any product of Fermi operators at time  $t$  can be written :

$$\langle \hat{c}_a^+(t) \dots \hat{c}_b(t) \dots \rangle = \sum_{q_a \dots q_b \dots} \sum G_{aa}^*(t, t_0) \dots G_{bb}(t, t_0) \dots \text{Tr} [\hat{\rho} \hat{c}_{q_a}^+ \dots \hat{c}_{q_b} \dots]$$

where  $\hat{c}_q = \hat{c}_q(t_0)$  and  $\hat{\rho}$  is the (initial) density matrix.

In the sequel we are interested in the occupancy  $n_a(t)$  of some state  $a$ . If we take the  $q$ -states as the eigenstates of  $H(t_0)$ , we get :

$$n_a(t) = \sum_q n_q^0 |G_{aq}(t, t_0)|^2 \quad (2.7)$$

where  $n_q^0$  is the initial  $q$ -state occupancy. If the system is initially thermalized,  $n_q^0 = n_q^0(\varepsilon_q)$  where  $n^0(\varepsilon)$  is the Fermi distribution function at considered temperature.

In charge transfer problems an atom leaves the surface and the  $\underline{a}$ -state is one of its orbitals. The time dependence of  $H(t)$  originates in the movement of this atom and its neighbours, regarded as classical particles (« trajectory approximation »). The substrate is initially thermalized. If the outgoing atom is initially (say for  $t < t_0 = 0$ ) part of it (sputtering), the final  $a$ -state occupancy reads :

$$n_a(\infty) = \int d\varepsilon n^0(\varepsilon) S(\varepsilon) \quad (2.8)$$

$$S(\varepsilon) = \sum_q \delta(\varepsilon - \varepsilon_q) |G_{aq}(\infty, 0)|^2. \quad (2.9)$$

In a scattering problem, the atom is initially (i.e. at  $t \rightarrow -\infty$ ) decoupled from the substrate. Then :

$$n_a(\infty) = n_a^0 |G_{aa}(\infty, -\infty)|^2 + \int d\varepsilon n^0(\varepsilon) S(\varepsilon) \quad (2.10)$$

$$S(\varepsilon) = \sum_{q \neq a} \delta(\varepsilon - \varepsilon_q) |G_{aq}(\infty, -\infty)|^2. \quad (2.11)$$

It is not always convenient to work with the eigenstates of  $H(t_0)$ , especially in the sputtering case where  $H(t_0)$  [i.e.  $H(0)$ ] describes the coupled atom-substrate system. Any reference to a particular basis set can be avoided by writing, instead of (2.9) :

$$\begin{aligned} S(\varepsilon) &= \langle a | G(\infty, 0) \delta(\varepsilon - H(0)) G^+(\infty, 0) | a \rangle = \\ &= -\frac{1}{\pi} \text{Im} \langle a | G(\infty, 0) g^{\text{ad}}(\varepsilon; 0) G^+(\infty, 0) | a \rangle. \end{aligned} \quad (2.12)$$

Finally, it can be noticed that (2.7), (2.8) and (2.10) remain valid if  $n_a$  and  $n^0$  are replaced by  $1 - n_a$  and  $1 - n^0$ , i.e. if holes are considered instead of electrons. This comes from the unitarity property of the Green operator :

$$\sum_q |G_{aq}(t, t_0)|^2 = 1$$

which entails, in the sputtering case :

$$\int d\varepsilon S(\varepsilon) = 1 \quad (2.13)$$

and, in the scattering case :

$$|G_{aa}(\infty, -\infty)|^2 + \int d\varepsilon S(\varepsilon) = 1. \quad (2.14)$$

### 3. Model.

Neglecting the movement of substrate atoms, assuming that at the outgoing atom only the  $a$ -orbital is involved in the charge transfer process and treating electrons as non-interacting, we can write the one-electron Hamiltonian as :

$$\left. \begin{aligned} H(t) &= H_s + H_a(t) + V(t) \\ H_a(t) &= |a\rangle \varepsilon_a(t) \langle a|, \quad \varepsilon_a(t) = \varepsilon_a^\infty + \eta(t) \end{aligned} \right\} \quad (3.1)$$

$H_s$  is the substrate Hamiltonian and  $V$  couples the  $a$ -state with substrate states. If  $H_s$  and  $V$  are expressed in terms of eigenstates of  $H_s$ , i.e.

$$\begin{aligned} H_s &= \sum_k |k\rangle \varepsilon_k \langle k| \\ V(t) &= \sum_k |k\rangle V_{ka}(t) \langle a| + h.c. \end{aligned}$$

then  $H$  (or rather its second-quantized counterpart  $\mathcal{H}$ ) takes the familiar form of the Newns-Anderson Hamiltonian without correlation. However this does not imply any assumption about the spectrum of  $\mathcal{H}_s$  which may include bands as well as discrete levels.

The first simplification to (3.1) is to suppose the  $a$ -state orthogonal to substrate states. The assumption is usual in charge transfer problems though it is really justified only when the atom is far from the surface. Its advantage is that the number of equations to solve to find the  $a$ -state Green function  $G_{aa}$  reduces to one :

$$G_{aa}(t, t') = G_a^0(t - t') + \iint d\tau d\tau' G_a^0(t - \tau) \Sigma(\tau, \tau') G_{aa}(\tau', t') \quad (3.2)$$

$$G_a^0(\tau) = -i \vartheta(\tau) e^{-i\varepsilon_a^\infty \tau}$$

$$\Sigma(t, t') = \eta(t) \delta(t - t') - i \langle a | V(t) e^{-iH_s(t-t')} V(t') | a \rangle \vartheta(t - t').$$

The other matrix elements of  $G$  are then obtained by (2.4). The adiabatic Green function  $g_{aa}^{\text{ad}}$  is, by (2.6) :

$$g_{aa}^{\text{ad}}(z; t) = [z - \varepsilon_a^\infty - \sigma^{\text{ad}}(z; t)]^{-1} \quad (3.3)$$

where  $\sigma^{\text{ad}}$  is the adiabatic self-energy :

$$\left. \begin{aligned} \sigma^{\text{ad}}(z; t) &= \eta(t) + \langle a | V(t) [z - H_s]^{-1} V(t) | a \rangle \\ &= \eta(t) + \sum_k \frac{|V_{ak}(t)|^2}{z - \varepsilon_k}. \end{aligned} \right\} \quad (3.4)$$

The other matrix elements of  $g^{\text{ad}}$  are again obtained by (2.6). It is important to note that the bound states and resonances in the adiabatic local electronic structure are given respectively by the real and complex poles of  $g_{aa}^{\text{ad}}(z; t)$ , i.e. the real and complex roots of :

$$z - \varepsilon_a^\infty - \sigma^{\text{ad}}(z; t) = 0. \quad (3.5)$$

The second simplification is to assume the same time dependence for all the  $V_{ka}$ 's :

$$V(t) = V(0) \xi(t) \quad (3.6)$$

where  $\xi$  is a real scalar function. Though setting some restrictions on the physical situations under consideration, this assumption can be justified in a number of interesting cases. One such case is when the atom-surface coupling can be described in a tight-binding model with one transfer integral or several equal transfer integrals (as in vertical desorption from a bridge or centre position on an ordered surface). Another case is when the  $V_{ka}$ 's form a continuum, but are sufficiently small for the resonance formed by the  $a$ -level to remain narrow. Then only the  $V_{ka}$ 's for  $\varepsilon_k$  near the resonance energy are important and, if the substrate density of states does not exhibit any sharp structure in this region, the relevant  $|V_{ka}|$ 's are expected to all evolve similarly. The same may not hold true as regards  $\arg V_{ka}$ , especially if the atom is moving fast with velocity  $\mathbf{v}$ , as in scattering of light atoms at grazing incidence. But this effect can be taken into account simply (and approximately) by substituting for  $n^0(\varepsilon)$  the distribution obtained with a Fermi sphere shifted by  $m_e \mathbf{v}$  in momentum space ( $m_e$  electron mass) [11].

The third simplification concerns the time dependence of the  $a$ -level energy :

$$\eta(t) = \eta(0) \xi^2(t) \quad (3.7)$$

and is designed to make the self-energy factorize :

$$\sigma^{\text{ad}}(z ; t) = \sigma(z) \xi^2(t) \quad (3.8)$$

$$\Sigma(t, t') = \xi(t) \Sigma_0(t - t') \xi(t') \quad (3.9)$$

where  $\sigma(z) = \sigma^{\text{ad}}(z ; 0)$  and  $\Sigma_0(\tau)$  is the Fourier transform of  $\sigma(z)$ . Of great importance in the sequel is its argument :

$$\varphi(\varepsilon) = -\arg \sigma(\varepsilon), \quad 0 \leq \varphi(\varepsilon) \leq \pi. \quad (3.10)$$

Physically,  $\eta$  comes from effects not allowed for by an independent-electron model. Among these, the image potential gives the contribution decaying the most slowly (as  $d^{-1}$ ) at large atom-surface separation  $d$ . Another effect is the splitting of the  $a$ -level due to the Coulomb repulsion between electrons of opposite spins or different orbital symmetries, as described (very crudely) in the Hartree-Fock approximation [28]. A third effect, specific of impact phenomena, is the overlap of core orbitals of collision partners, which produces a pseudopotential also contributing to  $\eta$ . The resulting  $\eta(t)$  has no reason to behave like  $V^2(t)$  as (3.7) would imply. In fact in a number of physically interesting situations,  $\varepsilon_a(t)$  need not be reproduced precisely at every time, but only during some important event (e.g. the crossing of the Fermi level by the sharp resonance formed by the  $a$ -level). It will then be advisable to choose  $\eta(0)$  and  $\xi_a^\infty$  so as to obtain the best  $\varepsilon_a(t)$  during that event, even if  $\varepsilon_a^\infty$  thus differs from the true atomic value. In other physical situations, the behaviour of  $\eta(t)$  over a longer time interval is important, but is actually not known precisely. Then (3.7) may serve as an interpolation.

It remains to specify  $\xi(t)$ . Since we deal primarily with slow atoms, it is essential to correctly reproduce the behaviour of  $\xi$  in the limit  $t \rightarrow \infty$ , which is (approximately) exponential. In the opposite limit  $t \rightarrow -\infty$ ,  $\xi$  tends to 1 in the sputtering case and assumes another exponential form in the scattering case. Interpolation between these limits will be dictated by mathematical convenience. We shall take :

$$\xi(t) = \vartheta(-t) + e^{-\mu t} \vartheta(t) \quad (3.11)$$

for sputtering, and :

$$\xi(t) = e^{\lambda t} \vartheta(-t) + e^{-\mu t} \vartheta(t) \quad (3.12)$$

for scattering, with  $\mu$  proportional to the (normal) emergence velocity and, in the scattering case,  $\lambda$  proportional to the incidence velocity. The absence of analyticity of (3.11) and (3.12) at  $t = 0$  is not unimportant, especially at low velocity, for the resulting discontinuity of  $d\xi/dt$  can induce excitations of very large energy which, in certain circumstances, turn out to dominate the final ionization probability. Fortunately, in the following analysis, it will be possible to identify the contribution of this singularity and to separate it from the « regular » contribution.

#### 4. The rate equation approach.

In a strict quantum-mechanical treatment, like the one described in chapter 2 and employed in the following chapters, the differential equation to be solved is Schrödinger's equation (or its variants) and the  $a$ -state occupancy  $n_a(t)$  is obtained by squaring probability amplitudes. Under certain conditions, listed below (Sect. 4.1), a differential equation can be derived for  $n_a(t)$  itself, in the form of a rate equation (or classical master equation). Used early and



widely in neutralization theories [2, 3], this approach is simple and suitable to one-electron as well as two-electron processes. As regards one-electron processes, its conditions of validity were briefly studied by Brako and Newns [6] and thoroughly by Geerlings [29] in the framework of the wide-band model. The model of chapter 3 will enable us to test it in more general conditions (Sect. 4.2) and thence to contribute to the debate concerning its validity (Sect. 4.3).

**4.1 CONDITIONS.** — Considering a substrate whose all states are distributed into bands and taking zero temperature for simplicity, we suppose the following conditions satisfied :

a) At any time  $t$  during the interval important for ion formation, the coupling  $V$  (Eq. (3.1)) remains weak, so that the  $a$ -level forms a narrow resonance (narrow as compared to band width) of centre  $\varepsilon_a(t)$  and half-width :

$$\Delta(t) = -\text{Im } \sigma^{\text{ad}}(\varepsilon_a(t); t). \quad (4.1)$$

Accordingly, excepted if  $\varepsilon_a$  is close to the Fermi energy  $\varepsilon_F$ , the adiabatic occupancy  $n_a^{\text{ad}}(t)$  is 0 or 1.

b) Either  $n_a^{\text{ad}}(t)$  changes in time, which implies  $\varepsilon_a(t)$  to cross the Fermi level or pass close to it, or the system is initially out of equilibrium (scattering case with  $n_a(-\infty) \neq n_a^{\text{ad}}(-\infty)$ ).

c) Let  $\tau$  be the time scale of variations of  $\varepsilon_a$  and  $\Delta$  (the corresponding energy uncertainty is therefore  $\tau^{-1}$ ). If  $\varepsilon_a$  crosses the Fermi level or any singularity in the density of states (e.g. band edge), the crossing is rapid at the scale of both  $1/\Delta$  and  $\tau$ , i.e.  $|\dot{\varepsilon}_a| \gg \Delta^2$  and  $\tau^{-2}$ . This important condition will be commented on in section 4.3.

d) All the time of ion formation, excepted during the short crossing of the Fermi level,  $\tau^{-1}$  is much less than the energy  $|\varepsilon_F - \varepsilon_a|$  required by a direct electron transfer, thus forbidding any other processes than strictly resonant ones. In particular  $\varepsilon_a$  and  $\Delta$  should be smooth functions.

In such conditions, the delay in restoration of equilibrium is the main cause of ion formation. According to Fermi's golden rule, equilibrium is restored at a rate  $2\Delta(t)$ .  $n_a(t)$  is thus expected to obey a rate equation :

$$dn_a/dt = 2\Delta(t)[n_a^{\text{ad}}(t) - n_a(t)]. \quad (4.2)$$

**4.2 APPLICATION TO THE MODEL OF CHAPTER 3.** — For simplicity, we assume  $\varepsilon_F > \varepsilon_a^\infty$ , so that the positive ion fraction is  $P = 1 - n_a(\infty)$ .

Consider first the sputtering case with  $\varepsilon_a$  initially above  $\varepsilon_F$  and crossing it at time  $t_c$ . Solving (4.2) gives :

$$P = \exp\left[-2 \int_{t_c}^{\infty} dt \Delta(t)\right] = \exp\left[-2 \int_{\varepsilon_a^\infty}^{\varepsilon_F} d\varepsilon_a \frac{\Delta}{(-d\varepsilon_a/dt)}\right]. \quad (4.3)$$

Using (3.8) and (3.11), we obtain :

$$d\varepsilon_a/dt = -2\mu\eta(t) = -2\mu \text{Re } \sigma^{\text{ad}}(\varepsilon_a(t); t)$$

whence, by (3.7) and (3.10) :

$$P \simeq \exp\left[-\frac{1}{\mu} \int_{\varepsilon_a^\infty}^{\varepsilon_F} d\varepsilon \tan \varphi(\varepsilon)\right]. \quad (4.4)$$

Condition (c) above implies  $\mu \eta(t_c) \gg \Delta^2(t_c)$  and  $\eta(t_c) \gg \mu$ . To be consistent these inequalities require  $\eta \gg \Delta$ , therefore  $\varphi \ll 1$ . (4.4) can thus be rewritten :

$$P \simeq \exp \left[ -\frac{1}{\mu} \int_{\varepsilon_a^\infty}^{\varepsilon_F} d\varepsilon \varphi(\varepsilon) \right]. \quad (4.5)$$

As will be seen in chapter 8, (4.5) is, up to a prefactor of minor importance, the exact  $P$  for arbitrary  $\varphi$  (therefore even for large  $\Delta$ ) under conditions equivalent to condition (d) above.

Remaining in the sputtering case, we can imagine  $\varepsilon_a$  to be initially close to  $\varepsilon_F$ , making  $n_a(0)$  fractionary. The extension of (4.5) is straightforward :

$$P \simeq [1 - n_a^{\text{ad}}(0)] \exp \left[ -\frac{1}{\mu} \int_{\varepsilon_a^\infty}^{\varepsilon_F} d\varepsilon \varphi(\varepsilon) \right]. \quad (4.6)$$

As will be seen in chapter 8, this is correct if the resonance is initially confined within an interval  $\sim \mu$  around  $\varepsilon_F$  and  $\varepsilon_F - \varepsilon_a^\infty \gg \mu$ . The rate equation approach is irrelevant if  $\varepsilon_a$  remains far below the Fermi level (see subsequent comments).

Turning to the scattering case with again  $\varepsilon_a$  crossing  $\varepsilon_F$ , we find, under the same conditions as for (4.5) :

$$P \simeq P_0 \exp \left[ -\left( \frac{1}{\lambda} + \frac{1}{\mu} \right) \int_{\varepsilon_a^\infty}^{\varepsilon_a(0)} d\varepsilon \varphi(\varepsilon) \right] + \left\{ 1 - \exp \left[ -\left( \frac{1}{\lambda} + \frac{1}{\mu} \right) \int_{\varepsilon_F}^{\varepsilon_a(0)} d\varepsilon \varphi(\varepsilon) \right] \right\} \times \\ \times \exp \left[ -\frac{1}{\mu} \int_{\varepsilon_a^\infty}^{\varepsilon_F} d\varepsilon \varphi(\varepsilon) \right]. \quad (4.7)$$

The first term is the product of  $P_0 \equiv 1 - n_a(-\infty)$  by the survival probability of the initial charge state. The second term comes from the successive electron exchanges from and to the  $\underline{a}$ -level when  $\varepsilon_a(t)$  is respectively above and below  $\varepsilon_F$ . If  $\varepsilon_a(t)$  remains above  $\varepsilon_F$  a sufficiently long time, (4.7) reduces to (4.5).

If, at  $t = 0$ , the resonance overlaps the Fermi level,  $P$  is still the sum of two terms, one being identical with the first term of (4.7), the other describing electron transfer to vacant substrate states around  $t = 0$  and being probably rather complicated since  $n_a^{\text{ad}}(t)$  varies rapidly then. However, as conditions (c) and (d) are now incompatible, the rate equation approaches becomes questionable. It is indeed invalid, for as will be seen the narrow resonance has not enough time to build up.

Finally, if  $\varepsilon_a$  remains well below  $\varepsilon_F$ .  $P$  can only be the survival probability of a supposedly ionic initial charge state. If  $\varepsilon_a(t)$  varies substantially, making  $\Delta(0) \ll \varepsilon_a(0) - \varepsilon_a^\infty$ ,  $P$  is given by the first term of (4.7). A similar expression holds if  $\varepsilon_a(t)$  varies in the opposite direction. Otherwise, it is as simple to write :

$$P \simeq P_0 \exp \left[ -\left( \frac{1}{\lambda} + \frac{1}{\mu} \right) \Delta(0) \right]$$

provided  $|\partial \text{Im} \sigma^{\text{ad}}(\varepsilon, t) / \partial \varepsilon| \ll 1$ .

4.3 COMMENTS. — Whenever  $\varepsilon_a$  was supposed to cross  $\varepsilon_F$ , condition (c) of section 4.1 led us to approximate  $n_a^{\text{ad}}(t)$  by a step function

$$n_a^{\text{ad}}(t) = \vartheta(\varepsilon_F - \varepsilon_a(t)) \quad (4.8)$$

in the resolution of (4.2). A fractionary  $n_a^{\text{ad}}$  was only used in (4.6) to describe an initial state effect in the very special case of  $\varepsilon_a$  being close to  $\varepsilon_F$  before the atom leaves the surface. Now suppose  $\varepsilon_a$  initially well below  $\varepsilon_F$ , always in the sputtering case. Since the resonance has a long lorentzian tail,  $n_a^{\text{ad}}(0)$  may not be completely negligible. Might an expression of the form

$$P \simeq [1 - n_a^{\text{ad}}(0)] \exp - \int_0^\infty dt \Delta(t)$$

generalize (4.6), at least approximately? The answer is negative. Exact calculations show that the true ion fraction is considerably smaller, either because of a smaller exponential, as happens if  $\varepsilon_a(t)$  and  $\Delta(t)$  are smooth functions (see for instance Sect. 5.2), or a smaller prefactor, as happens if they exhibit a singularity at  $t = 0$  (see Sects. 5.3 and 5.5). In fact, the occupancy defect  $1 - n_a^{\text{ad}}(0)$  is not of statistical origin, as the one produced by an incomplete neutralization, but is due to the admixture of the  $a$ -state with specific substrate states, viz. those above the Fermi level. Fermi's golden rule gives the decay rate of a discrete level coupled to a continuum. It is still applicable if the level spreads a little as a result of previous resonant processes. It cannot of course tell anything about possible transitions between states participating of a given resonance, which transitions would be the only way for the  $a$ -state to keep a memory of its overlap with empty states since the latter evolve adiabatically towards pure substrate states.

This is why, excepted in the special case leading to (4.6) and reconsidered later one, any attempt to correct  $n_a^{\text{ad}}$  for finite resonance width effects is irrelevant. The problem would be quite different for temperature effects, which are really of statistical nature. The substitution of a Fermi function for the step function (4.8) would then raise no difficulty and could even extend the range of validity of the rate equation approach [6, 29].

Besides static resonance effects, the  $a$ -level undergoes a dynamic broadening. If  $\varepsilon_a(t)$  and  $\Delta(t)$  are smooth functions and  $\tau$  is the time scale of their variations, this broadening is characterized by a width  $\tau^{-1}$  and an exponentially decaying lineshape can be ascribed to it to account for possible induced transitions. If  $\varepsilon_a(t)$  or  $\Delta(t)$  is singular, the exponential decay gives way to a power law decay at large energies, as will appear in the sequel. The correctness of (4.6) for a resonance initially confined within an interval  $\sim \mu$  around  $\varepsilon_F$  can be explained by this dynamic broadening, which redistributes the electrons between the various states inside the resonance, as if the occupancy defect was of statistical origin.

The broadening of the  $a$ -level is thus characterized by two parameters: statically,  $\Delta$ ; dynamically,  $\tau^{-1}$ . This is why the fast-crossing condition (c) of section 4.1 implies both  $\Delta^2$  and  $\tau^{-2} \ll \dot{\varepsilon}_a$ . In case of an exponentially decaying  $\Delta$  ( $\propto e^{-2\mu t}$ ) and an  $\varepsilon_a$  not varying more sharply than  $\Delta$  (i.e.  $|\ddot{\varepsilon}_a/\dot{\varepsilon}_a| \leq \dot{\Delta}/\Delta$ ), that double condition writes

$$|\dot{\varepsilon}_a| \gg \Delta^2 \quad \text{and} \quad \mu^2$$

and was previously obtained by Geerlings [29]. In practice the most important condition is a combination of them [6, 29]:

$$|\dot{\varepsilon}_a| \gg \mu \Delta. \quad (4.9)$$

This will be confirmed in section 4.7 in the framework of the wide-band model. For the model of chapter 3 (arbitrary density of states, similar behaviours of  $\varepsilon_a$  and  $\Delta$ ), (4.9) is equivalent to  $\varphi(\varepsilon) \ll 1$  and is a necessary condition for (4.5) to be well approximated by (4.4). On the contrary. Nørskov and Lang [30] found (4.9) a too strong criterion, but their criticism should probably be put down to a too specific case being considered.

**5. The wide-band case.**

The simplest approximation for  $\sigma^{ad}(z ; t)$  [defined by (3.4)] is to suppose it independent of  $z$  :

$$\sigma^{ad}(z ; t) = \Sigma(t) \equiv E(t) - i \Delta(t) . \tag{5.1}$$

A way to arrive at this form is to take  $V_{ak}(t) = V(t)$ , independent of  $k$  (contact interaction), and a substrate density of states  $\rho_s(\varepsilon)$  constant over an interval  $-D_1 < \varepsilon < D_2$  with  $D_1$  and  $D_2$  tending to infinity (wide-band approximation). Then :

$$\Delta(t) = \pi \rho_s |V(t)|^2 \tag{5.2}$$

$$E(t) = \eta(t) - \frac{1}{\pi} \Delta(t) \ln (D_2/D_1) \tag{5.3}$$

the last term coming from the Hilbert transform of  $\text{Im } \sigma^{ad}(\varepsilon ; t)$ .

This model, often called the wide-band model, is solvable exactly as recalled below in section 5.1. For few forms of  $\Sigma(t)$ ,  $S(\varepsilon)$  can be expressed with the aid of current mathematical functions (Sect. 5.2). In general however only the asymptotic  $S(\varepsilon)$  can be obtained explicitly. This is done in section 5.3 for the  $\Sigma(t)$  of chapter 3, in section 5.4 for a general, but analytic  $\Sigma(t)$  and in section 5.5 for a class of singular  $\Sigma(t)$ 's. The behaviour of  $S(\varepsilon)$  when  $\Sigma(t)$  passes from an analytic to singular form is examined in section 5.6. The use of the rate-equation approach is discussed in section 5.7.

**5.1 GENERAL SOLUTION.** — The wide-band model was solved early for sputtering [5] and scattering [27, 6]. Mathematically its simplicity is due to the local character of the kernel  $\Sigma(\tau, \tau')$  appearing in (3.2) [ $\Sigma(\tau, \tau') \propto \delta(\tau - \tau')$ ]. By derivation with respect to  $t$ , (3.2) becomes a first-order differential equation whose solution is :

$$G_{aa}(t, t') = -i \vartheta(t - t') \exp \left\{ -i \int_{t'}^t d\tau [\varepsilon_a^\infty + \Sigma(\tau)] \right\} .$$

Then the quantities of interest for the calculation of  $n_a(\infty)$  are readily obtained :

$$|G_{aa}(\infty, -\infty)|^2 = \exp \left[ -2 \int dt \Delta(t) \right] \tag{5.4}$$

$$S(\varepsilon) = \frac{1}{\pi} \left| \int dt \sqrt{\Delta(t)} \exp \left\{ i \int_t^\infty d\tau [\varepsilon - \varepsilon_a^\infty - \Sigma(\tau)] \right\} \right|^2 . \tag{5.5}$$

**5.2 TWO EXAMPLES AND AN INTERPRETATION.** — There are few forms of  $\Sigma(t)$  for which  $S(\varepsilon)$  can be expressed with the aid of current mathematical functions. The simplest example is :

$$\Sigma(t) = \Sigma_0' e^{-2\mu t} , \quad -\infty < t < \infty \tag{5.6}$$

for which :

$$S(\varepsilon) = \frac{\sin \varphi}{\mu} \frac{\exp[-(\varepsilon - \varepsilon_a^\infty) \varphi / \mu]}{1 + \exp[-\pi(\varepsilon - \varepsilon_a^\infty) / \mu]} \tag{5.7}$$

with  $\varphi = -\arg \Sigma_0$ . To derive this result, one integrates over  $\tau$ , changes to variable  $x = e^{-2\mu t}$  and uses, for real  $x$  :

$$\left| \Gamma \left( \frac{1}{2} + ix \right) \right|^2 = \pi \operatorname{sech} \pi x . \quad (5.8)$$

The unitarity relation (2.3) is easily proved by using :

$$\sin \varphi \int dx \frac{e^{-\varphi x}}{1 + e^{-\pi x}} = 1 \quad (5.9)$$

an identity useful in the sequel. The probability of hole formation  $P = 1 - n_a(\infty)$ , deduced from (2.8), may be written, at zero temperature :

$$P = \frac{2}{\pi} \sin \varphi \Theta_{2\varphi/\pi} \left( \tan^{-1} \exp \left[ -\frac{\mu(\varepsilon_F - \varepsilon_a^\infty)}{2\mu} \right] \right) \quad (5.10)$$

where  $\Theta_\nu(x) = \int_0^x du (\tan u)^{\nu-1}$ . If  $\varepsilon_F - \varepsilon_a^\infty \gg \mu$  :

$$P \simeq \frac{\sin \varphi}{\varphi} \exp - \frac{(\varepsilon_F - \varepsilon_a^\infty) \varphi}{\mu} . \quad (5.11)$$

Another example is :

$$\Sigma(t) = \Sigma_0 / (1 + e^{2\mu t}) , \quad \Sigma_0 = E_0 - i\Delta_0 . \quad (5.12)$$

The same change of variable as before transforms the integrand in (5.5) into a product of powers of  $x$  and  $1+x$ . The integral is a beta function, and, using (5.8) again, one obtains :

$$S(\varepsilon) = \frac{\Delta_0}{4\mu^2} \operatorname{sech} \frac{\pi(\varepsilon - \varepsilon_a^\infty)}{2\mu} \left| \Gamma \left( \frac{\varepsilon - \varepsilon_a^\infty - \Sigma_0}{2i\mu} \right) / \Gamma \left( \frac{i\Sigma_0}{2\mu} + \frac{1}{2} \right) \right|^2 .$$

For small  $\mu$  and  $\varepsilon > \varepsilon_a^\infty$ , this becomes :

$$\begin{aligned} S(\varepsilon) &\simeq \frac{\sin \psi(\varepsilon)}{\mu} \exp - \frac{C(\varepsilon)}{\mu} \\ C(\varepsilon) &= (\varepsilon - \varepsilon_a^\infty) \psi(\varepsilon) + \Delta_0 \ln \frac{\sin \psi(\varepsilon)}{\sin \varphi} - E_0 [\psi(\varepsilon) - \varphi] \\ \psi(\varepsilon) &= -\arg (\Sigma_0 + \varepsilon_a^\infty - \varepsilon) , \quad \varphi = -\arg \Sigma_0 \end{aligned} \quad (5.13)$$

with  $\varphi$  and  $\psi$  between 0 and  $\pi$ . Note that :

$$C(\varepsilon) = \int_{\varepsilon_a^\infty}^{\varepsilon} d\varepsilon' \psi(\varepsilon') .$$

The resulting  $P$  is :

$$P \simeq \frac{\sin \psi(\varepsilon_F)}{\psi(\varepsilon_F)} \exp - \frac{C(\varepsilon_F)}{\mu} . \quad (5.14)$$

If  $\varepsilon_F - \varepsilon_a^\infty \ll |\Sigma_0|$ ,  $\psi(\varepsilon < \varepsilon_F) \simeq \varphi$ , making (5.14) coincide with (5.11). If  $\varepsilon_F - \varepsilon_a^\infty \gg |\Sigma_0|$ ,

$\psi(\varepsilon_F)$  is close to  $\pi$ ; the prefactor is small, approximately  $\Delta_0/\pi(\varepsilon_F - \varepsilon_a^\infty)$ , and :

$$C(\varepsilon_F) \approx \pi(\varepsilon_F - \varepsilon_a^\infty) - \Delta_0 \ln \frac{e \sin \varphi (\varepsilon_F - \varepsilon_a^\infty - E_0)}{\Delta_0} - (\pi - \varphi) E_0. \quad (5.15)$$

What kind of processes do these results describe? Consider example (5.6) for  $\varphi \ll 1$  and  $\mu \ll \varepsilon_F - \varepsilon_a^\infty$ . The fact that (5.11) coincides with (4.5) clearly supports an interpretation in terms of resonant processes. The same holds for example (5.12) if  $\varepsilon_F - \varepsilon_a^\infty \ll E_0$ . Here resonant transitions occur when the narrow resonance formed by the  $a$ -state crosses occupied substrate levels and only act to restore equilibrium. Considering again (5.6), suppose  $\varphi$  close to  $\pi$ . The resonance is still narrow, but remains below the Fermi level. Charge transfer requires a minimum energy jump  $\varepsilon_F - \varepsilon_a^\infty$  whereas the variation of  $\Sigma$  with time can induce excitations of energy  $\sim \mu$ . Not unexpectedly,  $P$  is dominated by  $\exp[-\pi(\varepsilon_F - \varepsilon_a^\infty)/\mu]$  where it appears a Massey factor  $(\varepsilon_F - \varepsilon_a^\infty)/\mu$  [compare with (6.5)-(6.6) later on]. Here transitions destroy equilibrium. Example (5.12) is more instructive because the resonance initially lies at finite distance  $E_0$  from  $\varepsilon_a^\infty$  with a finite width  $2\Delta_0$ . If  $|E_0| \ll \varepsilon_F - \varepsilon_a^\infty$  and  $\Delta_0 \rightarrow 0$ , (5.15) gives :

$$C(\varepsilon_F) \approx \begin{cases} \pi(\varepsilon_F - \varepsilon_a^\infty - E_0) & E_0 > 0 \\ \pi(\varepsilon_F - \varepsilon_a^\infty) & E_0 < 0. \end{cases}$$

Again the Massey factor is proportional to the minimum energy jump. If  $\Delta_0 \neq 0$ , static resonance width effects come in and the minimum energy is ill-defined. The Massey factor is reduced, as (5.15) shows, but not in an obvious way. Should such transitions be called resonant processes? At least to describe the small velocity behaviour of  $P$ , a unique concept is desirable for mathematical reasons. As will be shown in section 5.4, if  $\Sigma(t)$  is an analytic function, electron exchange with a substrate level of energy  $\varepsilon$  can be regarded as taking place about some complex time  $t_{sp}$  such that  $\varepsilon$  equals the (complex) resonance energy  $\varepsilon_a^\infty + \Sigma(t_{sp})$ . This holds not only in case of a narrow resonance crossing the substrate level ( $t_{sp}$  is then nearly real) but also in case of a resonance remaining far from it ( $t_{sp}$  is then quite complex). To distinguish these cases, we shall speak of near and far resonance.

5.3 APPLICATION TO THE MODEL OF CHAPTER 3. — With the forms (3.11) and (3.12) for  $\xi(t)$ ,  $\Sigma(t)$  reads :

$$\begin{aligned} \Sigma(t) &= \Sigma_0 [e^{-2\mu t} \vartheta(t) + \vartheta(-t)] && \text{(sputtering)} \\ \Sigma(t) &= \Sigma_0 [e^{-2\mu t} \vartheta(t) + e^{2\lambda t} \vartheta(-t)] && \text{(scattering)} \end{aligned} \quad (5.16)$$

Let  $\Sigma_0 = E_0 - i\Delta_0 = |\Sigma_0| e^{-i\varphi}$  ( $0 < \varphi < \pi$ ). With the change of variable  $x = e^{-2\mu t}$  for  $t > 0$  and, in the scattering case,  $x = e^{2\lambda t}$  for  $t < 0$ , (5.5) becomes :

$$S(\varepsilon) = \frac{\Delta_0}{\pi} |I + J|^2$$

where

$$\begin{aligned} I &= \frac{1}{2\mu} \int_0^1 \frac{dx}{\sqrt{x}} x^{i(\varepsilon - \varepsilon_a^\infty)/2\mu} e^{\Sigma_0 x/2i\mu} \\ J &= \frac{i}{\varepsilon - \varepsilon_a^\infty - \Sigma_0} e^{\Sigma_0/2i\mu} && \text{(sputtering)} \\ J &= \frac{e^{\Sigma_0/2i\mu}}{2\lambda} \int_0^1 \frac{dx}{\sqrt{x}} x^{i(\varepsilon_a^\infty - \varepsilon)/2\lambda} e^{\Sigma_0(1-x)/2i\lambda} && \text{(scattering)}. \end{aligned}$$

In the scattering case, the survival probability of the initial state is simply :

$$|G_{aa}(\infty, -\infty)|^2 = \exp\left[-\left(\frac{1}{\lambda} + \frac{1}{\mu}\right) \Delta_0\right]. \quad (5.17)$$

Assume  $\varepsilon_F > \varepsilon_a^\infty$  and zero temperature. If  $\mu$  and  $\lambda$  are much smaller than at least one of the other energy parameters  $\varepsilon_F - \varepsilon_a^\infty$ ,  $E_0$  or  $\Delta_0$ , approximate expressions of  $P \equiv 1 - n_a(\infty)$  can be obtained.

a) Suppose first  $\Delta_0$  sufficiently large, so that  $J$  is negligible and  $I$  can be evaluated with the upper limit of integration moved to infinity. This means that the behaviour of  $\Sigma(t)$  for  $t < 0$  does not matter.  $S(\varepsilon)$  is then well approximated by (5.7) and  $P$  by (5.10). Two conditions are required for that :  $\Delta_0 \gg \lambda$  (automatically satisfied in the sputtering case) and  $\Delta_0 > (\varepsilon_F - \varepsilon_a^\infty) \varphi$  as comparison with the following case reveals.

b) When  $\varepsilon - \varepsilon_a^\infty$  is sufficiently large, the main contribution to  $I$  comes from the vicinity of  $x = 1$  and is comparable to  $J$ . Then :

$$S(\varepsilon) \simeq (\mu + \lambda)^2 R(\varepsilon) e^{-\Delta_0/\mu} \quad (5.18)$$

( $\lambda = 0$  in the sputtering case) where :

$$R(\varepsilon) = \frac{1}{\pi} \Delta_0 |\varepsilon - \varepsilon_a^\infty + \Sigma_0|^2 / |\varepsilon - \varepsilon_a^\infty - \Sigma_0|^6. \quad (5.19)$$

Consequently, if  $\varepsilon_F - \varepsilon_a^\infty$  is sufficiently large :

$$P \simeq (\mu + \lambda)^2 e^{-\Delta_0/\mu} \int_{\varepsilon_F}^{\infty} d\varepsilon R(\varepsilon) + P_0 \exp\left[-\left(\frac{1}{\lambda} + \frac{1}{\mu}\right) \Delta_0\right]. \quad (5.20)$$

The first term is due to transitions induced by the singularity at  $t = 0$  (notice the quantity  $\mu + \lambda$  proportional to the discontinuity of  $d\Sigma/dt$  and the survival factor  $e^{-\Delta_0/\mu}$ ). The second one, which is the memory of the initial ionic state in the scattering case, needs to be considered only if  $\Delta_0 \leq \lambda$ . A sufficiently large  $(\varepsilon_F - \varepsilon_a^\infty)$  means at least  $\varepsilon_F - \varepsilon_a^\infty \gg \mu$ . Furthermore comparison with case (a) shows that the condition

$$(\varepsilon_F - \varepsilon_a^\infty) \varphi - \Delta_0 \gg \mu$$

must also be satisfied. If  $(\varepsilon_F - \varepsilon_a^\infty) \varphi$  only exceeds  $\Delta_0$  by a quantity  $\sim \mu$ ,  $P$  is intermediate between (5.10) and (5.20).

c) In the sputtering case, when

$$|\varepsilon - \varepsilon_a^\infty - \Sigma_0| < \mu \ll \varepsilon - \varepsilon_a^\infty, \quad (5.21)$$

$I$  becomes much smaller than  $J$  and  $S(\varepsilon)$  may be written :

$$S(\varepsilon) \simeq \rho_a(\varepsilon) e^{-\Delta_0/\mu} \quad (5.22)$$

$\rho_a(\varepsilon)$  being the local density of states at  $t = 0$ . Consequently if (5.21) is satisfied for  $\varepsilon = \varepsilon_F$ , i.e. the  $a$ -level forms a narrow resonance lying initially close to the Fermi level and moving downwards,

$$P \simeq [1 - n_a^{\text{ad}}(0)] e^{-\Delta_0/\mu} \quad (5.23)$$

in agreement with (4.6) [notice that here  $(\varepsilon_F - \varepsilon_a^\infty) \varphi \approx E_0 \varphi \approx \Delta_0$ ]. As mentioned in chapter 4, there is no similar simplification in the scattering case for a narrow resonance moving up and down and overlapping the Fermi level at  $t = 0$ .

d) In the scattering case, if  $\lambda \sim \mu$  and

$$\Delta_0 \leq \mu \ll \varepsilon_F - \varepsilon_a^\infty < E_0 \tag{5.24}$$

i.e. the  $a$ -level forms a narrow resonance which crosses the Fermi level successively up and down,  $I$  and  $J$  are both of the order of  $\mu$  as far as  $|\varepsilon - \varepsilon_a^\infty| \leq E_0$ . To obtain  $P$ , it is not convenient to integrate  $S(\varepsilon)$  from  $\varepsilon_F$  to  $\infty$  because  $S(\varepsilon)$  has no simple expression for  $\varepsilon \approx \varepsilon_a^\infty + E_0$ , but we can integrate from  $-\infty$  to  $\varepsilon_F$  and use (5.9). For  $\varepsilon < \varepsilon_F$ ,  $I$  and  $J$  can be evaluated with the upper limit of integration moved to infinity. Finally, to lowest order in  $\Delta_0/(\varepsilon_F - \varepsilon_a^\infty - E_0)$ :

$$P \approx e^{-\frac{(\varepsilon_F - \varepsilon_a^\infty)\varphi}{\mu}} + \left[ P_0 - e^{\frac{(\varepsilon_F - \varepsilon_a^\infty)\varphi}{\lambda}} \right] e^{-\left(\frac{1}{\lambda} + \frac{1}{\mu}\right) \Delta_0} \tag{5.25}$$

in agreement with (4.7). In the sputtering case, upon conditions (5.24),  $P$  reduces to the first term of (5.25), in agreement with (4.5). In fact this case is included in case (a).

5.4 ASYMPTOTIC EXPRESSION FOR AN ANALYTIC  $\Sigma(t)$ . — If  $\Sigma(t)$  is analytic, the small-velocity behaviour of  $S(\varepsilon)$  is obtained by the saddle-point method, as done first by Brako and Newns [6]. The saddle point  $t_{sp}$  is a solution of

$$\varepsilon - \varepsilon_a^\infty - \Sigma(t_{sp}) = 0. \tag{5.26}$$

Asymptotically :

$$S(\varepsilon) \approx S_0(\varepsilon) \exp[-D(\varepsilon)] \tag{5.27}$$

$$S_0(\varepsilon) = 2 \left| \Delta(t_{sp}) / \dot{\Sigma}(t_{sp}) \right| \tag{5.28}$$

$$D(\varepsilon) = 2 \operatorname{Im} \int_{t_{sp}}^{\infty} d\tau [\varepsilon - \varepsilon_a^\infty - \Sigma(\tau)]$$

where  $\dot{\Sigma} = d\Sigma/dt$ .  $S_0$  and  $D$  are inversely proportional to the velocity. Considering  $t_{sp}$  as a function of  $\varepsilon$  through (5.26) and noticing that

$$dD/d\varepsilon = \partial D/\partial \varepsilon = -2 \operatorname{Im} t_{sp} \equiv \delta(\varepsilon)$$

we can also express  $D(\varepsilon)$  as

$$D(\varepsilon) = \int_{\varepsilon_a^\infty}^{\varepsilon} d\varepsilon' \delta(\varepsilon'). \tag{5.29}$$

Equation (5.26) has always several solutions. The reason is that, for  $n_a(\infty)$  to deviate from its adiabatic value,  $\Sigma(t)$  should decay faster than  $1/t$  as  $t \rightarrow \infty$  [5], so that (5.26) cannot be of first degree. (5.29) shows that, among several possible saddle points, the one lying closest to the real axis gives the dominant contribution to  $S(\varepsilon)$ . If  $\varepsilon > \varepsilon_a^\infty$  (resp.  $\varepsilon < \varepsilon_a^\infty$ ),  $t_{sp}$  should be in the lower (resp. upper) half-plane to make  $D(\varepsilon)$  positive. An illustration of these points is provided by examples of section 5.2.



To appreciate the accuracy of (5.27), let us push the expansion a step further :

$$S(\varepsilon) = S_0(\varepsilon) e^{-D(\varepsilon)} [1 + \text{Im } \mathcal{A}(t_{\text{sp}}) + \dots] \quad (5.30)$$

$$\mathcal{A}(t) = \frac{1}{2 \dot{\Sigma}} \left[ \frac{\dot{\Delta}^2}{2 \Delta^2} - \frac{\ddot{\Delta}}{\Delta} + \frac{\dot{\Delta} \ddot{\Sigma}}{\Delta \dot{\Sigma}} - \frac{5}{6} \left( \frac{\ddot{\Sigma}}{\dot{\Sigma}} \right)^2 + \frac{\ddot{\Sigma}}{2 \dot{\Sigma}} \right] \quad (5.31)$$

the corrective term  $\mathcal{A}$  being first order in velocity. If  $\Sigma(t)$  is a pure exponential [Eq. (5.6)],  $\text{Im } \mathcal{A}(t_{\text{sp}})$  vanishes ; in fact, as (5.7) shows, there is then no finite-order correction, only exponentially small ones. If  $\Sigma(t)$  is given by (5.12), it comes

$$\text{Im } \mathcal{A}(t_{\text{sp}}) = \frac{\mu}{3 \Delta_0} \left[ \sin^2 \psi(\varepsilon) + \frac{1}{2} \sin^2 \varphi \right].$$

Qualitatively, deviations of  $\Sigma(t)$  from an exponential restrain the asymptotic behaviour to lower velocities.

Knowing  $S(\varepsilon)$ , we can evaluate the ion fraction. If  $\varepsilon_{\text{F}} > \varepsilon_a^\infty$  :

$$P = P_0 \exp \left[ -2 \int dt \Delta(t) \right] + \frac{S_0(\varepsilon_{\text{F}})}{\delta(\varepsilon_{\text{F}})} \times e^{-D(\varepsilon_{\text{F}})} [1 + \text{Im } \mathcal{B}(\varepsilon_{\text{F}}) + \dots] \quad (5.32)$$

$$\mathcal{B}(\varepsilon) = \mathcal{A}(t_{\text{sp}}) + \frac{i}{\delta(\varepsilon) \dot{\Sigma}} \left( \frac{\dot{\Delta}}{\Delta} - \frac{\ddot{\Sigma}}{\dot{\Sigma}} + \frac{2i}{\delta(\varepsilon)} \right) \Big|_{t=t_{\text{sp}}} . \quad (5.33)$$

**5.5 INFLUENCE OF SINGULARITIES.** — Suppose that  $\Sigma(t)$  is continuous everywhere and analytic in each of intervals  $\mathbb{J}_+ = (0, \infty)$  and  $\mathbb{J}_- = (-\infty, 0)$ , but one or some of its derivatives are discontinuous at  $t = 0$ . If  $\varepsilon_a^\infty + E(t)$  remains far below the Fermi level and  $\Delta(t)$  does not become large, « regular » resonant processes are negligible.  $P$  is then dominated by transitions due to singularities of  $\Sigma(t)$  and can be evaluated in the following way.

Setting  $\varepsilon_0 = \varepsilon_a^\infty + E(0)$ , rewrite (5.5) as :

$$S(\varepsilon) = \frac{1}{\pi} \exp \left[ -2 \int_0^\infty dt \Delta(t) \right] |L_+(\varepsilon) - L_-(\varepsilon)|^2$$

$$L_\pm(\varepsilon) = \pm \int_{\mathbb{J}_\pm} dt \Lambda(t) \exp[-i(\varepsilon - \varepsilon_0)t]$$

$$\Lambda(t) = \sqrt{\Delta(t)} \exp \left\{ i \int_0^t d\tau [E(\tau) - E(0) - i\Delta(\tau)] \right\} .$$

By integration by parts,  $L_\pm(\varepsilon)$  can be expressed as an asymptotic series :

$$L_\pm(\varepsilon) = \frac{\Lambda(\pm 0)}{i(\varepsilon - \varepsilon_0)} + \frac{\dot{\Lambda}(\pm 0)}{[i(\varepsilon - \varepsilon_0)]^2} + \frac{\ddot{\Lambda}(\pm 0)}{[i(\varepsilon - \varepsilon_0)]^3} + \dots$$

whence

$$P = P_0 \exp \left[ -2 \int_{-\infty}^\infty dt \Delta(t) \right] + \frac{1}{4\pi} \exp \left[ -2 \int_0^\infty dt \Delta(t) \right] \times$$

$$\times \left\{ \frac{(\delta \dot{\Lambda})^2}{3 \Delta(0)(\varepsilon_{\text{F}} - \varepsilon_0)^3} + \frac{\delta \dot{\Lambda} \delta \dot{E}}{(\varepsilon_{\text{F}} - \varepsilon_0)^4} + \dots \right\} \quad (5.34)$$

with the notation  $\delta f = f(+0) - f(-0)$ . Again this is an asymptotic (i.e. divergent) series, meaningful only for large  $\epsilon_F - \epsilon_0$ . If only one of the functions  $\Delta(t)$  and  $E(t)$  is singular at  $t = 0$  with a discontinuity in its  $n$ -th derivative, the leading term within the curly brackets is, respectively :

$$\frac{1}{2n+1} \frac{[\delta\Delta^{(n)}]^2}{\Delta(0)(\epsilon_F - \epsilon_0)^{2n+1}} \quad \text{and} \quad \frac{1}{2n+3} \frac{\Delta(0)[\delta E^{(n)}]^2}{(\epsilon_F - \epsilon_0)^{2n+3}}$$

(5.20) is a special case of (5.34).

5.6 FROM SMOOTH TO SINGULAR  $\Sigma(t)$ . — Physically  $\Sigma(t)$  may vary more or less sharply depending on the way the considered atom (atom  $a$ ) leaves the surface. For instance suppose that this atom, initially at rest, is kicked off by a substrate atom  $b$  through a head-on binary collision governed by the interatomic potential

$$V_{\text{int}}(R) \propto \exp(-\beta_0 R)$$

( $R$  interatomic distance). Suppose further that, along the trajectory  $z(t)$  of atom  $a$ ,  $\Sigma$  varies as :

$$\Sigma(t) = \Sigma_0 \exp[-\alpha z(t)]$$

the movement starting at  $z = 0$ . Then, if  $v_0$  is the final velocity, an elementary calculation gives :

$$\Sigma(t) = \Sigma_0 [1 + \exp(\beta v_0 t)]^{-\alpha/\beta} \tag{5.35}$$

where  $2\beta = (1 + m_a/m_b)\beta_0$ ,  $m_a$  and  $m_b$  being atomic masses. Since  $V_{\text{int}}$  is due primarily to inner-shell interactions,  $\beta$  is expected to be larger than  $\alpha$ . The soft-collision case  $\beta = \alpha$  was treated in section 5.2. The hard-collision limit  $\beta \rightarrow \infty$  produces the singular form (5.16) with  $2\mu = \alpha v_0$ . Reality is somewhere between.

Our purpose is to investigate how, when  $\beta$  increases,  $S(\epsilon)$  passes from one asymptotic form to the other. For that we use (5.27)-(5.31) which give us the asymptotic  $S(\epsilon)$  and the first corrective term. We assume  $\epsilon > \epsilon_a^\infty$ . Setting :

$$r = \left( \frac{\epsilon - \epsilon_a^\infty}{\Sigma_0} \right)^{\beta/\alpha}$$

and  $\varphi = -\arg \Sigma_0$  ( $0 < \varphi < \pi$ ), we have :

$$S_0(\epsilon) = \frac{2 \sin \varphi}{\alpha v_0 |1 - r|}$$

$$\delta(\epsilon) = \begin{cases} \frac{2}{\beta v_0} \left[ \frac{\beta \varphi}{\alpha} - \text{Arg}(1 - r) \right] & (5.36a) \\ \frac{2}{\beta v_0} \left[ \pi - \text{Arg} \left( 1 - \frac{1}{r} \right) \right] & (5.37b) \end{cases}$$

$$\text{Im } \mathcal{A}(t_{\text{sp}}) = \frac{\beta v_0}{12(\epsilon - \epsilon_a^\infty)} \text{Im} \left[ \left( \frac{\alpha}{\beta} + \frac{\beta}{\alpha} - 1 \right) r + \frac{\beta}{\alpha} \frac{2}{1 - r} \right] \tag{5.37}$$

(5.36a) and (5.36b) are equivalent if the determination of the argument is not specified. Let us impose  $|\text{Arg}(\dots)| < \pi/2$ . Starting from the known case  $\beta = \alpha$  and arguing that

$\delta(\varepsilon)$  should be a continuous function of  $\beta$  (since a little difference in  $\beta$  should not produce a jump in the ion fraction), we find that (5.36a) and (5.36b) hold for  $|r| < 1$  and  $|r| > 1$  respectively. For  $|r| = 1$ , the continuity argument is of no use since  $S_0$  diverges and  $\delta$  is undefined whenever  $r = 1$ , i.e.  $\beta$  is a multiple of  $2\pi\alpha/\varphi$ .

We notice the following points :

a) If  $\varepsilon - \varepsilon_a^\infty \ll |\Sigma_0|$ , i.e. under near-resonance conditions, a large  $\beta/\alpha$  makes  $|r|$  extremely small and  $S(\varepsilon)$  coincides with (5.7). Whether (5.35), (5.16) or (5.6) is used for  $\Sigma(t)$  does not change  $S(\varepsilon)$ , only  $\Sigma(t)$  for  $t > 0$  being important.

b) If  $\varepsilon - \varepsilon_a^\infty = |\Sigma_0|$  and  $\beta$  is a multiple of  $2\pi\alpha/\varphi$ , the saddle-point method is inapplicable, giving a series of infinite terms. If  $\beta > 2\pi\alpha/\varphi$ ,  $\delta(\varepsilon)$  is discontinuous at  $\varepsilon = \varepsilon_a^\infty + |\Sigma_0|$ , dropping from  $\delta_+$  down to  $\delta_-$ , where :

$$\delta_{\pm} = \frac{2\pi}{\beta v_0} \left[ \frac{1}{2} + \frac{\beta\varphi}{2\pi\alpha} \pm \text{Int} \left( \frac{\beta\varphi}{2\pi\alpha} \right) \right]$$

Int denoting the integer part. If  $\beta/\alpha$  is large,  $\delta$  thus passes from a large to a small value. A similar jump occurred in the case of a singular  $\Sigma(t)$ , but at  $\varepsilon = \varepsilon_a^\infty + \Delta_0/\varphi$ , therefore below the present threshold (since  $|\Sigma_0| = \Delta_0/\sin\varphi$ ).

c) If  $\varepsilon - \varepsilon_a^\infty \gg |\Sigma_0|$ , i.e. under far-resonance conditions, a large  $\beta/\alpha$  makes  $|r|$  extremely large, so that the corrective term (5.37) cannot remain small (and therefore the asymptotic form valid) but for extremely small velocities, satisfying :

$$\alpha v_0 \ll 12(\varepsilon - \varepsilon_a^\infty)|r|(\beta/\alpha)^2.$$

If  $\beta$  is really much larger than  $\alpha$ , there must be some range of  $v_0$ , namely :

$$|\Sigma_0|/\beta \ll v_0 \ll \Delta_0/\alpha$$

in which  $S(\varepsilon)$  is well approximated by the result (5.20) obtained with a singular  $\Sigma(t)$ . Otherwise no universal velocity dependence of  $S(\varepsilon)$  emerges at velocities of practical interest.

**5.7 ON THE USE OF THE RATE-EQUATION APPROACH.** — The rate-equation approach is *a priori* well adapted to the case of a resonance crossing the Fermi level, but the definition of a crossing time may raise some difficulty. The wide-band model provides a convenient means to study this point. In this model, the resonance is centred at  $\varepsilon_a(t) \equiv \varepsilon_a^\infty + E(t)$  and the crossing time  $t_c$  is naturally defined by  $\varepsilon_a(t_c) = \varepsilon_F$ . For simplicity assume near-adiabatic conditions, i.e. very small velocity. The rate-equation approach result (4.3) is to be compared with the correct result :

$$P \simeq [S_0(\varepsilon_F)/\delta(\varepsilon_F)] \exp[-D(\varepsilon_F)] \quad (5.38)$$

[see (5.32)] which depends on  $t_{sp}$  [see (5.26)] for  $\varepsilon = \varepsilon_F$ .  $t_{sp}$  being close to  $t_c$ , we can expand :

$$t_{sp} - t_c = i \frac{\Delta}{\dot{\varepsilon}_a} \left[ 1 + i \frac{\dot{\Delta}}{\dot{\varepsilon}_a} \left( 1 - \frac{1}{2} \frac{\ddot{\varepsilon}_a \Delta}{\dot{\varepsilon}_a \dot{\Delta}} \right) + \dots \right]$$

where all quantities are to be taken at  $t = t_c$ . The expansion is in powers of  $\dot{\Delta}/\dot{\varepsilon}_a$  and  $\ddot{\varepsilon}_a/\dot{\varepsilon}_a$  is assumed not to be much larger than  $\dot{\Delta}/\Delta$ . Up to  $0(\dot{\Delta}^2/\dot{\varepsilon}_a^2)$ , the prefactor of (5.38) is

found to be unity, as in (4.3). The exponent is :

$$D(\varepsilon_F) = 2 \int_{t_c}^{\infty} dt \Delta(t) + \frac{\Delta^2}{\dot{\varepsilon}_a^2} \left( \dot{\Delta} - \frac{\Delta}{3} \frac{\ddot{\varepsilon}_a}{\dot{\varepsilon}_a} \right) + \dots$$

The first term is the rate-equation approach result. If  $\Delta(t) \propto e^{-2\mu t}$  and  $\varepsilon_a(t)$  behaves smoothly enough, the corrective term is much less than the leading term on condition that  $\dot{\varepsilon}_a \gg \mu \Delta$ , which confirms an assertion of section 4.3.

**6. The two-level case.**

In the context of charge transfer at surfaces, a two-level model (one level for atom *a*, one for the substrate) is of rather limited interest, for, if localized states may exist at surfaces (e.g. around an impurity), band states can rarely be ignored. However this model offers a twofold theoretical interest. First, it will serve us for testing the generality of results of chapters 8 and 9. Second, being the simplest of cluster models, it illustrates some of their properties, especially the absence of strict resonant processes since two coupled discrete levels cannot cross.

We thus consider one electron apt to occupy two orbitals *a* and *b*. In the basis set  $\{a, b\}$  the Hamiltonian reads :

$$H(t) = \begin{pmatrix} \varepsilon_a(t) & T(t) \\ T(t) & \varepsilon_b(t) \end{pmatrix}. \tag{6.1}$$

It has two eigenvectors  $|\pm\rangle$  with eigenvalues :

$$\varepsilon_{\pm} = \frac{1}{2} [\varepsilon_a + \varepsilon_b \pm \sqrt{(\varepsilon_b - \varepsilon_a)^2 + 4 T^2}].$$

We set  $E = \varepsilon_b - \varepsilon_a$  and  $\Omega = \varepsilon_+ - \varepsilon_-$ , all these quantities being functions of time.

**6.1 REVIEW.** — The problem of electron exchange between two levels is an old problem of atomic collision. From the first, two methods were used :

— the present trajectory approximation (TA) method, also called « impact parameter treatment » in the context of atomic collisions, which treats the nuclei as classical particles and leads to a time-dependent electron Hamiltonian of the form (6.1) ;

— the semiclassical method based on the JWKB approximation for the (stationary) wavefunction of the nuclear system, this wavefunction having two components corresponding to the two electron states and the variable being the internuclear distance *r*.

Both methods lead to a set of two coupled differential equations, which are first order in *t* in the first case, second order in *r* in the second case. The TA method is therefore simpler. However, perhaps because of its less generality, it does not seem to have been developed as systematically and rigorously as the semiclassical method.

For the sake of clarity, we first distinguish two opposite physical situations :

a) The first one is the case of avoided crossing (or pseudo-crossing) when *E* vanishes at  $r = r_c$  and *T* is small enough for  $\Omega$  to have a well-marked minimum there. The problem was solved by the TA method with the simplifying assumptions that, in the vicinity of the crossing, *T* is constant and *E* varies linearly with *t*. The resulting probability of electron transfer between the two orbitals is given by the Landau-Zener formula [31, 32] :

$$P \approx 4 \sin^2 \tau e^{-\gamma} (1 - e^{-\gamma}) \tag{6.2}$$

$$\gamma = 2 \pi T^2 / |\dot{E}| \tag{6.3}$$

where  $T$  and  $\dot{E}(=dE/dt)$  are evaluated at  $r_c$ . The factor  $\sin^2 \tau$  comes from interferences between transitions occurring at the two crossing times (when the atoms come nearer from one another and when they move away).  $\tau$  is approximately half the integral of  $\Omega(t)$  between the crossing times. As the validity of the treatment implies well separated crossing times,  $\tau$  is generally large and  $\sin^2 \tau$  is often replaced by  $1/2$ .

b) The opposite situation is when  $E$  is constant, so that  $\Omega$  increases with  $T$ . Electron transitions are then induced by the variation of  $T$  during the interval when  $\Omega$  is not too large ( $T \leq E$ ). By taking  $T \propto \text{sech}(\mu t)$ , Rosen and Zener obtained the following exact result [33]:

$$P = \frac{\sin^2 \tau}{\text{ch}^2(\gamma/2)} \quad (6.4)$$

$$\tau = \int T dt, \quad \gamma = \pi E/\mu. \quad (6.5)$$

The derivation of (6.2) and (6.4) relies on specific forms for  $E(t)$  and  $T(t)$ , but implies in principle no conditions on the magnitude of parameters. Alternatively, under near-adiabatic conditions (small velocity, large  $\gamma$ ),  $P$  can be calculated for any reasonable  $E(t)$  and  $T(t)$ . As expected from (6.2) and (6.4),  $P$  is then of the form:

$$P \simeq 4 \sin^2 \tau e^{-\gamma}. \quad (6.6)$$

The semiclassical theory of Stueckelberg [34] improved by Crothers [35] gave for  $\gamma$ :

$$\gamma = 2 \text{Im} \int_{r_0}^{r_0} (k_+ - k_-) dr \quad (6.7)$$

where  $k_j$  is the (local) wavenumber of the nuclear system when the electron is in state  $j$ ,  $r_0$  is the zero of  $k_+ - k_-$  lying closest to the real axis in the first quadrant and the lower limit of integration is on the real axis. We can translate (6.7) in the language of the TA method by identifying  $(k_+ - k_-) dr$  with  $\Omega dt$ :

$$\gamma = 2 \text{Im} \int_{r_0}^{r_0} \Omega dt \quad (6.8)$$

where  $\Omega(t_0) = 0$  and the lower limit is on the real axis. (6.8) was also obtained by the TA method by Dykhne [36] in the pseudo-crossing case without Zener's simplifying assumptions. As to the phase  $\tau$ , its semiclassical expression is [35]:

$$\tau = \text{Re} \left( \int_{r_+}^{r_0} k_+ dr - \int_{r_-}^{r_0} k_- dr \right) + \tau' \quad (6.9)$$

where  $r_+$  and  $r_-$  are the classical turning points corresponding to the two electron states and  $\tau'$  is a complicated function of the velocity which vanishes for  $\gamma = 0$  and  $\gamma = \infty$ . In a TA treatment, no distinction is made between  $r_+$  and  $r_-$ , both corresponding to the time  $t = 0$  of closest approach, and (6.9) is expected to simplify into:

$$\tau = \text{Re} \int_0^{t_0} \Omega dt. \quad (6.10)$$

Implicit in the derivation of (6.6), (6.8) and (6.10) is the assumption that the function  $\Omega(t)$  is even and analytic, as normally happens in a collision between two atoms under classical conditions. However it is not too difficult to extend the results to other forms of  $\Omega$ . Physically electron exchange occurs when  $\Omega$  is close to a minimum (as in the Landau-Zener case) or tends to it (as in the Rosen-Zener case where the minimum is at  $|t| = \infty$  and electron exchange spreads over the region  $T \leq E$ ). When  $\Omega$  is even and its minima are far from  $t = 0$ , (6.6) is easily interpreted as the sum of the contributions from the two minima, each equal to  $e^{-\gamma}$ , multiplied by an interference factor  $2 \sin^2 \tau$ . For any passage through a minimum of  $\Omega$  well separated from others, whether  $\Omega$  is even or not, such a contribution  $e^{-\gamma}$  is expected with  $\gamma$  calculated according to (6.8) with the form of  $\Omega$  appropriate in this region. Only the interference factor, usually  $\sim 1$ , depends on the behaviour of  $\Omega$  between the minima if there are more than one. The requirement that  $\Omega(t)$  is analytic cannot be relaxed similarly because a singularity can induce excitations of large energy and, even if it takes place in a region where  $\Omega$  is large, its contribution may dominate  $P$  in the near-adiabatic case, i.e. for large  $\gamma$ .

6.2 APPLICATION TO THE MODEL OF CHAPTER 3. — The assumptions made in chapter 3 lead to the following forms for  $T$  and  $E$ :

$$\left. \begin{aligned} T(t) &= T_0 \xi(t) \\ E(t) &= E_\infty + \eta_0 \xi^2(t) \end{aligned} \right\} \quad (6.11)$$

where, without loss of generality, we suppose  $E_\infty > 0$ . Though the variations of  $T$  and  $E$  are related, a diversity of physical situations, with or without pseudo-crossing, can be described by varying  $T_0$ ,  $E_\infty$  and  $\eta_0$ . Of central importance is the function  $\Omega$  which can be written:

$$\begin{aligned} \Omega &= |\eta_0| \sqrt{(\xi^2 - \xi_+^2)(\xi^2 - \xi_-^2)} \\ \xi_\pm &= (iT_0/\eta_0)(1 \pm \sqrt{1 - E_\infty \eta_0/T_0^2}). \end{aligned}$$

A boundary appears between the cases  $E_\infty \eta_0 < T_0^2$  and  $E_\infty \eta_0 > T_0^2$  in which  $\xi_\pm^2$  is respectively real and complex. This boundary is comparable, but not identical, with the boundary between the cases  $E_\infty \eta_0 < 2 T_0^2$  where  $\Omega$  is minimum at  $\xi = 0$  (e.g. Rosen-Zener case) and  $E_\infty \eta_0 > 2 T_0^2$  where  $\Omega$  is minimum at  $\xi \neq 0$  (e.g. Landau-Zener case).

The forms (3.11) and (3.12) proposed for  $\xi(t)$  are not analytic. There should thus be a contribution to  $P$  from the singularity at  $t = 0$ , which contribution cannot be calculated by (6.6) and will be considered in next section. We can formally get rid of it by letting  $|\eta_0|$  and  $T_0^2$  tend to infinity together, so that  $\Omega(0) = \infty$ . Doing this, we are also ensured that any minimum of  $\Omega$  is far from the singularity and, in the scattering case, far from the other minimum. We can thus evaluate  $\gamma$  by considering only the region  $t > 0$  in case (3.11) (the « sputtering case » which here would rather simulate a molecular dissociation induced by a projectile not involved in electron transfer) and by treating separately the regions  $t > 0$  and  $t < 0$  in case (3.12) (« scattering case »).

Let us calculate  $\gamma$ , as given by (6.8), for the region  $t > 0$ . Taking  $\xi = e^{-\mu t}$  as variable of integration, we must choose a contour going from anywhere on the positive real half-axis to  $\xi_-$  such that  $\text{Re } \xi_- \geq 0$ . If  $E_\infty \eta_0 < T_0^2$ , whatever the sign of  $\eta_0$ ,  $\xi_-$  is on the imaginary axis and it is convenient to use a contour composed of three parts, a segment on the real axis, another on the imaginary axis and, joining them, a quarter circle of infinitesimal radius centred at the origin. Only the latter contributes to the imaginary part in (6.8), giving

$\gamma = \pi E_\infty / \mu$ . If  $E_\infty \eta_0 > T_0^2$ ,  $\xi_-$  is off the imaginary axis. By integrating along the arc  $|\xi| = |\xi_-|$ , one finds  $\gamma = \pi T_0^2 / \mu \eta_0$ . To summarize :

$$\gamma = \frac{\pi}{\mu \eta_0} \text{Inf} (E_\infty \eta_0, T_0^2). \quad (6.12)$$

In the « sputtering case »,  $P$  is simply  $e^{-\gamma}$ . In the « scattering case » this term has to be supplemented by the contribution of the region  $t < 0$  which only differs from it by the substitution of  $\lambda$  for  $\mu$ . Since  $\tau = \infty$ , it is reasonable to neglect the interference factor.

For  $E_\infty \eta_0 < T_0^2$ , (6.12) shows that  $\gamma$  is independent of  $\eta_0$  and therefore coincides with the Rosen-Zener results (6.5). This is understandable since,  $\Omega$  being minimum at  $t = \infty$ , only the asymptotic value of  $E(t)$  should be important. More remarkable is the fact that (6.12) coincides with the Landau-Zener result (6.3) in the entire range  $E_\infty \eta_0 > T_0^2$  although (6.3) was established under rather different assumptions (constant  $T$ , linear  $E$ ) and that range covers not only cases where  $\Omega$  has a marked minimum ( $E_\infty \eta_0 \gg T_0^2$ ), but also cases where  $\Omega$  has no minimum at finite time ( $T_0^2 < E_\infty \eta_0 < 2 T_0^2$ ).

**6.3 AN EXACT TREATMENT.** — As already mentioned, the treatment of the preceding subsection ignores the contribution of the singularity of  $\xi$  at  $t = 0$ . Though from a physical point of view the singularity is unwanted, it may be useful to know its contribution in view of the frequent use of non analytic forms in numerical or literal calculations.

An exact treatment requires to solve a set of two coupled first-order differential equations. For simplicity let us limit ourselves to the case  $\eta_0 = 0$  (similar to the Rosen-Zener case) with  $\xi$  given by (3.11) (« sputtering case »). If we suppose the electron to be initially in the lower eigenstate  $|-\rangle$ , the probability  $P$  of electron exchange is the probability of final occupation of state  $b$  :

$$P = |\langle b | G(\infty, 0) |-\rangle|^2$$

where  $G$  is the solution of (2.3). Projecting  $|-\rangle$  onto  $|a\rangle$  and  $|b\rangle$ , we obtain :

$$P = \frac{\varepsilon_+(0) |1 - rT_0/\varepsilon_+(0)|^2}{\Omega(0) (1 + |r|^2)} \quad (6.13)$$

where :

$$r = \frac{G_{bb}(\infty, 0)}{G_{ba}(\infty, 0)} = - \frac{i}{T_0} \frac{\partial}{\partial t} \ln G_{ba}(\infty, t) \Big|_{t=0}$$

the last equality being deduced from (2.3).  $G_{ba}$  obeys a second-order differential equation. Setting :

$$s = \frac{T_0}{\mu} e^{-\mu t}, \quad s' = \frac{T_0}{\mu} e^{-\mu t'}, \quad \nu = \frac{1}{2} \left( 1 - i \frac{E_\infty}{\mu} \right)$$

we find :

$$G_{ba}(t, t') \propto s \left( \frac{s'}{s} \right)^\nu [J_\nu(s) J_{-\nu}(s') - J_{-\nu}(s) J_\nu(s')]$$

( $J_\nu$  Bessel function), whence :

$$r = i \frac{d}{ds} \ln [s^\nu J_\nu(s)] \Big|_{s=T_0/\mu} = i J_{\nu-1} \left( \frac{T_0}{\mu} \right) / J_\nu \left( \frac{T_0}{\mu} \right). \quad (6.14)$$

Formulae (6.13)-(6.14) give the exact  $P$  for the particular model considered ( $\eta_0 = 0$ , « sputtering case »). For the special value  $E_\infty = 0$  (resonant case), not considered previously, one verifies that  $P = 1/2$ . Coming to the near-adiabatic regime ( $\mu$  small) and  $E_\infty > 0$ , we can distinguish two situations. If  $\mu \ll T_0 \sim E_\infty$ , we get, from the behaviour of the Bessel function for large and comparable values of its index and argument :

$$P = \mu^2 \frac{E_\infty^2 T_0^2}{(E_\infty^2 + 4 T_0^2)^3} + O(\mu^4). \tag{6.15}$$

If  $T_0$  is extremely large, the large-argument limit must be taken first, giving :

$$P \simeq \exp(-\pi E_\infty / \mu). \tag{6.16}$$

Comparing with (6.15), one sees that (6.16) is valid only if  $T_0$  satisfies :

$$\left(\frac{T_0}{E_\infty}\right)^2 \gg \frac{\mu}{8 E_\infty} \exp \frac{\pi E_\infty}{2 \mu}$$

which is indeed very large if  $E_\infty \gg \mu$ . (6.16) is the « regular » contribution, identical with (6.12). (6.15) is the contribution of the singularity of  $\xi$  at  $t = 0$ , proportional to the square of the slope discontinuity as in the wide-band model. The regular contribution can thus easily be masked by the singular one.

Though (6.15) was derived for  $\eta_0 = 0$  and a form of  $\xi$  corresponding to sputtering, it is not too difficult to generalize it, as only parameters at  $t = 0$  should enter it. These parameters are three :  $E(0) = E_\infty + \eta_0$ ,  $T(0) = T_0$  and  $\mu + \lambda$  (resp.  $\mu$ ), the discontinuity of  $\dot{\xi}(0)$  in the scattering (resp. sputtering) case. To generalize (6.15) one must therefore simply substitute  $E_\infty + \eta_0$  for  $E_\infty$  and, in the scattering case,  $\mu + \lambda$  for  $\mu$ . Results of chapters of chapters 8 and 9 will confirm it.

### 7. Exact series solution.

Coming back to the model of chapter 3, we now derive exact expressions for  $S(\varepsilon)$  and  $|G_{aa}(\infty, -\infty)|^2$ , the quantities of interest for the calculation of  $n_a(\infty)$ . The method is based on the exponential form of  $\xi(t)$  [Eqs. (3.11) and (3.12)], but implies no assumption on  $\sigma(z)$  [Eq. (3.8)]. The sputtering case is treated in section 7.1, the scattering case in section 7.2 and some computational problems are discussed in section 7.3.

**7.1 SPUTTERING CASE.** — The content of this section is essentially a reproduction of old results [27]. The Laplace transform method used there was also employed independently by Brako and Newns in a somewhat different case [17].

We first solve (3.2) for  $t$  and  $t' > 0$ , when  $\xi(t) = e^{-\mu t}$ .  $\Sigma(t, t')$  is given by (3.9). We define :

$$g_{aa}(z, t') = \int dt e^{iz(t-t')} G_{aa}(t, t') \tag{7.1}$$

(3.2) becomes :

$$g_{aa}(z, t') = \frac{1}{z - \varepsilon_a^\infty} [1 + \sigma(z + i\mu) g_{aa}(z + 2i\mu, t') e^{-2\mu t'}]$$



whose iteration gives :

$$\begin{aligned}
 g_{aa}(z, t') &= \Psi(z, t') / (z - \varepsilon_a^\infty) \\
 \Psi(z, t') &= \sum_{n=0}^{\infty} \psi_n(z) e^{-2n\mu t'} \\
 \psi_n(z) &= \prod_{p=1}^n \frac{\sigma(z + (2p-1)i\mu)}{z - \varepsilon_a^\infty + 2pi\mu}, \quad \psi = 1.
 \end{aligned}
 \tag{7.2}$$

We recover  $G_{aa}$  by inverting (7.1) :

$$G_{aa}(t, t') = \int_C \frac{dz}{2\pi} e^{-iz(t-t')} g_{aa}(z, t')$$

where contour C encloses the lower half-plane. The poles of  $\Psi(z, t')$  are all below the real axis. So, as  $t \rightarrow \infty$ , only the pole  $z = \varepsilon_a^\infty$  of  $g_{aa}(z, t')$  contributes to  $G_{aa}$  :

$$iG_{aa}(\infty, t) = \Psi(\varepsilon_a^\infty, t) e^{i\varepsilon_a^\infty t}$$

where an unimportant phase factor  $\exp(-i\varepsilon_a^\infty \infty)$  has been omitted. Thus :

$$iG_{aa}(\infty, 0) = \sum_n \psi_n(\varepsilon_a^\infty)
 \tag{7.3}$$

and, by (2.4b) :

$$\begin{aligned}
 iG_{ak}(\infty, 0) &= V_{ak} \int_0^\infty dt G_{aa}(\infty, t) e^{-(\mu + i\varepsilon_k)t} \\
 &= V_{ak} \sum_n \frac{\psi_n(\varepsilon_a^\infty)}{\varepsilon_a^\infty - \varepsilon_k + (2n+1)i\mu}.
 \end{aligned}
 \tag{7.4}$$

To obtain  $S(\varepsilon)$ , we expand (2.12), using (3.3) and (2.6) :

$$\begin{aligned}
 S(\varepsilon) &= -\frac{1}{\pi} \text{Im} \left\{ \sum_k \frac{|G_{ak}|^2}{\varepsilon - \varepsilon_k + i0} + \frac{1}{\varepsilon - \varepsilon_a^\infty - \sigma(\varepsilon)} \left[ |G_{aa}|^2 + G_{aa} \sum_k \frac{G_{ak}^* V_{ak}}{\varepsilon - \varepsilon_k + i0} \right. \right. \\
 &\quad \left. \left. + G_{aa}^* \sum_k \frac{G_{ak} V_{ka}}{\varepsilon - \varepsilon_k + i0} + \sum_k \frac{G_{ak} V_{ka}}{\varepsilon - \varepsilon_k + i0} \sum_{k'} \frac{G_{ak'}^* V_{ak'}}{\varepsilon - \varepsilon_{k'} + i0} \right] \right\}
 \end{aligned}$$

where  $G_{aa} = G_{aa}(\infty, 0)$  etc. Using then (7.3), (7.4) and the identity :

$$\sum_k \frac{|V_{ak}|^2}{(a - \varepsilon_k)(b - \varepsilon_k)} = \frac{\sigma(a) - \sigma(b)}{b - a}
 \tag{7.5}$$

we obtain, after some simplifications :

$$S(\varepsilon) = \rho_a(\varepsilon) |X(\varepsilon)|^2
 \tag{7.6}$$

$$\rho_a(\varepsilon) = -\frac{1}{\pi} \text{Im} \frac{1}{\varepsilon - \varepsilon_a^\infty - \sigma(\varepsilon)}
 \tag{7.7}$$

$$X(\varepsilon) = i\mu \sum_{n=0}^{\infty} \frac{(2n+1)\tau_n - 2(n+1)\tau_{n+1}}{\varepsilon - \varepsilon_a^\infty - i(2n+1)\mu}
 \tag{7.8}$$

$$\tau_n \equiv \psi_n(\varepsilon_a^\infty) = \prod_{p=1}^n \frac{\sigma(\varepsilon_a^\infty + (2p-1)i\mu)}{2pi\mu}, \quad \tau_0 = 1 \tag{7.9}$$

$\rho_a(\varepsilon)$  is the local density of states at  $t = 0$ .

7.2 SCATTERING CASE. — We need  $G_{aa}(\infty, -\infty)$  and  $G_{ak}(\infty, -\infty)$ , which we can decompose as :

$$-iG_{aa}(\infty, -\infty) = G_{aa}(\infty, 0)G_{aa}(0, -\infty) + \sum_k G_{ak}(\infty, 0)G_{ka}(0, -\infty) \tag{7.10}$$

$$-iG_{ak}(\infty, -\infty) = G_{aa}(\infty, 0)G_{ak}(0, -\infty) + \sum_{k'} G_{ak'}(\infty, 0)G_{k'k}(0, -\infty). \tag{7.11}$$

We already know  $G_{aa}(\infty, 0)$  and  $G_{ak}(\infty, 0)$ . To obtain the matrix elements of  $G(0, -\infty)$ , we must solve (3.2) for  $t$  and  $t' < 0$ , when  $\xi(t) = e^{\lambda t}$ . We define :

$$g_{aa}(t, z) = \int dt' e^{iz(t-t')} G_{aa}(t, t')$$

and write (3.2) in reverse form :

$$G_{aa} = G_a^0 + G_{aa} \Sigma G_a^0$$

where time integrations are implicit. It comes :

$$g_{aa}(t, z) = \frac{1}{z - \varepsilon_a^\infty} [1 + e^{2\lambda t} g_{aa}(t, z + 2i\lambda) \sigma(z + i\lambda)]$$

whose iteration gives :

$$g_{aa}(t, z) = \Phi(z, t)/(z - \varepsilon_a^\infty) \tag{7.12}$$

$$\Phi(z, t) = \sum_{n=0}^\infty \varphi_n(z) e^{2n\lambda t}$$

$$\varphi_n(z) = \prod_{p=1}^n \frac{\sigma(z + (2p-1)i\lambda)}{z - \varepsilon_a^\infty + 2pi\lambda}, \quad \varphi_0 = 1. \tag{7.13}$$

Proceeding as in section 7.1, we obtain :

$$iG_{aa}(t, -\infty) = \Phi(\varepsilon_a^\infty, t) e^{-i\varepsilon_a^\infty t}$$

an unimportant factor  $\exp(i\varepsilon_a^\infty \infty)$  being omitted. Similarly to (7.3) and (7.4) :

$$iG_{aa}(0, -\infty) = \sum_n \varphi_n(\varepsilon_a^\infty)$$

$$iG_{ka}(0, -\infty) = V_{ka} \sum_n \frac{\varphi_n(\varepsilon_a^\infty)}{\varepsilon_a^\infty - \varepsilon_k + (2n+1)i\lambda}.$$

To calculate  $G_{ka}(0, -\infty)$  and  $G_{kk'}(0, -\infty)$ , we need  $G_{ak}(t, -\infty)$ . Using (2.4b) and (7.12), we have, always neglecting a factor  $\exp(i\varepsilon_a^\infty \infty)$  :

$$\begin{aligned} iG_{ak}(t, -\infty) &= V_{ak} \int_{-\infty}^t d\tau G_{aa}(t, \tau) e^{(\lambda - i\varepsilon_k)\tau} \\ &= -iV_{ak} e^{(\lambda - i\varepsilon_k)t} \int \frac{d\omega}{2\pi} \frac{\Phi(\omega, t)}{(\omega - \varepsilon_a^\infty + i0)(\omega - \varepsilon_k - i\lambda)}. \end{aligned}$$

It is here convenient to close the contour of integration in the upper half-plane where  $\Phi(z, t)$  has no pole :

$$iG_{ak}(t, -\infty) = V_{ak} e^{(\lambda - i\varepsilon_k)t} \frac{\Phi(\varepsilon_k + i\lambda, t)}{\varepsilon_k - \varepsilon_a^\infty + i\lambda}.$$

Then :

$$iG_{ak}(0, -\infty) = \frac{V_{ak}}{\varepsilon_k - \varepsilon_a^\infty + i\lambda} \sum_n \varphi_n(\varepsilon_k + i\lambda)$$

and, by (2.4a) :

$$iG_{k'k}(0, -\infty) = \delta_{kk'} + \frac{V_{k'a} V_{ak}}{\varepsilon_k - \varepsilon_a^\infty + i\lambda} \sum_n \frac{\varphi_n(\varepsilon_k + i\lambda)}{\varepsilon_k - \varepsilon_{k'} + 2i(n+1)\lambda}.$$

We can now evaluate (7.10) and (7.11) and, by (2.11), deduce  $S(\xi)$ . Using (7.5) again, we obtain :

$$\begin{aligned} iG_{aa}(\infty, -\infty) &= \sum_{m=0}^\infty \sum_{n=0}^\infty \tau_n \varphi_m(\varepsilon_a^\infty) \left[ 1 - \frac{\sigma(\varepsilon_a^\infty + (2n+1)i\mu) - \sigma(\varepsilon_a^\infty + (2m+1)i\lambda)}{(2n+1)i\mu - (2m+1)i\lambda} \right] \\ &= \frac{1}{2} \sum_{m=0}^\infty \sum_{n=0}^\infty \tau_n \varphi_m(\varepsilon_a^\infty) \sum_{\pm} \frac{2(n\mu + m\lambda) + \mu + \lambda \mp i\delta}{\pm 2(n\mu - m\lambda) + \mu + \lambda \mp i\delta} \end{aligned} \tag{7.14}$$

where  $\delta$  is an infinitesimal, and :

$$S(\varepsilon) = -\frac{1}{\pi} \text{Im } \sigma(\varepsilon) |Y(\varepsilon)|^2 \tag{7.15}$$

$$\begin{aligned} Y(\varepsilon) &= \sum_{n=0}^\infty \frac{\tau_n}{\varepsilon_a^\infty - \varepsilon + i(2n+1)\mu} + \sum_{m=0}^\infty \sum_{n=0}^\infty \frac{\tau_n \varphi_m(\varepsilon + i\lambda)}{\varepsilon - \varepsilon_a^\infty + i\lambda} \times \\ &\times \left[ 1 + \frac{\sigma(\varepsilon_a^\infty + i(2n+1)\mu) - \sigma(\varepsilon + 2i(m+1)\lambda)}{\varepsilon - \varepsilon_a^\infty + 2i(m+1)\lambda - i(2n+1)\mu} \right] \\ &= \frac{i}{\varepsilon - \varepsilon_a^\infty + i\lambda} \sum_{m=0}^\infty \sum_{n=0}^\infty \tau_n \varphi_m(\varepsilon + i\lambda) \times \\ &\times \left[ \frac{2n\mu}{\varepsilon - \varepsilon_a^\infty + 2i(m+1)\lambda - i(2n-1)\mu} \right] - \frac{(2n+1)\mu + \lambda}{\varepsilon - \varepsilon_a^\infty + 2im\lambda - i(2n+1)\mu}. \end{aligned} \tag{7.16}$$

Two expressions have been given for both  $G_{aa}(\infty, -\infty)$  and  $Y(\varepsilon)$ . On the first one, the important simplifications which occur in the wide-band case ( $\sigma$  constant) are quite apparent.

**7.3 ABOUT THE COMPUTATION OF THE SERIES.** — Results (7.6)-(7.9) and (7.14)-(7.16) can either be converted into approximate, but more transparent expressions, as will be done later on, or be treated numerically. In the latter case, the convergence properties of the series are of interest.

Consider first (7.8). Its convergence properties are essentially those of the series  $\sum \tau_n$ . For the sake of discussion, suppose  $\sigma(z)$  constant. Setting  $\alpha = i\sigma/2\mu$  ( $\text{Re } \alpha > 0$ ), we have :

$$\tau_n = \frac{(-\alpha)^n}{n!} \quad \text{whence} \quad \sum_n \tau_n = e^{-\alpha}.$$

The convergence is pretty fast. However the series is basically a large- $\mu$  expansion, whereas in practice  $\mu$  ( $\propto$  velocity) is rather small. For instance in previous calculations [25],  $|\alpha|$  might exceed 50. For such large  $|\alpha|$ , the problem is not the number of terms required to evaluate the series with given accuracy, which number only increases as  $|\alpha|$ , but the accuracy required to evaluate the largest terms, these being  $\sim \exp|\alpha|$  whereas the series itself is much more smaller. In numerical calculations double precision is generally a minimum requirement. Quadruple precision was used in the quoted calculations [25].

The convergence of the double series (7.14) is related to that of the two series  $\sum \tau_n$  and  $\sum \varphi_m(\varepsilon_a^\infty)$  which only differ by the exchange of  $\mu$  and  $\lambda$ . The problem is therefore of the same nature as above, yet apparently more serious. In fact, if  $\lambda$  is small, the first term at rhs of (2.10) is generally negligible as compared with the second one, making  $G_{aa}(\infty, -\infty)$  useless.

The convergence of the double series (7.16) depends on that of  $\sum \tau_n$  and  $\sum \varphi_m(\varepsilon)$ . For constant  $\sigma$  :

$$\varphi_m(\varepsilon) = \prod_{p=1}^n \frac{\sigma}{\varepsilon - \varepsilon_a^\infty + 2pi\lambda} .$$

By carrying out the  $\varepsilon$ -integration in (2.10) over either occupied or empty states (see the last remark of chapter 2), it is always possible to impose  $|\varepsilon - \varepsilon_a^\infty| > |\varepsilon_F - \varepsilon_a^\infty|$ , so that  $\varphi_m(\varepsilon)$  remains finite when  $\lambda \rightarrow 0$ . The accuracy problem in the evaluation of the largest terms in the series is thus not substantially more serious than for (7.8). However if  $|\sigma|/|\varepsilon - \varepsilon_a^\infty|$  is not small,  $|\varphi_m(\varepsilon)|$  begins to decrease rapidly with  $m$  only for  $m \gg |\varepsilon - \varepsilon_a^\infty|/\lambda$ , so that it may be necessary to retain more terms in the sum over  $m$  than in the sum over  $n$ .

**8. Asymptotic expressions : the sputtering case.**

In most physical situations,  $\mu$  lies in an energy range low enough to justify the use of an approximate  $S(\varepsilon)$ , in general a small- $\mu$  asymptotic expression. Such approximations are derived in sections 8.1-8.4. The resulting ion fraction is calculated in section 8.5.

**8.1 INTEGRAL REPRESENTATION.** — Owing to the form of  $\tau_n$ , (7.8) is essentially a large- $\mu$  expansion. To obtain the small- $\mu$  behaviour, an integral representation is more convenient. We first get rid of the denominator by writing

$$X(\varepsilon) = - \int_0^\infty dt e^{i(\varepsilon_a^\infty - \varepsilon)t - \mu t} \left[ \mu + (\varepsilon^{2\mu t} - 1) \frac{d}{dt} \right] Q(e^{-2\mu t}) \tag{8.1}$$

or, setting  $x = e^{-2\mu t}$  :

$$X(\varepsilon) = \int_0^1 dx x^{\frac{\varepsilon_a^\infty - \varepsilon}{2i\mu} - \frac{1}{2}} \left[ -\frac{1}{2} + (1-x) \frac{d}{dx} \right] Q(x) \tag{8.2}$$

where :

$$Q(x) = \sum_{n=0}^\infty \tau_n x^n = \sum_{n=0}^\infty \prod_{p=1}^n \frac{x\sigma(\varepsilon_a^\infty + (2p-1)i\mu)}{2pi\mu} . \tag{8.3}$$

When  $\mu$  is small, since  $\sigma(z)$  is analytic in the upper half-plane,  $\sigma(\varepsilon_a^\infty + (2p-1)i\mu)$  varies little between two consecutive and large  $p$ 's. This remains true for two any consecutive  $p$ 's if  $\sigma(z)$  has no pole near  $\varepsilon_a^\infty$ . A pole of  $\sigma(z)$  on the real axis corresponds to a bound state of  $H_s$ . The case of  $\varepsilon_a^\infty$  close to a bound state (or quasi-bound state) of the substrate will not be considered here.

Rewriting  $Q$  as :

$$Q(x) = \sum_{n=0}^{\infty} \frac{1}{n!} \left( \frac{x}{2i\mu} \right)^n \exp \frac{W_n}{2i\mu}$$

$$W_n = 2i\mu \sum_{p=1}^n \ln \sigma(\varepsilon_a^\infty + (2p-1)i\mu) \quad (8.4)$$

we can now expand

$$W_n = \int_{\varepsilon_a^\infty}^{\varepsilon_a^\infty + 2ni\mu} dz \ln \sigma(z) + O(\mu^2). \quad (8.5)$$

The higher terms, which depend on the successive derivatives of  $\sigma(z)$  at  $z = \varepsilon_a^\infty$  and  $z = \varepsilon_a^\infty + 2ni\mu$ , are given in appendix. By (8.5),  $W_n$  can be continued to any  $n$ , real or complex, so we write :

$$W_n = W(\varepsilon_a^\infty + 2ni\mu). \quad (8.6)$$

The sum over  $n$  cannot be transformed in the same way as the sum over  $p$  since, when  $\mu$  is small, there are strong differences between successive terms. But, treating  $W$  as an analytic function, we can write :

$$Q(x) = \int dq \exp \frac{W(\varepsilon_a^\infty + 2qi\mu)}{2i\mu} \sum_{n=0}^{\infty} \frac{1}{n!} \left( \frac{x}{2i\mu} \right)^n \delta(q-n).$$

Then, using the integral representation of the  $\delta$ -function, we sum over  $n$  to get :

$$Q(x) = \iint \frac{dq dr}{2\pi} e^{-iqr} \exp \left\{ \frac{1}{2i\mu} [W(\varepsilon_a^\infty + 2qi\mu) + x e^{ir}] \right\}$$

or, in terms of new variables  $w = \varepsilon_a^\infty + 2qi\mu$  and  $s = -ir$  (and with a proper modification of integration contours) :

$$Q(x) = \iint \frac{dw ds}{4\pi\mu} \exp \left\{ \frac{1}{2i\mu} [x e^{-s} + (w - \varepsilon_a^\infty) s + W(w)] \right\}. \quad (8.7)$$

For small  $\mu$ ,  $Q$  is evaluated by the saddle-point method. For a function of two variables the appropriate formula is :

$$\iint dx dy \exp \frac{f(x, y)}{\mu} \simeq 2\pi\mu \left[ \frac{\partial^2 f}{\partial x^2} \frac{\partial^2 f}{\partial y^2} - \left( \frac{\partial^2 f}{\partial x \partial y} \right)^2 \right]^{-1/2} \exp \frac{f}{\mu}$$

where, at rhs,  $f$  and its derivatives are to be calculated at the saddle point defined by  $\partial f/\partial x = \partial f/\partial y = 0$ . We obtain :

$$Q(x) \simeq [1 - x\sigma'(u)]^{-1/2} \exp \frac{F(x)}{2i\mu} \quad (8.8)$$

$$F(x) = G(u) \equiv \int_{\varepsilon_a^\infty}^u dz \left[ 1 + \ln \frac{\sigma(z)}{\sigma(u)} \right] \quad (8.9)$$

where  $\sigma'(u) = d\sigma/du$  and  $u$  is related to  $x$  by :

$$u - \varepsilon_a^\infty - x\sigma(u) = 0 \tag{8.10}$$

to be compared with (3.5). The following relations will be useful :

$$\begin{aligned} \frac{du}{dx} &= \frac{\sigma(u)}{1 - x\sigma'(u)}, \\ \frac{dF}{dx} &= \sigma(u) = \frac{u - \varepsilon_a^\infty}{x} \end{aligned} \tag{8.11}$$

(8.8) may lead to ambiguities, for, excepted in the wide-band case, (8.10) has always several solutions for  $u$ . This point will be reconsidered when a solution of (8.10) will be needed actually.

Substituting (8.8) for  $Q$  in (8.2), we have :

$$X(\varepsilon) \approx -\frac{1}{2\mu} \int_0^1 \frac{dx}{\sqrt{x}} \frac{\mu + i(1-x)\sigma(u)}{\sqrt{1-x\sigma'(u)}} \exp \frac{A(x)}{2i\mu} \tag{8.12}$$

$$A(x) = (\varepsilon_a^\infty - \varepsilon) \ln x + F(x). \tag{8.13}$$

Let us distort the line of integration into a contour  $C$  along which either  $\text{Re } A$  is constant or  $\text{Im } A = -\infty$  (such a contour exists necessarily). For small  $\mu$  the dominant contribution to  $X(\varepsilon)$  comes from the vicinity of the point  $M$  of  $C$  where  $\text{Im } A$  is maximum.  $M$  may be either a saddle point, i.e. a solution of  $dA/dx = 0$ , or a limit of integration, 0 or 1. However the limit  $x = 0$  must be excluded because it cannot be approached with a constant  $\text{Re } A$  (owing to  $\ln x$ ), only with  $\text{Im } A = -\infty$ . A saddle point and  $x = 1$  are thus the only possibilities for  $M$ . Their respective contributions are calculated in sections 8.2 and 8.3, and compared in section 8.4.

**8.2 M IS A SADDLE POINT.** — On account of (8.11) the saddle-point equation reads :

$$\frac{dA}{dx} = \frac{u - \varepsilon}{x} = 0$$

whence  $u = \varepsilon$  or, by (8.10) :

$$\varepsilon - \varepsilon_a^\infty - x\sigma(\varepsilon) = 0. \tag{8.14}$$

If  $M$  is a saddle point and does not coincide with the limit  $x = 1$ , (8.12) becomes, for  $\mu \ll |\varepsilon - \varepsilon_a^\infty|$  :

$$X(\varepsilon) \approx \sqrt{\frac{i\pi}{\mu}} \frac{\varepsilon - \varepsilon_a^\infty - \sigma(\varepsilon)}{\sqrt{\sigma(\varepsilon)}} \exp \left\{ \frac{1}{2i\mu} \int_{\varepsilon_a^\infty}^\varepsilon dz \left[ 1 + \ln \frac{\sigma(z)}{\varepsilon - \varepsilon_a^\infty} \right] \right\}. \tag{8.15}$$

If  $|\varepsilon - \varepsilon_a^\infty|$  is so small that  $|\varepsilon - \varepsilon_a^\infty| \leq \mu \ll |\sigma(\varepsilon)|$ , an expansion of  $F(x)$  around  $x = 0$  gives :

$$X(\varepsilon) \approx - \left( \frac{2\mu}{i\sigma(\varepsilon)} \right)^{\frac{\varepsilon_a^\infty - \varepsilon}{2i\mu} - \frac{1}{2}} \Gamma \left( \frac{\varepsilon_a^\infty - \varepsilon}{2i\mu} + \frac{1}{2} \right). \tag{8.16}$$

From (8.15) and (8.16) two expressions of  $S(\varepsilon)$  are deduced. With the aid of (5.8) they can be

merged into a unique expression valid if either  $|\varepsilon - \varepsilon_a^\infty|$  or  $|\sigma(\varepsilon)|$  is much larger than  $\mu$  :

$$S(\varepsilon) \simeq \frac{\sin \varphi(\varepsilon)}{\mu} \frac{\exp[-C(\varepsilon)/\mu]}{1 + \exp[-\pi(\varepsilon - \varepsilon_a^\infty)/\mu]} \quad (8.17)$$

where  $\varphi(\varepsilon)$  is defined by (3.10) and :

$$C(\varepsilon) = \int_{\varepsilon_a^\infty}^{\varepsilon} d\varepsilon \varphi(\varepsilon). \quad (8.18)$$

If  $\mu \ll |\varepsilon - \varepsilon_a^\infty|$ ,  $S(\varepsilon)$  becomes simply :

$$S(\varepsilon) \simeq \frac{\sin \varphi(\varepsilon)}{\mu} e^{-\tilde{C}(\varepsilon)/\mu} \quad (8.19)$$

where

$$\tilde{C}(\varepsilon) = \begin{cases} C(\varepsilon) & \varepsilon > \varepsilon_a^\infty \\ \pi(\varepsilon_a^\infty - \varepsilon) + C(\varepsilon) & \varepsilon < \varepsilon_a^\infty \end{cases}. \quad (8.20)$$

Notice that, though (8.10) does not define  $u$  uniquely,  $x$ , as given by (8.14), always exists and is unique. In fact to derive (8.17) the calculation of an approximate  $Q(x)$  and the use of the saddle-point method itself are not necessary. Since the limit of integration  $x = 1$  is here unimportant, it can be removed and (8.2) integrated till infinity. Physically this amounts to taking  $\xi(t) = e^{-\mu t}$  for  $-\infty < t < \infty$ . After having substituted (8.7) for  $Q$  in (8.2), one integrates over  $x$  first. This is done in appendix. The method is not only simpler, but also more powerful, for one can keep the entire expansion of  $W(w)$  in powers of  $\mu$  and find the asymptotic expansion of  $S(\varepsilon)$  to every order [see Eqs. (A.3)-(A.4)]. Nevertheless the method used in this section enables us to treat properly the problem of the limit of integration.

Some properties of (8.17) can be noted :

a) If  $\varepsilon$  lies within an energy gap,  $\varphi(\varepsilon) = 0$  or  $\pi$ , so  $S(\varepsilon)$  vanishes as it should to make  $n_a(\infty)$  independent of  $n^0(\varepsilon)$ .

b)  $S(\varepsilon)$  is invariant in the simultaneous interchange of  $\varepsilon$  and  $\varepsilon_a^\infty$  on one hand,  $\varphi$  and  $\pi - \varphi$  on the other hand (electron-hole symmetry).

c) (8.17), which is correct up to  $0(\mu)$ , obeys within the same approximation the unitarity relation (2.13) [to prove it, argue that, for small  $\mu$ ,  $S(\varepsilon)$  is strongly peaked, take a constant  $\varphi(\varepsilon)$  in the peak region and use (5.9)].

A close parallel exists between the present derivation of the asymptotic form (8.19) and that of (5.27) in section 5.4, the saddle-point equation (8.14) being a generalization of (5.26) to an energy-dependent  $\sigma^{\text{ad}}$ , yet restricted to an exponential time dependence since  $x = e^{-2\mu t}$ . (8.19) thus describes resonant processes in the sense given that word in section 5.2, near-resonant processes if  $\varphi$  is small, far-resonant ones if  $\varphi$  is close to  $\pi$ , with the additional complication that,  $\varphi$  being now energy dependent, both kinds of processes may occur.

**8.3 M IS AT  $x = 1$ .** — Define  $u_0$  by :

$$u_0 - \varepsilon_a^\infty - \sigma(u_0) = 0 \quad (8.21)$$

$u_0$  is the value of  $u$  for  $x = 1$ , therefore a solution of (3.5) for  $t = 0$ , and physically represents a resonance in the initial local electronic structure. If M is at  $x = 1$ , we obtain  $X(\varepsilon)$  by

expanding  $A(x)$  around this point. Two cases appear :

a) If  $\mu \ll |\varepsilon - u_0|$ ,  $M$  is distinct from the saddle point and a first-order expansion suffices :

$$X(\varepsilon) = \frac{i\mu}{\sqrt{1 - \sigma'(u_0)}} \frac{\varepsilon + u_0 - 2\varepsilon_a^\infty}{(\varepsilon - u_0)^2} \exp \frac{G(u_0)}{2i\mu} \quad (8.22)$$

whence :

$$S(\varepsilon) \simeq \mu^2 R(\varepsilon) \exp(-C_2/\mu) \quad (8.23)$$

$$C_2 = -\text{Im } G(u_0) \quad (8.24)$$

$$R(\varepsilon) = \frac{\rho_a(\varepsilon)}{|1 - \sigma'(u_0)|} \frac{|\varepsilon + u_0 - 2\varepsilon_a^\infty|^2}{|\varepsilon - u_0|^4} \quad (8.25)$$

with definitions (8.9) for  $G$  and (7.7) for  $\rho_a$ . Notice that, if  $u_0$  is real (i.e. the resonance reduces to a bound state),  $C_2 = \tilde{C}(u_0)$ . (8.23) is a generalization of (5.18) and similarly describes transitions induced by the singularity of  $\xi$  at  $t = 0$ . These transitions occur between the substrate level of energy  $\varepsilon$  and the resonance of (complex) energy  $u_0$ . The survival factor  $\exp(-C_2/\mu)$  however depends on « regular » resonant processes taking place at  $t > 0$ .

b) If  $|\varepsilon - u_0|$  is so small that :

$$|\varepsilon - u_0| \leq \mu \ll |\varepsilon - \varepsilon_a^\infty| \quad (8.26)$$

which implies a real or nearly real  $u_0$ ,  $M$  coincides practically with the saddle point and a second-order expansion is necessary, giving :

$$X(\varepsilon) \simeq -\sqrt{1 - \sigma'(u_0)} \exp[G(u_0)/2i\mu] \quad (8.27)$$

whence :

$$S(\varepsilon) \simeq \rho_a(\varepsilon) |1 - \sigma'(u_0)| \exp(-C_2/\mu). \quad (8.28)$$

The exponentials in (8.28) and (8.19) are nearly equal since, to lowest order in  $(\varepsilon - u_0)$  :

$$C_2 - \tilde{C}(\varepsilon) \simeq -\frac{1}{2} \text{Im} \left[ (\varepsilon - u_0)^2 \frac{1 - \sigma'(\varepsilon)}{\varepsilon - \varepsilon_a^\infty} \right] \quad (8.29)$$

but, owing to (8.26), the prefactor of (8.28) is larger. (8.28) generalizes (5.22). If  $u_0$  is complex, (8.28) describes resonant processes when, initially, the resonance is narrow and overlaps the substrate level of energy  $\varepsilon$  (but does not necessarily remains narrow afterwards). If  $u_0$  is real, corresponding to a bound state, (8.28) reduces to :

$$S(\varepsilon) \simeq \delta(\varepsilon - u_0) \exp(-C_2/\mu) \quad (8.30)$$

where  $C_2 = \tilde{C}(u_0)$ .

These results pose the problem of the choice of  $u_0$ , for, as we mentioned in connection with (8.10), an equation such as (8.21) generally has several solutions. Thus in a cluster model (e.g. the two-level model of chap. 6), there are as many  $u_0$ 's as levels. In the presence of bands of finite width,  $\sigma(z)$  possesses branch points at band edges and several analytic continuations are possible, each defining a Riemann sheet. Since  $u_0$  represents a resonance in the local



electronic structure at  $t = 0$ , the condition  $\text{Im } u_0 \leq 0$  and simple physical considerations are normally sufficient to determine the correct Riemann sheet. The choice of  $u_0$  among the various possible resonances may be more delicate. It seems that, if one of them evolves adiabatically to the bare  $a$ -state when the atom-surface coupling vanishes, it is the correct  $u_0$  to be used in the calculation of  $S(\varepsilon)$ . This assertion is supported by several examples : the two-level case (see later on), the semi-infinite chain [24] and a substrate density of states composed of both a finite band and a discrete level superposed on a wide band [25]. Sometimes (see the two-level case in section 8.5), other resonances may give subdominant contributions of physical interest.

**8.4 WHERE IS M ?** — When (8.26) is satisfied, the saddle point is very close to  $x = 1$  and (8.28) is the sole possible  $S(\varepsilon)$ . In a discrete-level model also, since  $\sin \varphi(\varepsilon)$  vanishes everywhere excepted at isolated points, the relevant  $S(\varepsilon)$  is readily identified. Otherwise  $S(\varepsilon)$  is given by (8.17) or (8.23) depending on whether M is at the saddle point or at  $x = 1$ . If the saddle point lies on contour  $C$ , the correct  $S(\varepsilon)$  is of course the larger. If the saddle point is not on  $C$ , (8.17) is irrelevant and  $S(\varepsilon)$  is given by (8.23). In the latter case can we state that (8.17) is smaller than (8.23) ? If the statement is true, a simple comparison of (8.17) and (8.23) will give the correct  $S(\varepsilon)$  in any case, which is a much more convenient method than to construct contour  $C$  and locate the saddle point. A general proof of the statement is not easy. Numerical confirmations have been obtained in two cases : the semi-infinite chain considered previously [24] for which the numerical calculation was done by Jardin and Quazza (unpublished) and a model for copper sputtering for which the two possible contributions to  $S(\varepsilon)$  were compared carefully [25]. Hereafter we present a direct proof of the statement in the simple wide-band case.

With notations of section 5.3, we have :

$$Q(x) = \exp(\Sigma_0 x/2 i \mu)$$

so  $X(\varepsilon)$  is given exactly by (8.12) where  $\sigma' = 0$  and :

$$A(x) = (\varepsilon_a^\infty - \varepsilon) \ln x + \Sigma_0 x.$$

For simplicity we assume  $\varepsilon > \varepsilon_a^\infty$ . Figure 1 shows some of the stationary-phase paths  $\text{Re } A(x) = \text{constant}$ . They are symmetrical with respect to the line OS whose angle with the real axis is  $\varphi$ . S is the saddle point and lies at  $x_S = (\varepsilon - \varepsilon_a^\infty)/\Sigma_0$ . The path passing through S intersects the positive real half-axis at one (if  $\varphi \geq \pi/2$ ) or two points (if  $\varphi < \pi/2$ ), the closer to the origin being J such that :

$$x_J = \gamma(\varepsilon - \varepsilon_a^\infty)/|\Sigma_0|$$

where  $\gamma$  is the smaller solution of  $1 + \ln \gamma = \gamma \cos \varphi$ .

Contour  $C$  must go from  $x = 0$  to  $x = 1$  with always either  $\text{Re } A = \text{constant}$  or  $\text{Im } A = -\infty$ . Let us follow it backwards. Depending on  $x_J$ , three cases appear :

a) If  $x_J > 1$ ,  $C$  ends at a point such as I at lhs of J. Descending the stationary-phase path passing through I, we recurrently follow a closed loop enclosing O.  $A(x)$  is multivalued and, at each turn,  $\text{Im } A$  decreases by  $2\pi(\varepsilon_a^\infty - \varepsilon)$ . After infinitely many turns,  $\text{Im } A = -\infty$  and we can leave the loop to join O along any radius. S is not on  $C$ . On the real axis,  $\text{Im } A(x) = -\Delta_0 x$ , therefore :

$$\text{Im } A(x_I) > \text{Im } A(x_J) > \text{Im } A(x_S).$$

So (8.17), here irrelevant, is smaller than (8.23).

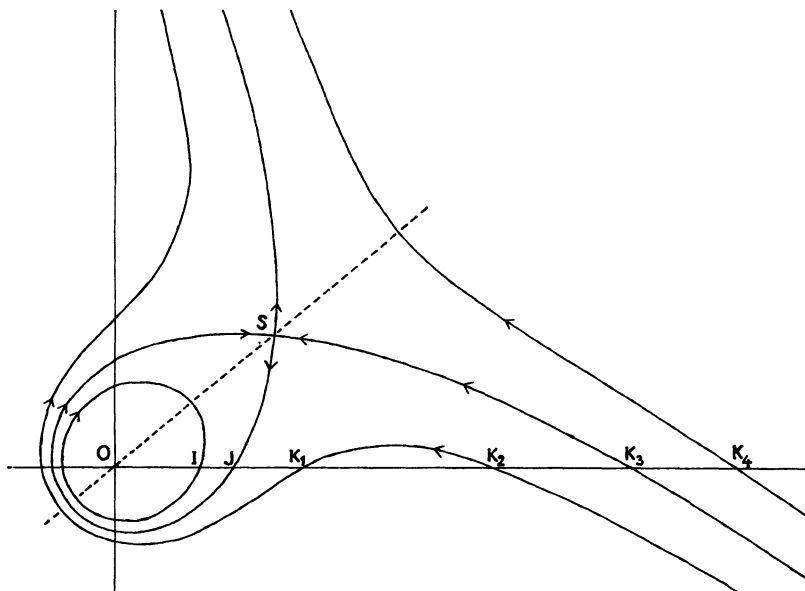


Fig. 1. — The stationary-phase paths  $\text{Re } A = \text{Const.}$  in the complex  $x$ -plane.  $S$  is the saddle point.  $\text{Im } A$  increases in the direction of arrows.

b) If  $x_J = 1$ ,  $C$  ends at  $J$ . It is again a closed loop, its peculiarity being to make a right angle at  $S$ .  $S(\epsilon)$  is still given by (8.23).

c) If  $x_J < 1$ ,  $C$  ends at a point such as one of the  $K_i$ 's at rhs of  $J$ . In a first step (unnecessary if  $i = 3$ ), we descend the stationary-phase path passing through  $K_i$  till infinity (where  $\text{Im } A = -\infty$ ) to join the stationary-phase path passing through  $S$ . In a second step, we follow the latter. We cross  $S$  straight a first time, describe a loop, cross  $S$  again, but now at right angle, and continue as in case (b). Depending on parameters,  $\text{Im } A$  may be maximum at  $K_i$  or at the first crossing of  $S$ . The higher maximum determines  $S(\epsilon)$ .

Notice that the topology of  $C$  is a consequence of the choice of  $x$  as variable of integration [Eq. (8.2)]. If  $t$  had been used instead [Eq. (8.1)], the exponent would have been single-valued and  $C$  composed of an infinity of branches. In case (c) above,  $C$  would have crossed an infinity of saddle points, one straight and the others at right angle.

**8.5 ION FRACTION.** — Once  $S(\epsilon)$  is known, application of (2.8) gives the ion fraction  $P$ . In a number of cases the integration involved in (2.8) can be done, at least approximately. Such cases are considered below. For simplicity we assume  $\epsilon_F > \epsilon_a^\infty$  and zero temperature. Thus :

$$P = \int_{\epsilon_F}^{\infty} d\epsilon S(\epsilon).$$

Further, as mentioned below (8.3),  $\epsilon_a^\infty$  is supposed not to be in the vicinity of a discrete substrate level.

Excluding for the moment the case of  $\epsilon_F$  close to a narrow resonance or within a gap of substrate states, consider increasing values of  $\epsilon_F - \epsilon_a^\infty$  :

a) If  $\epsilon_F - \epsilon_a^\infty \lesssim \mu$ , the relevant  $S(\epsilon)$  is (8.17). If  $\varphi(\epsilon)$  varies little over an interval  $\sim \mu / \varphi(\epsilon_F)$ ,  $P$  is given by (5.10).

b) If  $\varepsilon_F - \varepsilon_a^\infty \gg \mu$ , the relevant  $S(\varepsilon)$  may be (8.19) or (8.23). Let  $\varepsilon_c$  be such that  $C(\varepsilon_F) = C_2$ . If  $\varepsilon_F < \varepsilon_c$ , only (8.19) needs to be considered, giving :

$$P \simeq \frac{\sin \varphi(\varepsilon_F)}{\varphi(\varepsilon_F)} \exp\left(-\frac{C_1}{\mu}\right) \quad (8.31)$$

where  $C_1 = C(\varepsilon_F)$ . This result is valid both if  $\varphi(\varepsilon)$  varies little over an interval  $\sim \mu/\varphi(\varepsilon_F)$  above  $\varepsilon_F$ , thus generalizing (5.11), and if  $\varphi(\varepsilon)$  remains small (but not necessarily constant) for  $\varepsilon > \varepsilon_F$ , then generalizing (4.5). Note that these conditions do not forbid the presence of band edges above or below  $\varepsilon_F$ . (8.31) can be interpreted in terms of resonant processes as done in sections 5.2 and 8.2.

c) Assume now  $\varepsilon_F - \varepsilon_c \sim \mu/\varphi(\varepsilon_c)$ . For  $\varepsilon \simeq \varepsilon_F$ , (8.19) and (8.23) are of the same order of magnitude, (8.23) having a larger exponential, (8.19) a larger prefactor. Contour  $C$  passes the saddle point, so (8.15) and (8.22) should be added before being squared to give  $S(\varepsilon)$  [see (7.6)]. The expression of  $P$  is not very simple.

d) If  $\varepsilon_F - \varepsilon_c \gg \mu/\varphi(\varepsilon_c)$ , (8.23) gives :

$$P \simeq \mu^2 e^{-C_2/\mu} \int_{\varepsilon_F}^{\infty} d\varepsilon R(\varepsilon) \quad (8.32)$$

which generalizes (5.20). Ionization is provoked by the discontinuity of  $d\xi/dt$  at  $t = 0$ , subsequent resonant processes acting to partially restore equilibrium.

Turning to the case of  $\varepsilon_F$  near a narrow resonance (within a band), suppose (8.26) satisfied for  $\varepsilon = \varepsilon_F$ . (8.30) gives :

$$P \simeq (1 - \nu) \exp(-C_2/\mu) \quad (8.33)$$

where  $1 - \nu = \frac{1}{\pi} \arg(\varepsilon_F - u_0)$ .  $\nu$  represents the fraction of area of the resonance peak below the Fermi level. For a single resonance,  $\nu = n_a^{\text{ad}}(0)$ . (8.33) generalizes (4.6) and (5.23), reducing to (4.6) for a single resonance.

Finally consider a discrete-level system with  $\varepsilon_a^\infty$  not coinciding with any of the eigenvalues  $\varepsilon_1, \varepsilon_2, \dots, \varepsilon_N$  of  $H_s$ . Exact resonance is thus excluded. When the atom-substrate coupling is switched on, the eigenvalues of  $H$  tend continuously to a set  $\{u_i\}$  ( $i = 1, \dots, N + 1$ ), one of them passing from  $\varepsilon_a^\infty$  to  $u_a$  (one of the  $u_i$ 's). There is one  $u_i$  in each of intervals  $(-\infty, \varepsilon_1), (\varepsilon_i, \varepsilon_{i+1}), (\varepsilon_N, \infty)$ ,  $u_a$  being in the same interval as  $\varepsilon_a^\infty$ .  $\varphi(\varepsilon)$  drops down from  $\pi$  to 0 whenever  $\varepsilon$  passes one of the  $\varepsilon_i$ 's and goes up from 0 to  $\pi$  once in each of intervals  $(\varepsilon_i, \varepsilon_{i+1})$ . By (8.21),  $\varphi(u_a) = 0$  if  $u_a > \varepsilon_a^\infty$ ,  $\pi$  if  $u_a < \varepsilon_a^\infty$ . Consequently,  $\varphi(\varepsilon)$  is constant between  $\varepsilon_a^\infty$  and  $u_a$ , entailing  $\tilde{C}(u_a) = 0$ . With the choice  $u_0 = u_a$  in (8.23) or (8.30), we obtain  $C_2 = 0$ . (8.30) is relevant only if  $u_a > \varepsilon_F$  and leads to the trivial result  $P \simeq 1$ . In the interesting case  $u_a < \varepsilon_F$ , (8.23) gives :

$$P \simeq \frac{\mu^2}{|1 - \sigma'(u_a)|} \sum_{u_i > \varepsilon_F} \frac{|u_i + u_a - 2\varepsilon_a^\infty|^2}{|1 - \sigma'(u_i)| |u_i - u_a|^4}. \quad (8.34)$$

The choice  $u_0 = u_a$  was discussed in section 8.3. Notice that any other choice would probably give  $C_2 > 0$  and therefore an exponentially smaller  $P$  (or contribution to  $P$ ). Physically (8.34) must be valid if the distance between  $u_a(t)$ , the eigenvalue of  $H(t)$  such that  $u_a(\infty) = \varepsilon_a^\infty$ , and the closest other eigenvalue of  $H(t)$  is always much larger than  $\mu$ .

A special case is the two-level model studied in section 6.2. The electron being supposed initially in the lower state,  $|-\rangle$ , we must take  $u_a = \varepsilon_-(0)$  and  $u_i = \varepsilon_+(0)$ . With notation (6.11) and  $E_0 = E_\infty + \eta_0$ , (8.34) gives :

$$P \simeq \mu^2 \frac{T_0^2 (E_0 + 2 \eta_0)^2}{(E_0^2 + 4 T_0^2)^3} \tag{8.35}$$

which reduces to (6.15) for  $\eta_0 = 0$ . Like (8.34), (8.35) is due to the singularity of  $\xi$  at  $t = 0$  and can be eliminated by taking  $|\eta_0|$  or  $T_0$  extremely large. Then making  $u_0 = \varepsilon_+(0)$  in (8.30), we obtain  $P \simeq e^{-\gamma}$  where :

$$\gamma = \frac{1}{\mu} \tilde{C}(u_0) = \frac{\pi}{\mu \eta_0} \text{Inf}(E_\infty, \eta_0, T_0^2)$$

in agreement with (6.12).

**9. Asymptotic expressions : the scattering case.**

In the scattering case,  $P$  depends on two quantities, the square modulus of  $G_{aa}(\infty, -\infty)$ , which gives the survival probability of the initial charge state, and  $S(\varepsilon)$ . Approximations for these are derived in sections 9.1 and 9.2 respectively. The resulting ion fraction is calculated in section 9.3. Notations of section 8 are kept.

**9.1 EVALUATION OF  $G_{aa}$ .** — Similarly to  $Q(x)$ , we define :

$$P(y) = \sum_{n=0}^{\infty} \varphi_n(\varepsilon_a^\infty) y^n$$

which only differs from  $Q(y)$  by the substitution of  $\lambda$  for  $\mu$ . Choosing the infinitesimal  $\delta$  as real and positive, we can rewrite (7.14) as :

$$iG_{aa}(\infty, -\infty) = \frac{1}{2} \sum_{\pm} \pm \int_0^{i\infty} dt e^{i\delta t \mp (\mu + \lambda)t} [(\mu + \lambda \mp i\delta) PQ + \dot{P}Q - P\dot{Q}]$$

where  $P \equiv P(e^{2\lambda t})$ ,  $Q \equiv Q(e^{-2\mu t})$  and the dot denotes derivation with respect to  $t$ . Using approximation (8.8) for  $Q(x)$  and a similar expression for  $P(y)$ , we get, owing to (8.11) :

$$\begin{aligned} \dot{Q} &\simeq i(u_> - \varepsilon_a^\infty) Q \\ \dot{P} &\simeq -i(u_< - \varepsilon_a^\infty) P \end{aligned}$$

where  $u_<$  and  $u_>$  are the functions of  $t$  defined by :

$$\begin{aligned} u_> - \varepsilon_a^\infty - e^{-2\mu t} \sigma(u_>) &= 0 \\ u_< - \varepsilon_a^\infty - e^{2\lambda t} \sigma(u_<) &= 0. \end{aligned}$$

As in chapter 8,  $\varepsilon_a^\infty$  is supposed different from a discrete substrate level.

When  $\lambda$  and  $\mu$  are small, the integrand is dominated by the factor [see (8.8)]

$$\exp \frac{1}{2i} \left[ \frac{1}{\lambda} F(e^{2\lambda t}) + \frac{1}{\mu} F(e^{-2\mu t}) \right].$$

A priori its modulus can be maximum at two points on the contour of integration : the saddle point  $t_{sp}$  or the limit of integration  $t = 0$ . Owing to (8.11) the saddle-point equation is

$$\frac{d}{dt} \left[ \frac{1}{2\lambda} F(e^{2\lambda t}) + \frac{1}{2\mu} F(e^{-2\mu t}) \right] = u_{<} - u_{>} = 0$$

whence  $e^{2(\lambda + \mu)t} = 1$ . The real solution of  $t_{sp} = 0$  coincides with the limit of integration. There are therefore three possibilities :

a) The maximum is at this saddle point. Expanding  $F$  to second order in  $t$  and letting  $\delta \rightarrow 0$ , we obtain :

$$G_{aa}(\infty, -\infty) \simeq -i \exp \left[ -\frac{i}{2} \left( \frac{1}{\lambda} + \frac{1}{\mu} \right) G(u_0) \right] \quad (9.1)$$

whence

$$|G_{aa}(\infty, -\infty)|^2 \simeq \exp \left[ - \left( \frac{1}{\lambda} + \frac{1}{\mu} \right) C_2 \right] \quad (9.2)$$

with definitions (8.24), (8.21) and (8.9).

b) The maximum is at  $t = 0$ , but no saddle point lies there. This implies that  $u_{<}(0)$  and  $u_{>}(0)$  represent two different resonances, say  $u_1$  and  $u_2$ . Then :

$$G_{aa}(\infty, -\infty) \simeq \frac{(\mu + \lambda)(2\varepsilon_a^\infty - u_1 - u_2)}{(u_1 - u_2)^2 \sqrt{1 - \sigma'(u_1)} \sqrt{1 - \sigma'(u_2)}} \exp \left[ \frac{G(u_1)}{2i\lambda} + \frac{G(u_2)}{2i\mu} \right]. \quad (9.3)$$

But, as  $u_0$  is chosen in (9.1) so as to minimize  $C_2$ , (9.3) is necessarily exponentially smaller than (9.1) and therefore irrelevant.

c) The maximum is at an imaginary  $t_{sp}$ . However examination of simple examples (wide-band or two-level models) never leads to a physically reasonable  $C_2$ .

Finally the correct asymptotic expression is (9.1). In the wide-band model,  $C_2 = \Delta_0$  and we retrieve (5.17). In the case of a narrow resonance, such that  $[-\arg \sigma(u_0)]$  is close to 0 or  $\pi$ ,  $C_2 \simeq \tilde{C}(\text{Re } u_0)$ . In particular, if  $\text{Re } u_0 \simeq \eta(0) > 0$ ,

$$|G_{aa}(\infty, -\infty)|^2 \simeq \exp \left[ - \left( \frac{1}{\lambda} + \frac{1}{\mu} \right) \int_{\varepsilon_a^\infty}^{\varepsilon_a(0)} d\varepsilon \varphi(\varepsilon) \right]$$

in agreement with the first term of (4.7). In the two-level model,  $C_2 = 0$ . The asymptotic  $G_{aa}(\infty, -\infty)$  is then insufficient to give an estimate of the decay of the initial charge state.

## 9.2 EVALUATION OF $S(\varepsilon)$ . — Defining :

$$M(y) = \sum_{n=0}^{\infty} \varphi_n(\varepsilon + i\lambda) y^n = \sum_{n=0}^{\infty} \prod_{m=1}^n \frac{y\sigma(\varepsilon + 2mi\lambda)}{\varepsilon - \varepsilon_a^\infty + (2m+1)i\lambda} \quad (9.4)$$

we can rewrite (7.16) as :

$$(\varepsilon - \varepsilon_a^\infty + i\lambda) Y(\varepsilon) = \int_0^\infty dt e^{i(\varepsilon_a^\infty - \varepsilon)t - \mu t} M(e^{2\lambda t}) \times \left[ \lambda + \mu + (e^{2(\mu + \lambda)t} - 1) \frac{d}{dt} \right] Q(e^{-2\mu t}) \quad (9.5)$$

where the upper limit of integration is  $i\infty \text{ sgn}(\varepsilon_a^\infty - \varepsilon)$ .

When we evaluated  $Q(x)$  in section 8.1, we excluded the case of  $\sigma(z)$  having a pole at  $\varepsilon_a^\infty$  to avoid strong variations of  $\sigma(\varepsilon_a^\infty + (2p - 1)i\mu)$  between consecutive  $p$ 's. A similar requirement about  $M(y)$  would lead us to exclude the possibility for  $\sigma(z)$  to have a pole at  $\varepsilon$ , therefore anywhere on the real axis. We shall not lay down such a restriction. We are however led to treat separately the discrete and continuous parts of the spectrum of  $H_s$ , only assuming that, if  $\varepsilon_0$  designates a pole of  $\sigma(z)$ , either  $\text{Im } \varepsilon_0 = 0$  or  $(-\text{Im } \varepsilon_0) \gg \lambda$ .

9.2.1  $S(\varepsilon)$  in the continuous spectrum. — Using the identity :

$$\prod_{m=1}^n \frac{1}{m+a} = \frac{a}{n!} \int_0^1 ds s^{a-1} (1-s)^n$$

valid for  $\text{Re } a > 0$ , we can rewrite  $M(y)$  as :

$$M(y) = \frac{\varepsilon - \varepsilon_a^\infty + i\lambda}{2i\lambda} \int_0^1 \frac{ds}{\sqrt{s}} s^{(\varepsilon - \varepsilon_a^\infty)/2i\lambda} N((1-s)y)$$

where

$$N(z) = \sum_{n=0}^\infty \prod_{m=1}^n \frac{z\sigma(\varepsilon + 2mi\lambda)}{2mi\lambda}.$$

With the change of variable  $x = e^{-2\mu t}$ , (9.5) becomes :

$$Y(\varepsilon) = \frac{1}{2i\lambda} \int_0^1 \frac{ds}{\sqrt{s}} s^{\frac{\varepsilon - \varepsilon_a^\infty}{2i\lambda}} \int_0^1 \frac{dx}{\sqrt{x}} x^{\frac{\varepsilon_a^\infty - \varepsilon}{2i\mu}} N(z) \left[ \frac{\lambda + \mu}{2\mu} + (x-y) \frac{d}{dx} \right] Q(x)$$

where  $y = x^{-\lambda/\mu}$  and  $z = (1-s)y$ .

$N(z)$  just differs from  $Q(z)$  by the substitution of  $\lambda$  for  $\mu$  and  $\varepsilon + i\lambda$  for  $\varepsilon_a^\infty$ . Its asymptotic expression is deduced from (8.8) :

$$N(z) \approx \left[ \frac{\sigma(v)/\sigma(\varepsilon)}{1 - z\sigma'(v)} \right]^{1/2} \exp \frac{K(z)}{2i\lambda}$$

$$K(z) = \int_\varepsilon^v d\zeta \left[ 1 + \ln \frac{\sigma(\zeta)}{\sigma(v)} \right]$$

where  $v$  is the function of  $z$  defined by :

$$v - \varepsilon - z\sigma(v) = 0.$$

Similarly to (8.11), we have

$$\frac{dv}{dz} = \frac{\sigma(v)}{1 - z\sigma'(v)}, \quad \frac{dK}{dz} = \sigma(v) = \frac{v - \varepsilon}{z}. \tag{9.6}$$

For small  $\lambda$  and  $\mu$ ,  $Y(\varepsilon)$  can thus be written :

$$Y(\varepsilon) \approx \frac{1}{4i\lambda\mu} \int_0^1 \frac{ds}{\sqrt{s}} \int_0^1 \frac{dx}{\sqrt{x}} \frac{\lambda + \mu + i(y-x)\sigma(u)}{\sqrt{1-x\sigma'(u)}\sqrt{1-z\sigma'(v)}} \sqrt{\frac{\sigma(v)}{\sigma(\varepsilon)}} \exp \frac{L(s,x)}{2i\lambda}$$

$$L(s,x) = (\varepsilon - \varepsilon_a^\infty) \ln(sy) + K(z) + \frac{\lambda}{\mu} F(x)$$

where  $u$  defined by (8.10) and  $y, z$  and  $v$  as above.

The regions apt to contribute significantly to  $S(\varepsilon)$  are the vicinity of the saddle point  $S$  (such that  $\partial L/\partial x = \partial L/\partial s = 0$ ) and the vicinity of lines  $x = 1$  and  $s = 1$  (i.e. the limits of integration). Since, by (8.11) and (9.6) :

$$\frac{\partial L}{\partial x} = \frac{\mu}{\lambda} \frac{u-v}{x}$$

$$\frac{\partial L}{\partial s} = \frac{\varepsilon - \varepsilon_a^\infty - s(v - \varepsilon_a^\infty)}{s(1-s)} = \frac{v - \varepsilon_a^\infty - x^{-\lambda/\mu} \sigma(v)}{s} \quad (9.7)$$

$S$  is such that  $x^{1+\lambda/\mu} = 1$ . As in section 9.1, a complex  $x$  does not seem to correspond to a relevant saddle point (therefore either the latter is not on the contour of integration or, if it is, its contribution is not significant).  $S$  is therefore on the line  $x = 1$ . The sole regions to be explored are thus the lines  $x = 1$  and  $s = 1$ .

**9.2.2 The line  $s = 1$ .** —  $s = 1$  implies  $v = \varepsilon$ . The saddle point  $x_{sp}$  for the  $x$ -integral is such that  $u = \varepsilon$ , therefore is given by (8.14). The situation is strongly reminiscent of the sputtering case. For the moment we calculate each contribution to  $S(\varepsilon)$  separately, as if it was dominant.

a) The contribution of the vicinity of  $x_{sp}$  is again given by (8.17) :

$$S(\varepsilon) \simeq \frac{\sin \varphi(\varepsilon)}{\mu} \frac{\exp[-C(\varepsilon)/\mu]}{1 + \exp[-\pi(\varepsilon - \varepsilon_a^\infty)/\mu]} \quad (9.8)$$

reducing to (8.19) for  $\mu \ll |\varepsilon - \varepsilon_a^\infty|$ . The conditions of validity and interpretation are the same as in section 8.2.

b) The contribution of the vicinity of the limit  $x = 1$  is :

$$S(\varepsilon) \simeq (\mu + \lambda)^2 R(\varepsilon) \exp(-C_2/\mu) \quad (9.9)$$

only differing from (8.23) by the factor  $(\mu + \lambda)^2$  instead of  $\mu^2$ . In both cases  $S(\varepsilon)$  is proportional to the square of the discontinuity of  $d\xi/dt$  and describes transitions induced by this discontinuity between the level of energy  $\varepsilon$  and the resonance of (complex) energy  $u_0$ . The validity of (9.9) is however more limited than that of (8.23), for it implies  $\varepsilon$  not too close to a narrow resonance.

c) A more general expression for the contribution of the vicinity of  $x = 1$ , provided  $|\varepsilon - u_0| \gg \lambda$  and  $\mu$ , is :

$$S(\varepsilon) \simeq (\mu + \lambda)^2 \tilde{R}(\varepsilon) \exp(-C_2/\mu) \quad (9.10)$$

$$\tilde{R}(\varepsilon) = \frac{\tilde{\rho}_a(\varepsilon)}{|1 - \sigma'(u_0)|} \frac{|\varepsilon + u_0 - 2\varepsilon_a^\infty|^2}{|\varepsilon - u_0|^4}$$

$$\tilde{\rho}_a(\varepsilon) = \frac{\sin \varphi(\varepsilon)}{4\lambda |1 - \sigma'(\varepsilon)|} f(p) = \rho_a(\varepsilon) \pi |p|^2 f(p)$$

$$p = \frac{\varepsilon - \varepsilon_a^\infty - \sigma(\varepsilon)}{2\sqrt{\lambda \sigma(\varepsilon)[1 - \sigma'(\varepsilon)]}}$$

where  $f$  is defined for any  $p$  such that  $\text{Im } p \geq 0$  by :

$$f(p) = \frac{4}{\pi} \left| \int_0^\infty dt \exp i(t^2 + 2tp) \right|^2$$

and is such that  $f(0) = 1$ . Setting  $p = p_1 + ip_2$ , the approximation

$$f(p) \approx 1/\pi |p|^2$$

holds in the following cases: (i)  $p_2 \gg 1$ ; (ii)  $p_1 \gg p_2$ ; (iii)  $p_1$  negative such that  $p_2 \gg \ln |p_1|/|p_1|$ . Then  $\tilde{\rho}_a(\varepsilon)$  reduces to  $\rho_a(\varepsilon)$  and (9.10) to (9.9). This happens if no narrow resonance is present or, if there is one, for  $\varepsilon$  sufficiently far from it. If  $p_2$  is small, there is a range of negative  $p_1$ 's, such that  $p_2 \ll \ln |p_1|/|p_1|$ , in which

$$f(p) \approx 4 \exp(4 p_1 p_2).$$

This happens in presence of a narrow resonance. Consider such a resonance of energy  $u_b = \varepsilon_a^\infty + E_b - i\Delta_b$  with  $\Delta_b \ll \sqrt{\lambda E_b} \ll E_b$  and suppose  $\sigma'(\varepsilon)$  negligible in the region of interest.  $\tilde{\rho}_a(\varepsilon)$  is well approximated as

$$\tilde{\rho}_a(\varepsilon) \approx \frac{\varphi}{\lambda} \exp\left[(\varepsilon - \varepsilon_a^\infty - E_b) \frac{\varphi}{\lambda}\right] \tag{9.11}$$

( $\varphi = -\arg \sigma \approx \Delta_b/E_b$ ) over an interval of width  $\sim \lambda/\varphi$  below  $\varepsilon_a^\infty + E_b$ , therefore as far as the exponential is neither negligible nor larger than 1. Outside this interval, the profile of  $\tilde{\rho}_a(\varepsilon)$  evolves towards the lorentzian decay of  $\rho_a(\varepsilon)$ . Physically the resonance has not enough time to build up, so its spreads over the energy range corresponding to the shift of the resonance peak during the time  $1/\Delta_b$ . Put in another way, (9.11) describes the influence of resonant processes taking place at  $t < 0$ . A remarkable property of  $f(p)$  is, for  $p_2 > 0$ :

$$\int dp_1 f(p) = 1/p_2.$$

For a narrow resonance, this entails

$$\int d\varepsilon \tilde{\rho}_a(\varepsilon) \approx \int d\varepsilon \rho_a(\varepsilon) \tag{9.12}$$

which the above example confirms.

d) If  $\varepsilon$  is close to  $u_0$  (which implies the resonance  $u_0$  to be narrow),  $x_{sp}$  is close to 1. If the condition

$$|\varepsilon - u_0| \leq (\mu \text{ and } \lambda) \ll |\varepsilon - \varepsilon_a^\infty|$$

is realized, it comes:

$$S(\varepsilon) \approx \frac{\sin \varphi(\varepsilon)}{4 \mu} g\left(\frac{\lambda}{\mu}\right) \exp\left(-\frac{C_2}{\mu}\right) \tag{9.13}$$

where

$$g(x) = \left(\sqrt{x} + \frac{1}{x}\right)^2 \left| \int_0^{\pi/2} d\vartheta \frac{\cos \vartheta}{1 + i \sqrt{x} \sin 2 \vartheta} \right|^2.$$

In comparison with the sputtering case [Eq. (8.28)], the peak of  $S(\varepsilon)$  undergoes a strong spreading, again due to the delay in resonance formation. An analysis of its profile would require a more general expression, interpolating between (9.9) and (9.13) in a manner similar to (9.10). Such an expression is rather complicated and will not be considered here.



The relative importance of the various contributions (9.8), (9.9), (9.10) and (9.13) depends on  $\varepsilon$ . If  $\varepsilon$  is far from a narrow resonance, the choice is between (9.8) and (9.9), and considerations of section 8.4 remain valid. If  $\varepsilon$  lies near a narrow resonance, say  $u_\varepsilon$ , and the system possesses at least two resonances, (9.10) and (9.13) are two possible  $S(\varepsilon)$ 's. In (9.10),  $C_2$  is calculated with  $u_0 \neq u_\varepsilon$ , in (9.13) with  $u_0 = u_\varepsilon$ . The relevant  $S(\varepsilon)$  normally corresponds to the smaller  $C_2$ .

9.2.3 *The line  $x = 1$ .* —  $x = 1$  implies  $u = u_1$ , a resonance [i.e. a solution of (8.21)]. As the case  $s = 1$  has been treated above, only the case  $s = s_{sp} \neq 1$  needs to be considered,  $s_{sp}$  denoting the saddle point for the  $s$ -integral.  $s_{sp}$  is the solution of  $\partial L/\partial s = 0$ . Using successively the two expressions of  $\partial L/\partial s$  given by (9.7), we obtain :

$$s_{sp} = (\varepsilon - \varepsilon_a^\infty)/(v - \varepsilon_a^\infty)$$

and, since  $x = 1$ ,  $v = u_0$  where  $u_0$  is a resonance, identical with  $u_1$  or not. There are thus two possibilities :

a)  $u_1 = u_0$ . Then :

$$S(\varepsilon) \simeq \frac{\sin \varphi(\varepsilon)}{\lambda} \frac{\exp \left[ - \left( \frac{1}{\lambda} + \frac{1}{\mu} \right) C_2 + \frac{B(\varepsilon)}{\lambda} \right]}{1 + \exp [\pi (\varepsilon_a^\infty - \varepsilon)/\lambda]} \tag{9.14}$$

where

$$B(\varepsilon) = \int_{\varepsilon_a^\infty}^{\varepsilon} d\varepsilon [-\arg \sigma(\varepsilon)] \tag{9.15}$$

$B(\varepsilon)$  is formally identical with  $C(\varepsilon)$  [Eq. (8.18)], but for the moment we do not dispose of a firm criterion enabling us to specify the determination of  $\arg \sigma$ . Approximation (9.14) is correct under two conditions. First, integration over  $x$  requires :

$$\mu \ll |\sigma(u_0)| . \tag{9.16}$$

Second,  $s_{sp}$  should not be too close to 1. This implies :

$$\lambda \ll |\varepsilon - u_0| . \tag{9.17}$$

Of course, for (9.14) to be relevant, it is necessary that  $s_{sp}$  lies on the contour of  $s$ -integration. If  $u_0$  is close to the real axis on the right (resp. left) side of  $\varepsilon_a^\infty$ , this almost certainly implies  $\text{Re } s_{sp} < 1$ , therefore, by (9.13) :

$$\varepsilon < \text{Re } u_0 \text{ (resp. } \varepsilon > \text{Re } u_0) . \tag{9.18}$$

If a positive determination is taken for  $[-\arg \sigma(\varepsilon)]$ , (9.14) thus ceases being relevant when becoming too large.

b)  $u_1 \neq u_0$ . Then :

$$S(\varepsilon) \simeq \frac{(\lambda + \mu)^2 |u_0 + u_1 - 2 \varepsilon_a^\infty|^2}{|1 - \sigma'(u_0)| |1 - \sigma'(u_1)| |u_0 - u_1|^4} \times \frac{\sin \varphi(\varepsilon)}{\lambda} \frac{\exp \left[ - \frac{C_2(u_1)}{\mu} - \frac{C_2(u_0) - B(\varepsilon)}{\lambda} \right]}{1 + \exp [\pi (\varepsilon_a^\infty - \varepsilon)/\lambda]} \tag{9.19}$$

where, generalizing (8.24) :

$$C_2(u_i) = - \text{Im } G(u_i) . \tag{9.20}$$

Besides (9.16) and (9.17), the condition  $|u_1 - u_0| \gg \mu$  should be satisfied, as well as (9.18) if  $u_0$  is close to the real axis.

(9.14) describes the influence of resonant processes occurring at  $t < 0$ . An example will show it best. Consider the wide-band model under condition (5.24). For  $\varepsilon < \varepsilon_a^\infty + E_0$ ,  $S(\varepsilon)$  is deduced from (5.25) :

$$S(\varepsilon) = - \left. \frac{dP}{d\varepsilon_F} \right|_{\varepsilon_F = \varepsilon} \simeq \frac{\varphi}{\mu} e^{- (\varepsilon - \varepsilon_a^\infty) \frac{\varphi}{\mu}} + \frac{\varphi}{\lambda} e^{(\varepsilon - \varepsilon_a^\infty) \frac{\varphi}{\mu}} - \left( \frac{1}{\lambda} + \frac{1}{\mu} \right) A_0 . \tag{9.21}$$

This is just the sum of (9.8) and (9.14) (within these particular model and conditions) if the determination  $[- \arg \sigma(\varepsilon)] = \varphi(\varepsilon)$  is chosen. The two terms correspond to the two crossings of the substrate level of energy  $\varepsilon$  by the resonance, downwards (at  $t > 0$ ) and upwards (at  $t < 0$ ) respectively. For  $\varepsilon \simeq \varepsilon_a^\infty + E_0$ , the two exponents in (9.21) become equal, but, as condition (9.17) is violated, the approximation breaks down. For  $\varepsilon > \varepsilon_a^\infty + E_0$ , (9.18) is violated (there is no more crossing) and (9.14) is irrelevant [so is (9.8) moreover].

To unravel the question of the determination of  $\arg \sigma(\varepsilon)$ , consider the same model, but change the sign of  $\varepsilon_F - \varepsilon_a^\infty$  and  $E_0$  in condition (5.24) (thus  $E_0 < 0$  and  $\varepsilon_F < \varepsilon_a^\infty$ ). To respect electron-hole symmetry, we should choose  $[- \arg \sigma(\varepsilon)] = \varphi(\varepsilon) - \pi$ . The two terms of  $S(\varepsilon)$  have equal exponents again for  $\varepsilon \simeq \varepsilon_a^\infty + E_0$  and the approximation breaks down for  $\varepsilon \leq \varepsilon_a^\infty + E_0$ . In both cases  $\arg \sigma(\varepsilon)$  should be chosen in such a way that (9.14) becomes comparable to (9.8) just when (9.17) is violated and never exceeds it.

The example also points out that, unlike previous expressions of  $S(\varepsilon)$ , (9.14) is not a dominant contribution. It is at most of the same order of magnitude as (9.8) and should therefore be added to it. More exactly, the terms to be added are the corresponding contributions to  $Y(\varepsilon)$ , not  $S(\varepsilon)$ . But the crossed terms are always oscillating functions of  $\varepsilon$  whose contribution to the ion fraction is negligible.

(9.19) also describes the influence of resonant processes at  $t < 0$ , but in a situation where vertical transitions due to the discontinuity of  $d\xi/dt$  at  $t = 0$  play a major role. For this contribution not to be masked by (9.9) or (9.10),  $[C_2(u_0) - B(\varepsilon)]/\lambda$  must not be large, which implies the resonance  $u_0$  to be relatively narrow and  $\varepsilon$  not far from it. But then  $s_{sp}$  is close to 1, which is the situation treated in § 9.2.2.c. In fact for a narrow resonance (9.19) is a duplication of (9.10). This is quite apparent when (9.11) is carried back into (9.10) and one takes  $B(\varepsilon) = C(\varepsilon) \simeq (\varepsilon - \varepsilon_a^\infty) \varphi$  and  $C_2(u_0) \simeq C(\varepsilon_a^\infty + E_b)$  in (9.19).

**9.2.4  $S(\varepsilon)$  in the discrete spectrum.** — Let  $\varepsilon_0$  be a pole of  $\sigma(z)$ , therefore a bound state of  $H_s$ . Its distance to  $\varepsilon_a^\infty$  or any other pole will be supposed  $\gg \lambda$ . It is convenient to introduce  $\gamma(z)$ , analytic at  $\varepsilon_0$ , such that :

$$\sigma(z) = [\gamma(z)]^2 / (z - \varepsilon_0) .$$

Consider an interval of  $\varepsilon$  only containing  $\varepsilon_0$  as eigenvalue of  $H_s$ . In this interval (7.15) becomes :

$$S(\varepsilon) = \delta(\varepsilon - \varepsilon_0) |\gamma(\varepsilon_0) Y(\varepsilon_0)|^2 .$$

We need  $M(y)$  for  $\varepsilon = \varepsilon_0$  :

$$M(y) = \sum_{n=0}^{\infty} \frac{1}{n!} \left[ \frac{\sqrt{y}}{2i\lambda} \right]^{2n} \frac{\Gamma\left(\frac{E}{2i\lambda} + \frac{3}{2}\right)}{\Gamma\left(n + \frac{E}{2i\lambda} + \frac{3}{2}\right)} \exp \frac{U_n}{i\lambda}$$

where  $E = \varepsilon_0 - \varepsilon_a^\infty$  and

$$U_n = 2i\lambda \sum_{p=1}^n \ln \gamma(\varepsilon_0 + 2pi\lambda).$$

The last expression is quite comparable to (8.4) and can be approximated similarly. Setting

$$U_n = U(\varepsilon_0 + 2ni\mu)$$

as in (8.6), introducing  $\delta$ -functions and writing them in integral representation as in section 8.1, we get :

$$M(y) = \iint \frac{dq dr}{2\pi} e^{-iqr} \exp \frac{U(\varepsilon_0 + 2qi\lambda)}{i\lambda} \sum_{n=0}^{\infty} \frac{1}{n!} \left[ \frac{\sqrt{y} e^{ir/2}}{2i\lambda} \right]^{2n} \frac{\Gamma \left[ \frac{E}{2i\lambda} + \frac{3}{2} \right]}{\Gamma \left( n + \frac{E}{2i\lambda} + \frac{3}{2} \right)}.$$

To sum the series, we use the identity :

$$\sum_{n=0}^{\infty} \frac{(x/2i)^{2n}}{n! \Gamma \left( n + \nu + \frac{3}{2} \right)} = \frac{1}{\sqrt{\pi} \Gamma(\nu + 1)} \int_{-1}^1 ds (1-s^2)^\nu e^{-isx}$$

obtained by comparing the series and integral representations of the Bessel function. The rest of the calculation consists in repeated applications of the saddle-point method. Integration over  $q$  and  $r$  gives, to lowest order in  $\lambda$  :

$$M(y) \approx \frac{1}{\gamma(\varepsilon_0)} \sqrt{\frac{E}{2\pi i \lambda}} \int_{-1}^1 ds \frac{\gamma(v)}{\sqrt{1-s} \sqrt{y} \gamma'(v)} \exp \frac{I(y, s)}{2i\lambda}$$

$$I(y, s) = E \ln(1-s^2) + 2 \int_{\varepsilon_0}^v dz \left[ 1 + \ln \frac{\gamma(z)}{\gamma(v)} \right]$$

where  $v$  is defined by :

$$v = \varepsilon_0 - s \sqrt{y} \gamma(v) = 0. \quad (9.22)$$

Note the similarity with (8.8)-(8.10). The similarity can be made more complete by rewriting  $M(y)$  in terms of  $\sigma$  :

$$M(y) \approx \frac{1}{\gamma(\varepsilon_0)} \sqrt{\frac{Ey}{\pi i \lambda}} \int_{-1}^1 ds \frac{s\sigma(v)}{\sqrt{1-s^2} y \sigma'(v)} \exp \frac{I(y, s)}{2i\lambda}$$

$$I(y, s) = E \ln(1-s^2) + \int_{\varepsilon_0}^v dz \left[ 1 + \ln \frac{\sigma(z)}{\sigma(v)} \right]$$

with the definition :

$$v - \varepsilon_0 - s^2 y \sigma(v) = 0, \quad v \neq \varepsilon_0$$

equivalent to (9.22). To integrate over  $s$ , we observe that the stationary-phase path  $\text{Re } I = \text{Const.}$  must coil around each of the limits of integration and therefore reach its

highest point at a saddle point between them. It comes :

$$M(y) \approx \frac{1}{\gamma(\epsilon_0)} \frac{E}{\sqrt{y} \sqrt{1-y\sigma'(w)}} \exp \frac{I(y)}{2i\lambda}$$

$$I(y) = E \ln \frac{E}{w - \epsilon_a^\infty} + \int_{\epsilon_0}^w dz \left[ 1 + \ln \frac{\sigma(z)}{\sigma(w)} \right]$$

$$= G(w) - \int_{\epsilon_a^\infty}^{\epsilon_0} dz \left[ 1 + \ln \frac{y\sigma(z)}{E} \right]$$

where  $w$  is related to  $y$  in the same way as  $u$  to  $x$  [Eq. (8.10)] :

$$w - \epsilon_a^\infty - y\sigma(w) = 0 .$$

We can now return to  $Y(\epsilon_0)$ . With the change of variable  $x = e^{-2\mu t}$ , (9.5) becomes :

$$\gamma(\epsilon_0) Y(\epsilon_0) \approx \frac{1}{2\mu} \int_0^1 \frac{dx}{\sqrt{xy}} \frac{\lambda + \mu + i(y-x)\sigma(u)}{\sqrt{1-x\sigma'(u)} \sqrt{1-y\sigma'(w)}} \exp \frac{J(x)}{2i\mu}$$

$$J(x) = F(x) - E \ln x + \frac{\mu}{\lambda} I(y)$$

where  $y = x^{-\lambda/\mu}$ . The analysis is then quite similar to that of section 9.1. As :

$$dJ/dx = (u - w)/x$$

the saddle point  $x_{sp}$  is such that  $x_{sp}^{1+\lambda/\mu} = 1$ . The possibility for the maximum of  $\text{Im } J$  on the contour of integration to be at a complex  $x_{sp}$  should again be dismissed. It remains two cases :

a) The maximum is at the real saddle point  $x = 1$ , here coinciding with the limit of integration. It comes :

$$\gamma(\epsilon_0) Y(\epsilon_0) \approx \exp [J(1)/2i\mu] \tag{9.23}$$

on condition that  $\lambda \sim \mu \ll |u_0 - \epsilon_a^\infty|$ . Using definitions (8.24) and (9.15), we obtain :

$$S(\epsilon) \approx \delta(\epsilon - \epsilon_0) \exp \left[ - \left( \frac{1}{\lambda} + \frac{1}{\mu} \right) C_2 + \frac{1}{\lambda} B(\epsilon_0) \right] . \tag{9.24}$$

b) The maximum is at  $x = 1$ , but this point is not a saddle point. Then,  $u_1$  and  $u_2$  being two different resonances, we obtain, on condition that  $\lambda \sim \mu \ll |u_1 - u_2|$  :

$$S(\epsilon) \approx \delta(\epsilon - \epsilon_0) \frac{(\mu + \lambda)^2 |u_1 + u_2 - 2\epsilon_a^\infty|^2}{|1 - \sigma'(u_1)| |1 - \sigma'(u_2)| |u_1 - u_2|^4} \times$$

$$\times \exp \left[ - \frac{C_2(u_1)}{\mu} - \frac{C_2(u_2) - B(\epsilon_0)}{\lambda} \right] . \tag{9.25}$$

(9.24) and (9.25) show some analogy with formulae (8.30) and (8.23) of the sputtering case. This will be more apparent in next section.

**9.3 ION FRACTION.** — As in the sputtering case, we restrict ourselves to situations leading to relatively simple expressions for the ion fraction  $P$ . We again assume  $\epsilon_F > \epsilon_a^\infty$ , zero

temperature and no discrete substrate level in the vicinity of  $\varepsilon_a^\infty$ . Here :

$$P = P_0 |G_{aa}(\infty, -\infty)|^2 + \int_{\varepsilon_F}^{\infty} d\varepsilon S(\varepsilon). \quad (9.26)$$

First, suppose the resonance(s) sufficiently broad or distant from  $\varepsilon_a^\infty$  to ensure  $C_2(u_i) \gg \lambda$ , whether  $u_i$  designates  $u_a$ , the resonance formed adiabatically by the a-level, or any other resonance. Then, the memory of the charge state at  $t = -\infty$  is lost during scattering and  $P$  reduces to the last term of (9.26). The relevant  $S(\varepsilon)$  may be (9.8), (9.9) or exceptionally (9.25) if a discrete substrate level is shifted into a band as the result of interaction with the a-level. The analysis of paragraph 8.5.a to 8.5.d is still valid, the sole modification to the results being the replacement of (8.32) by :

$$P \simeq (\mu + \lambda)^2 e^{-C_2/\mu} \int_{\varepsilon_F}^{\infty} d\varepsilon R(\varepsilon). \quad (9.27)$$

Next, consider a relatively narrow resonance  $u_a$  ( $C_2(u_a) \sim \lambda \sim \mu$ ). If it crosses the Fermi level markedly ( $\varepsilon_F - \varepsilon_a^\infty$  and  $|u_a - \varepsilon_F| \gg \lambda$ ), both (9.8) and (9.14) contribute to  $S(\varepsilon)$ . To integrate over  $\varepsilon$ , it is convenient to proceed as in paragraph 5.3.d to avoid using  $S(\varepsilon)$  for  $\varepsilon \simeq Re u_a$ , which is badly known. Adding the survival probability of the initial charge state, given by (9.2), we obtain

$$P \simeq e^{-C_1/\mu} - e^{-\left(\frac{1}{\lambda} + \frac{1}{\mu}\right) C_2} [e^{C_1/\lambda} - P_0] \quad (9.28)$$

where  $C_2 = C_2(u_a)$ . In practice (9.28) reduces to the rate-equation result (4.7). If the resonance does not cross the Fermi level,  $P$  is the sum of the survival probability of the initial charge state

$$P_0 \exp\left[-\left(\frac{1}{\lambda} + \frac{1}{\mu}\right) C_2\right] \quad (9.29)$$

and the contribution of transitions at  $t = 0$  induced by the singularity of  $\xi$ , again given by (9.27). (9.29) has a smaller exponential than (9.27), but a larger prefactor if  $P_0 = 1$ , so the two contributions can be comparable. If the resonance  $u_a$  overlaps the Fermi level at  $t = 0$ , it follows from considerations of paragraph 9.2.2.d that  $P$  is still proportional to  $\exp(-C_2/\mu)$ , but with a small (and complicated) prefactor, in contrast with the sputtering results (8.33).

Now, suppose the adiabatic a-level discrete at any time, which entails  $C_2(u_a) = \tilde{C}(u_a) = 0$ . The case  $P_0 = 1$  leads to the trivial result  $P \simeq 1$  and need not be considered any longer. For  $P_0 = 0$ ,  $P$  is dominated by transitions due to the discontinuity of  $d\xi/dt$  at  $t = 0$ . If, for  $\varepsilon > \varepsilon_F$ ,  $\rho_a(\varepsilon)$  is sufficiently smooth (which means that no narrow resonance lies there), the relevant  $S(\varepsilon)$  is (9.9), giving :

$$P \simeq (\mu + \lambda)^2 \int_{\varepsilon_F}^{\infty} d\varepsilon R(\varepsilon) \quad (9.30)$$

where  $R(\varepsilon)$  is evaluated with  $u_0 = u_a$ . In presence of narrow resonances above  $\varepsilon_F$ , the appropriate  $S(\varepsilon)$  is (9.10) and  $R(\varepsilon)$  is replaced by the much smoother function  $\tilde{R}(\varepsilon)$ . For simplicity suppose that there is only one narrow resonance, say  $u_b$ , above  $\varepsilon_F$ . If, adiabatically, the latter remains a sufficiently long time above  $\varepsilon_F$  to satisfy the condition

$$C_2(u_b) - C(\varepsilon_F) \gg \lambda$$

(in fact an equilibration condition), the broad peak of  $\tilde{R}(\varepsilon)$  is entirely above  $\varepsilon_F$  and, owing to (9.11), the result is practically the same as (9.30). Otherwise the fraction of this peak below  $\varepsilon_F$  should be subtracted, meaning that the resonance  $u_b$  is not completely vacant and therefore apt to receive an electron from the  $a$ -level.

To illustrate this situation, imagine substrate states composed of a semi-infinite conduction band ( $\varepsilon > \varepsilon_c$ ) and a bound or quasi-bound state of energy  $\varepsilon_b < \varepsilon_F$ , an adsorbate state for instance. Initially the  $a$ -level is occupied and lies below the conduction band ( $\varepsilon_a^\infty < \varepsilon_c$ ). During scattering, the  $a$ -state mixes with the  $b$ -state in such a way that the adiabatic  $a$ -level remains below  $\varepsilon_c$  while the resonance  $u_b$  crosses  $\varepsilon_F$ . As in paragraph 9.2.2.c, set  $u_b = \varepsilon_a^\infty + E_b - i\Delta_b$  and assume  $\Delta_b \ll \sqrt{\lambda E_b} \ll E_b$  (therefore  $\varphi \approx \Delta_b/E_b$ ) and  $\sigma'(\varepsilon) \approx 0$  for  $\varepsilon > \varepsilon_F$ . To get a rough estimate of  $P$ , neglect the variation of  $\varepsilon - u_a$  between  $\varepsilon_F$  and  $\text{Re } u_b$ . It comes :

$$P \approx \frac{(\mu + \lambda)^2 |u_a + u_b - 2\varepsilon_a^\infty|^2}{|1 - \sigma'(u_a)| |u_b - u_a|^4} \left[ 1 - \exp\left(-\frac{\varepsilon_a^\infty + E_b - \varepsilon_F}{\lambda} \varphi\right) \right]. \quad (9.31)$$

Two factors appear. The first one is the transition probability between the  $a$ -state and the resonance  $u_b$  at  $t = 0$ . The second one is the probability that the  $b$ -state has previously transferred its electron to empty states of the conduction band through resonant processes, as use of the rate-equation approach would show easily.

Finally consider a discrete-level system with  $P_0 = 0$ . The possible  $S(\varepsilon)$ 's are (9.24) and (9.25). Asymptotically, the dominant one is (9.25), which describes the influence of the singularity at  $t = 0$ . As in section 8.5, we note  $\varepsilon_i$  the eigenvalues of  $H_s$ ,  $u_i$  those of  $H(t = 0)$ .  $\varepsilon_0$  is one of the  $\varepsilon_i$ 's above  $\varepsilon_F$ , therefore above  $\varepsilon_a^\infty$ . The choice  $u_1 = u_a$  entails  $C_2(u_1) = 0$ . Taking for  $u_2$  the nearest  $u_i$  above  $\varepsilon_0$  and observing that  $\varphi(\varepsilon) = 0$  in the interval  $\varepsilon_0 < \varepsilon < u_2$  [since  $\varphi(\varepsilon)$  makes no more than one jump between two consecutive  $\varepsilon_i$ 's, starts from 0 just above an  $\varepsilon_i$  and  $\text{sign } \sigma(u_i) = \text{sign}(u_i - \varepsilon_a^\infty) > 0$ ], we obtain  $C_2(u_2) = C(\varepsilon_0)$ . With the determination  $B(\varepsilon) = C(\varepsilon)$ , the exponential takes its highest possible value, 1. Finally, summing over the various  $\varepsilon_i$ 's above  $\varepsilon_F$ , we retrieve the sputtering result (8.34) just modified by the substitution of  $(\mu + \lambda)^2$  for  $\mu^2$ .

In the special case of the two-level model, it is possible as in section 8.5, to go further and retrieve the « regular »  $P$  due to continuous transitions between the two levels (« weakly resonant processes » in the sense of section 5.2) and not to transitions at  $t = 0$ . This implies an extremely large  $|\eta_0|$  or  $T_0$  and therefore well separated transitions along the inward ( $t < 0$ ) and outward ( $t > 0$ ) trips. The relevant  $S(\varepsilon)$  is here (9.24), with  $\varepsilon_0 = \varepsilon_b$ .  $C_2[\equiv C_2(u_0)]$  can be evaluated either with  $u_0 = u_a = \varepsilon_-(0)$ , giving  $C_2 = 0$ , or with  $u_0 = u_b = \varepsilon_+(0)$ , giving  $C_2 = \mu\gamma$  where  $\gamma$  is defined by (6.12). The first choice gives the contribution of transitions along the inward trip.  $B(\varepsilon_b)$  should then be evaluated with the determination

$$\arg \sigma(\varepsilon) = \begin{cases} 0 & \sigma(\varepsilon) > 0 \\ \pi & \sigma(\varepsilon) < 0 \end{cases}$$

giving  $B(\varepsilon_b) = -C(\varepsilon_b) = -C(u_b) = -\mu\gamma$ . The second choice for  $u_0$  gives the contribution of transitions along the outward trip. The (more usual) determination  $[-\arg \sigma(\varepsilon)] = \varphi(\varepsilon)$ , giving  $B(\varepsilon_b) = C(\varepsilon_b)$ , is then appropriate. Collecting the two contributions, we obtain :

$$P \approx e^{-\gamma} + e^{-(\mu/\lambda)\gamma}. \quad (9.32)$$

To retrieve (6.6) in the case  $\lambda = \mu$ , an interference term

$$- 2 \cos (2 \tau) \exp \left[ - \frac{\gamma}{2} \left( 1 + \frac{\mu}{\lambda} \right) \right]$$

should be added. In fact the correct procedure would be to add contributions from  $Y(\varepsilon)$  [Eq. (9.23)], instead of  $S(\varepsilon)$ , and square afterwards. The crossed term is the interference term.  $\tau$  could be calculated, but, as it is very sensitive to the form of  $T(t)$  and  $E(t)$  between the regions where transitions occur, which form is here rather artificial, its value is of no physical interest.

## 10. Conclusion.

The main results of this study are the expressions of the ionization probability  $P$  of slow atomic particles scattered or sputtered from surfaces, obtained in chapters 8 and 9 in an independent-electron model under the assumptions of exponential variations of atom-substrate coupling matrix elements with a single time constant  $\mu^{-1}$  (resp.  $\lambda^{-1}$ ) along the outward (resp. inward) trajectory and matching conditions at  $t = 0$  such that the matrix elements are continuous, but not their derivatives. Essentially two possible behaviours are obtained. If ion formation results from continuous non-adiabatic transitions, especially if the resonance formed by the atomic level crosses the Fermi level,  $P$  behaves as

$$P \sim \exp(-C_1/\mu) \quad (10.1)$$

in the sputtering case. In the scattering case a second exponential term may be significant if the coupling is not too strong, as well as interference terms if substrate levels are discrete. A different behaviour is obtained when ion formation results from transitions induced by the singular variation of the coupling at  $t = 0$ , viz.

$$P \propto (\mu + \lambda)^2 e^{-C_2/\mu} \quad (10.2)$$

or more complicated expressions, with  $C_2 = 0$  for a discrete-level substrate.

Though (10.1) was obtained under rather restrictive assumptions, any regular (i.e. analytic) variation of atom-substrate coupling matrix elements should lead to a similar form (possibly corrected by an interference factor in the scattering case if discrete substrate levels are involved) asymptotically, i.e. for sufficiently small  $\mu$ , provided the trajectory approximation remains justified and temperature effects can be ignored. (5.32) and (6.6) show it for as different models as wide-band and two-level models. The conclusion seems still to hold if electron correlation is taken into account [17, 21]. However it does not tell us within which range of velocities (10.1) is a good approximation. Qualitatively, as noticed in sections 5.4 and 5.6, (10.1) is better when the law of variation of coupling matrix elements is closer to an exponential and, as appears from appendix, when  $\sigma(\varepsilon)$  is smoother. Thus deviations from (10.1) will be more easily observed if the coupling displays sharp or non-monotoneous variations or the Fermi level is close to a sharp structure (e.g. band edge) in the density of states. An example of sharp and non-monotoneous variation of the coupling is the one resulting from the collapse of the transfer integral between the He 1s-orbital and some Si orbitals when the atoms are in close contact, leading effectively to a large increase of the He<sup>+</sup> ion fraction at low velocities [23]. (10.1) cannot allow for such effects, which require specific calculations. But, in contrast with many model calculations employing the same exponential time dependence for coupling matrix elements, it is not restricted to a particular substrate. Through the expressions of  $C_1$  and the prefactor (given in chapter 8), a dynamic property, the ionization probability, is directly related to a static property, the function  $\varphi(\varepsilon)$ , making a quick evaluation of  $P$  possible in a number of non-trivial cases.

The interest of (10.2) and akin expressions is more limited since they result from the assumed matching conditions at  $t = 0$ . However they give an insight into the possible contribution of an abrupt change in the variation of some parameters. If this change is of physical origin, due to a collision for instance, (10.2) may be an acceptable approximation in some range of velocities, as analysed in section 5.6. Another use of (10.2) is to estimate the influence of artificial matching conditions in numerical simulations. In particular, if calculations are made with clusters, a crossover from (10.1) to (10.2) (with  $C_2 = 0$ ) is expected when the level separation becomes comparable with the energy uncertainty  $1/\mu$ .

One-electron processes involved in charge exchange are often called resonant processes. The concept is clear when the a-level forms a narrow resonance and charge exchange proceeds quasi-isoenergetically so as to restore equilibrium, justifying use of the rate equation approach. But charge exchange can also proceed through transitions between levels of different energies, whether these can be easily identified (e.g. discrete levels) or they belong to broad resonances. Mathematically there is no border-line between the two kinds of processes, which were called near- and far-resonant processes in section 5.2 and are both described by (10.1) or akin expressions. However far-resonant processes have a low probability [for discrete levels separated by  $\Delta E$ , this decays as  $\exp(-\pi \Delta E/\mu)$ ], making the corresponding  $C_1$  large. So, for a positive (resp. negative) ion fraction of slow sputtered or scattered atoms to be detectable, it is usually required that the resonance formed by the atomic level penetrates into a band of vacant (resp. occupied) substrate states, unless (as regards ion scattering) an incomplete neutralization can be invoked.

The potentialities of the present results have already been illustrated in model cases, the detachment of the end atom from a semi-infinite chain and the knocking-off of an atom a by an atom b itself coupled to a wide-band substrate [24], and in the physical case of secondary  $\text{Cu}^+$  emission [25]. In view of further physical applications, the following points should be minded. The above calculations rely on a law of variation of coupling matrix elements characterized by time constants  $\mu$  and  $\lambda$  and imply a unique trajectory, not influenced by charge exchange.  $\mu$  and  $\lambda$  are proportional to outward and inward velocities. In a real situation, velocities influence other parameters, such as the magnitude of the coupling at  $t = 0$ . Also the assumption of a unique trajectory for given initial and final velocities is not always justified in scattering and is probably never in sputtering. In the latter case a quantitative comparison with experiment would require a statistics of ejection processes. Lastly, at low exit energies, the recoil due to charge transfer invalidates the trajectory approximation. However, if the point at which this transfer occurs is relatively well defined, the final energy of the ion just needs to be corrected by the a-level energy variation beyond this point, essentially due to the image force.

### Appendix.

As mentioned in section 8.2, when the contribution (8.17) is dominant, its asymptotic expansion can be derived to every order. This is done in this appendix.

Since, in the present case, the truncation of the interval of integration at  $x = 1$  in (8.2) is supposed to produce only exponentially smaller terms, we remove this upper limit. Substituting (8.7) for  $Q$  in (8.2) and integrating over  $x$  from 0 to  $\infty$ , we get :

$$X(\varepsilon) = \Gamma \left( \frac{\varepsilon_a^\infty - \varepsilon}{2i\mu} + \frac{1}{2} \right) (-2i\mu)^{\frac{\varepsilon_a^\infty - \varepsilon}{2i\mu} - \frac{1}{2}} \bar{X}(\varepsilon)$$

$$\bar{X}(\varepsilon) = \iint \frac{dw ds}{4\pi\mu} e^{\frac{W(w)}{2i\mu}} \left[ (\varepsilon - \varepsilon_a^\infty) e^{\frac{w - \varepsilon + i\mu_s}{2i\mu}} - e^{\frac{w - \varepsilon - i\mu_s}{2i\mu}} \right].$$



Integration over  $s$  gives two  $\delta$ -functions, whence :

$$\bar{X}(\varepsilon) = (\varepsilon - \varepsilon_a^\infty) \exp \frac{W(\varepsilon - i\mu)}{2i\mu} - \exp \frac{W(\varepsilon + i\mu)}{2i\mu}$$

$W(z)$  is defined by (8.6). We wish its expansion in powers of  $\mu$  beyond the first term given by (8.5). We use the formula :

$$\sum_{p=1}^n f((2p-1)\mu) = \frac{1}{2\mu} \int_0^{2n\mu} dx f(x) + \frac{1}{2} \sum_{m=1}^{\infty} c_m \mu^{2m-1} [f^{(2m-1)}(2n\mu) - f^{(2m-1)}(0)] \quad (\text{A.1})$$

where  $f^{(m)}$  denotes the  $m$ -th derivative of  $f$  and the  $c_m$ 's are the coefficients of the Taylor expansion of  $x \operatorname{csch} x$  at the origin, also given in terms of Bernoulli's numbers  $B_m$  as :

$$c_m = 2(-1)^m (2^{2m-1} - 1) B_m / (2m)! \quad (\text{A.2})$$

It comes :

$$W(z) = \int_{\varepsilon_a^\infty}^z dx \ln \sigma(x) + \sum_{m=1}^{\infty} (-1)^m c_m \mu^{2m} \left[ \frac{d^{2m-1}}{dx^{2m-1}} \ln \sigma(x) \right]_{\varepsilon_a^\infty}^z.$$

Using (A.1) again, we deduce :

$$2i\mu \ln \sigma(\varepsilon) = W(\varepsilon + i\mu) - W(\varepsilon - i\mu)$$

whence :

$$\bar{X}(\varepsilon) = \frac{\varepsilon - \varepsilon_a^\infty - \sigma(\varepsilon)}{\sqrt{\sigma(\varepsilon)}} \exp \frac{W(\varepsilon + i\mu) + W(\varepsilon - i\mu)}{4i\mu}.$$

Finally, using (7.6) and (5.8), we obtain :

$$S(\varepsilon) = \frac{\sin \varphi(\varepsilon)}{\mu} \frac{\exp[-C(\varepsilon)/\mu]}{1 + \exp[-\pi(\varepsilon - \varepsilon_a^\infty)/\mu]} \quad (\text{A.3})$$

where :

$$\begin{aligned} C(\varepsilon) &= -\frac{1}{2} \operatorname{Im} [W(\varepsilon + i\mu) + W(\varepsilon - i\mu)] = -\sum_{n=0}^{\infty} \frac{(-1)^n \mu^{2n}}{(2n)!} \operatorname{Im} W^{(2n)}(\varepsilon) \\ &= C(\varepsilon) + \sum_{p=1}^{\infty} (-1)^p \mu^{2p} [b_p \varphi^{(2p-1)}(\varepsilon) - c_p \varphi^{(2p-1)}(\varepsilon_a^\infty)] \end{aligned} \quad (\text{A.4})$$

$C(\varepsilon)$  is given by (8.18),  $\varphi(\varepsilon)$  by (3.10),  $c_p$  by (A.2) and :

$$b_p = \sum_{n=0}^p \frac{c_{p-n}}{(2n)!}.$$

The beginning of the expansion is :

$$C(\varepsilon) = C(\varepsilon) - \frac{\mu^2}{6} [2\varphi'(\varepsilon) + \varphi'(\varepsilon_a^\infty)] - \frac{\mu^4}{360} [8\varphi'''(\varepsilon) + 7\varphi'''(\varepsilon_a^\infty)] - \dots$$

For large  $p$ ,  $c_p \simeq -b_p \simeq 2(-1)^p \pi^{-2p}$ .

We emphasize that (A.4) is generally an asymptotic (i.e. divergent) series, the trivial case of a constant  $\varphi(\varepsilon)$  being probably the sole exception. Supposing that one manages to resum the series, one could only be sure of the result up to exponentially small terms (i.e. of the form  $e^{-\alpha/\mu}$ ) and  $S(\varepsilon)$  could not be known better than with a similar relative uncertainty.

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