PERGAMON

Solid State Communications xx (0000) xxx–xxx

solid state communications

www.elsevier.com/locate/ssc

A new approach to Auger and quasi-resonant processes in ion–surface collisions

R.T. Pepino, G.G. Kleiman*

Instituto de Física 'Gleb Wataghin', Universidade Estadual de Campinas, Caixa Postal 6165, 13083-970 Campinas, SP, Brazil

Received 8 August 2002; received in revised form 8 August 2002; accepted 25 September 2002 by C.E.T. Goncalves da Silva

Abstract

We present a theoretical model of charge exchange between an ion and a solid surface which includes resonant transfer and Auger-coupling processes. The Auger processes are treated through an equation of motion approach which results in an Auger self-energy identical to that obtained through the second-order Keldysh–Green functions formalism. The model which we report involves a Lorentzian-shaped level width for the resonant processes and a wide band form for the Auger processes. It permits an exact solution of the problem in terms of well-known functions. The roles played by the characteristic parameters of the problem, which are related to the atom velocity, energy level positions, interaction potential and band structure are illustrated in some simple cases. © 2002 Published by Elsevier Science Ltd.

PACS: xxx; xxx; xxx

Keywords: xxx; xxx; xxx

1. Introduction

Understanding the mechanisms of charge exchange is an essential ingredient in the full description of the interaction of moving atoms, molecules and ions with solid surfaces. A considerable theoretical literature has developed over the years on the application of the Anderson–Newns Hamiltonian [1,2] to the problem of charge exchange between surfaces and atoms which are either scattered or sputtered. Those investigations which solve the equations of motion generally concentrate on the mechanism of resonant charge transfer and can be divided between single particle and many body theories. The single particle theories describe the atom as having one nondegenerate electronic state and vary in the way they model the surface's electronic properties. Descriptions of the solid include the wide band [3,4], linear chain [5–7], and surface layer coupling [8] models. The many body theories account for multiple and degenerate atomic orbitals and treat the intra-atomic Coulomb repulsion explicitly [9–11]. The influence of Auger processes on charge exchange with jellium metals has also been studied [12,13].

The parameters of the single particle problem include the velocity of the atom, its coupling with the metal, the position of its energy level and the characteristics of the metallic electronic structure. Closed form solutions exist for the extreme cases of the wide band [3] and two level [14] models, whose applicability is somewhat limited. Studies of other models of the solid involve numerical calculations, which are, in general, extremely lengthy and preclude exhaustive examination of the influence of the various parameters of the problem.

In this paper, we study, in the single particle picture, the combined influence of resonant transfer and Auger coupling on the charge exchanged between an ion and a solid surface. By considering the operator equations of motions, we derive expressions for the relevant self energies, which we model. These models permit us to derive closed form solutions of the equations of motion which recover the limits of the wide band and two level models. Furthermore, the model allows for efficient calculations and systematic studies of the relative importance of resonance and Auger effects and its

* Corresponding author. Tel.: +55-1937885365; fax: +55-1937885376.

E-mail address: kleiman@ifi.unicamp.br (G.G. Kleiman).

0038-1098/02/$ - see front matter © 2002 Published by Elsevier Science Ltd.
PII: S0038-1098(02)00596-3

predictions are sensitive to the influence of the various parameters of the theory. In another paper [15], we report the predictions of the model and comparisons with experiments. Here, we concentrate on presenting the model.

2. Theoretical model

We model the problem with the Hamiltonian of Eqs. (1a)–(d) [12,13]:

$$H(t) = H_0 + V_R(t) + V_A(t), \tag{1a}$$

$$H_0 = \sum_\mu \varepsilon_\mu c_\mu^+ c_\mu + \varepsilon_a(t) c_a^+ c_a, \tag{1b}$$

$$V_R(t) = \sum_\mu [V_{a\mu}(t) c_a^+ c_\mu + V_{a\mu}^*(t) c_\mu^+ c_a], \tag{1c}$$

$$V_A(t) = \sum_{k\ell\ell'} [W_{k\ell\ell'}(t) c_k^+ c_a^+ c_\ell c_{\ell'} + W_{k\ell\ell'}^*(t) c_{\ell'}^+ c_\ell^+ c_a c_k]. \tag{1d}$$

In Eqs. (1a)–(d), H_0 refers to bands of states in the solid and to the localized level of the ion, characterized, respectively, by the one-electron energies ε_μ and $\varepsilon_a(t)$ (assumed to vary with time t). The potential $V_R(t)$ represents a one-electron (quasi-resonant) coupling between the atomic level and the band of states $\{\mu\}$, while $V_A(t)$ corresponds to Auger processes involving the atomic level and the states $\{\ell\}$ and $\{k\}$. The quantities $c_{k,\mu,\ell}^+$ ($c_{k,\mu,\ell}$), c_a^+ (c_a) represent the Schrödinger creation (annihilation) operators for electrons in the corresponding one-electron states of the surface and of the atom, which we assume to be orthogonal. We suppose that the state labeled by k is initially unoccupied (only Auger capture by the ion is allowable). We make the usual assumption [3,13] of separable time and state dependences of the potentials: that is, we assume that $W_{k\ell\ell'}(t) = W_{k\ell\ell'} u_A(t)$ and $V_\mu(t) = V_\mu u_R(t)$ [4].

To determine the charge transferred between the subsystems, it is necessary to calculate the atomic occupation as a function of time, $n_a(t) = \langle \Phi_0 | c_a^+(t) c_a(t) | \Phi_0 \rangle$, where $|\Phi_0\rangle$ is the state of the system as $t = t_0 \to -\infty$ (here we use the Heisenberg representation for the operators). A direct method of calculation is based on the evolution equations of the creation (annihilation) operators. Defining the energy difference $\varepsilon_{\ell\ell' k} = \varepsilon_\ell + \varepsilon_{\ell'} - \varepsilon_k$ and the three fermion operators $\hat{A}_{k\ell\ell'}(t) = c_k^+(t) c_\ell(t) c_{\ell'}(t)$ and $\hat{A}(t) = \sum_{k\ell\ell'} W_{k\ell\ell'}(t) \hat{A}_{k\ell\ell'}(t)$, we can show that [15]:

$$\begin{aligned} i \frac{d\tilde{c}_a(t)}{dt} &= \sum_\mu V_\mu^*(t) c_\mu(-\infty) \exp\left(i \int_{-\infty}^t dt' (\varepsilon_a(t') - \varepsilon_\mu) \right) \\ &\quad - \sum_{k\ell\ell'} W_{k\ell\ell'}(t) \hat{A}_{k\ell\ell'}(-\infty) \\ &\quad \exp\left(i \int_{-\infty}^t dt' (\varepsilon_a(t') - \varepsilon_{\ell\ell' k}) \right) - i \int_{-\infty}^t d\tau \\ &\quad \exp\left(i \int_\tau^t dt' \varepsilon_a(t') \right) \tilde{c}_a(\tau) \left(\Sigma_R(t,\tau) + \hat{\Sigma}_A(t,\tau) \right), \end{aligned} \tag{2}$$

where $\tilde{c}_a(t) = c_a(t) \exp(i \int_{-\infty}^t dt' \varepsilon_a(t'))$ and:

$$\begin{aligned} \Sigma_R(t,\tau) &= \sum_\mu V_\mu^*(t) V_\mu(\tau) e^{i\varepsilon_\mu(\tau - t)} \\ &= u_R(t) u_R(\tau) \int_{-\infty}^{\infty} d\varepsilon \Delta_R(\varepsilon) e^{-i\varepsilon(t-\tau)}, \end{aligned} \tag{3}$$

$$\begin{aligned} \hat{\Sigma}_A(t,\tau) &= \sum_{\substack{k_1 \ell_1 \ell_1' \\ k_2 \ell_2 \ell_2'}} W_{k_1 \ell_1 \ell_1'}(t) W_{k_2 \ell_2 \ell_2'}^*(\tau) \\ &\quad e^{i\varepsilon_{\ell_1 \ell_1' k_1}(\tau - t)} \{ \hat{A}_{k_1 \ell_1 \ell_1'}(\tau), \hat{A}_{k_2 \ell_2 \ell_2'}^+(\tau) \}, \end{aligned} \tag{4}$$

In Eq. (3), $\Delta_R(\varepsilon) \equiv \pi \sum_\mu |V_\mu|^2 \delta(\varepsilon - \varepsilon_\mu)$ and we use units such that $\hbar = 1$. No approximations were made in the derivation of Eq. (2). Note, however, that, whereas $\Sigma_R(t,\tau)$ is a scalar, $\hat{\Sigma}_A(t,\tau)$ is an operator, which complicates the solution of Eq. (2).

We can proceed further by supposing that the dominant Auger transitions satisfy a quasi-conservative condition: that is, $\varepsilon_\ell + \varepsilon_{\ell'} - \varepsilon_k - \varepsilon_a(t) = \eta(t) \approx 0$, so that the exchange of energy between the Auger electrons and the ion is small. We expect this condition to be valid if the characteristic time of a transition, related to $\hbar/\varepsilon_{ll'k}$, is much smaller than that of the Auger interaction, related to the time variation of $W_{k\ell\ell'}(t)$. This approximation simplifies the problem, permitting us to replace the operator $\hat{\Sigma}_A(t,\tau)$ with the scalar quantity in Eq. (5) [15]:

$$\Sigma_C(t,\tau) = \sum_{k\ell\ell'} |W_{k\ell\ell'}|^2 u_A(t) u_A^*(\tau) e^{i\varepsilon_{\ell_1 \ell_1' k_1}(\tau - t)} n_\ell^0 n_{\ell'}^0, \tag{5}$$

where n_ℓ^0 is the initial occupation of the state ℓ and the state k is unoccupied. This Auger self-energy is identical to the second order result for Auger capture processes [12,13] obtained through an approach based on Keldysh–Green functions [16] (as in Ref. [13], here we neglect the contributions from loss and exchange self energies, and discuss them elsewhere [15]).

Supposing that the matrix elements in Eq. (5) vary slowly on the scale of the band energies (i.e. $|W_{k\ell\ell'}| \approx W$, which is a common approximation for Auger wide band valence spectra [17]), we can rewrite the equation in a form that involves the Fourier transforms of ρ_k, the density of final states, and of the auto-convolution of the density of occupied states in the band $\{\ell\}$, defined by $\rho_\ell^0(\varepsilon) = \sum_\ell n_\ell^0 \delta(\varepsilon - \varepsilon_\ell)$, so that:

$$\begin{aligned} \Sigma_C(t,\tau) \approx W^2 \int_{-\infty}^{\infty} d\omega\, e^{i\omega(t-\tau)} \rho_k(\omega) \int_{-\infty}^{\infty} d\varepsilon' e^{i\varepsilon'(t-\tau)} \int_{-\infty}^{\infty} \\ d\varepsilon'' \rho_\ell^0(\varepsilon' - \varepsilon'') \rho_\ell^0(\varepsilon''). \end{aligned} \tag{6}$$

Assuming a slowly varying final state density of states, (i.e. $\rho_k(\varepsilon) \approx \rho_0$, a constant), we find that:

$$\Sigma_C(t,\tau) \cong \Lambda_0 |u_A(t)|^2 \delta(t - \tau), \tag{7a}$$

$$\Lambda_0 \equiv W^2 \rho_0 \int_{-\infty}^{+\infty} d\varepsilon' \, d\varepsilon'' \rho_\ell^0(\varepsilon' - \varepsilon'') \rho_\ell^0(\varepsilon''). \tag{7b}$$

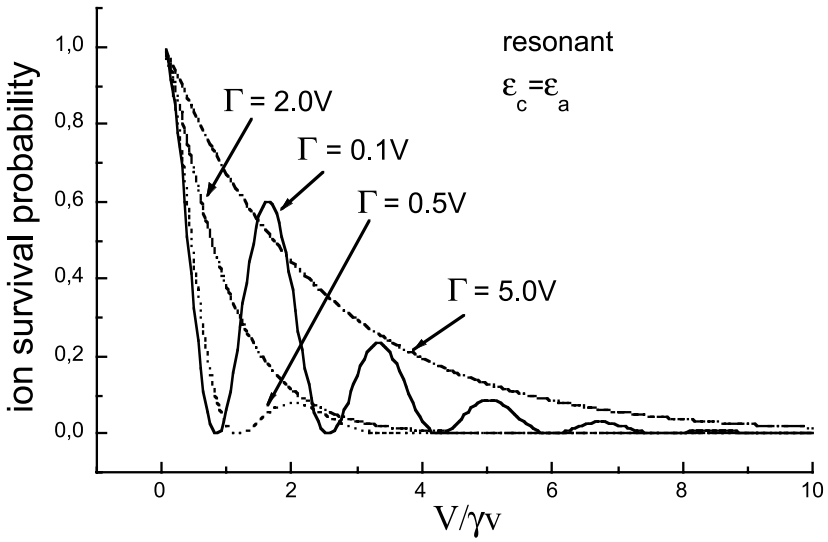

Fig. 1. The ion survival probability, $P^+(\infty)$, as a function of $V/\gamma\nu$ for some representative values of Γ, in the case $\varepsilon_a = \varepsilon_c$ and $\Lambda_0 = 0$. The transition between oscillatory and purely damped behavior occurs for $\Gamma = 2V$.

Eqs. (7a) and (b) are consistent with the independent results [13] that the Auger self energy is localized in time and that its real (or dispersive) part is negligible because of the rapidity of the Auger transitions compared to the time scale of W. Neglecting $V_R(t)$ in Eq. (2) results in a semiclassical master equation of the same form as that in Ref. [13]. It appears, therefore, that Eqs. (7a) and (b) constitute a reasonable approximation to the Auger self energy.

In accordance with our stated objective of finding closed form solutions of Eq. (2), we note that the form Eqs. (7a) and (b) (when substituted into Eq. (2)) is mathematically identical to that of the wide band model for resonant processes, which is, of course, exactly soluble [3]. We can remove the dependence upon Λ_0 by defining a new operator $\tilde{b}_a(t) = \tilde{c}_a(t)\exp(i\int_0^t dt'\Lambda_0|u_2(t')|^2)$. The resulting equation for $\tilde{b}_a(t)$ is similar in form to the standard equation for resonant transfer [3,15] (i.e. Eq. (2) with $\Lambda_0 = 0$). In order to formulate an exactly soluble form for the resonant term, we observe that, for large ε, the interaction between the ion and the surface is dominated by the Auger processes even if we allow $\Delta_R(\varepsilon)$ (which, from its definition, has a finite width) to have a decaying tail. By choosing a Lorentzian band model, as in Eq. (8), we can convert Eq. (2) into a second-order nonhomogeneous differential equation in time which leads to solutions in terms of known functions [15].

$$\Delta_R(\varepsilon) = V^2 \frac{\Gamma}{(\varepsilon - \varepsilon_c)^2 + \Gamma^2}, \tag{8}$$

The form of Eq. (8) allows us to investigate effects related to the band-width Γ and the relative position of the band center, ε_c and interference effects between Auger and quasi-resonant processes can be investigated in the combined model. A Lorentzian model was used earlier in exploring the validity of the WKB approximation for resonant transfer [18]. A previous study combining Auger and resonant processes did not allow for interference effects [19].

3. Some calculational results

As an example of the application of the model, we consider constant $\varepsilon_a(t)$ and let $u_R(t) = u_A(t) = \exp(-\gamma\nu|t|)$. The solution in this case, expressible in terms of confluent hypergeometrical functions, can be found elsewhere [15]. In particular, if, initially, the band is full while the atomic state is empty, we find that the survival probability of the ion, $P^+(\infty) = 1 - n_a(\infty)$, is given by:

$$P^+(\infty) = \left|e^{-c}\left(\Phi_a^{-b^2/c}(c)\Phi_a^{a+b^2/c}(-c) - (b/a)^2 Phi;{}^{1-b^2/c}_{1+a}(c)\Phi_{1+a}^{a+b^2/c}(-c)\right)\right|^2 \tag{9a}$$

where $a = 1/2 + \Gamma/2\gamma\nu + i(\varepsilon_a - \varepsilon_c)/2\gamma\nu$, $b = V/2\gamma\nu$, $c = \Lambda_0/2\gamma\nu$ and $\Phi_a^b(c)$ is the confluent hypergeometrical function given in Eq. (9b),

$$\Phi_a^b(c) = \sum_{n=0}^{\infty} \frac{\Gamma(b+n)}{\Gamma(b)} \frac{\Gamma(a)}{\Gamma(a+n)} \frac{c^n}{n!}, \tag{9b}$$

and $\Gamma(a)$ is the gamma function.

In Fig. (1), we present a graph of $P^+(\infty)$ as function of $V/\gamma\nu$ for different values of Γ/V in the resonant situation ($\varepsilon_a - \varepsilon_c = 0$) for $\Lambda_0 = 0$. Damped oscillatory behavior is manifested for $\Gamma/V \leq 2$, while a purely damped behavior occurs otherwise. Those oscillations are reminiscent of the two level problem (limit $\Gamma \to 0$), which in the present case corresponds to the Demkov model of charge transfer in atomic collisions [14,20]. Their origin is in the quantum interference between the localized levels, whose phases

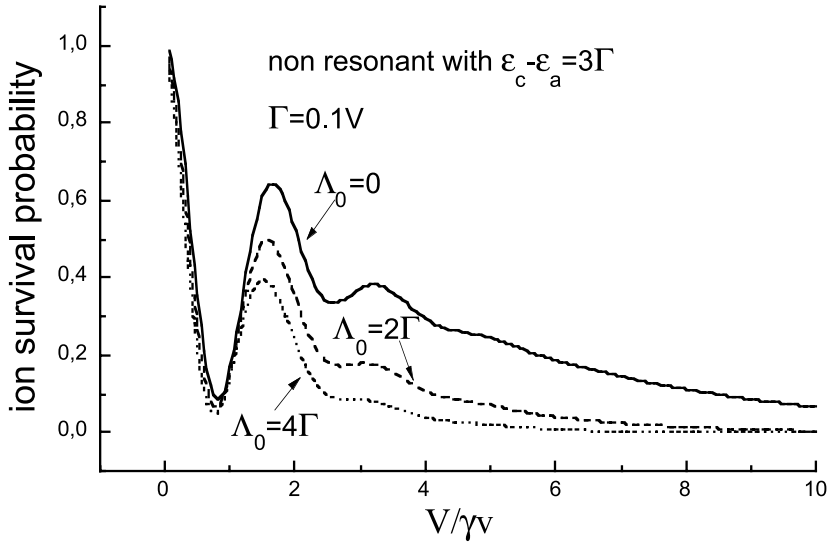

Fig. 2. Effects of $\varepsilon_a - \varepsilon_c$ and Λ_0 on $P^+(\infty)$. Both parameters have damping effects, but increasing Λ_0 also shifts the peaks to higher velocities. Their roles are more important at intermediate to low velocities.

differ by V. On the other hand, if we think of the band as a virtual atomic level of energy ε_c broadened by width Γ, the damping is readily associated with Γ. It is clear that the interference becomes more intense the stronger the potential V, which explains why the onset of the oscillations depends on Γ/V. The wide band limit is a particular case of the present model, as one can see by taking the limit $\Gamma \to \infty$, while keeping V^2/Γ constant. Oscillatory behavior cannot occur in this limit, since $\Gamma \gg V$. It is interesting to note that the contribution from the tail of the Lorentzian has a wide band type of behavior [3], even when $\Gamma_0 = 0$, allowing us to associate the tail with weak Auger processes [15].

In Fig. (2) we take into account effects of nonzero $\varepsilon_a - \varepsilon_c$ and Λ_0. We distinguish between high velocities, for which $\Gamma/\gamma v \ll 1/2$, low velocities, for which $\Gamma/\gamma v \gg 1/2$ and intermediate velocities otherwise. Λ_0 has purely damping effects (related to e^{-c} in Eq. (9a)), which results in shifts of the peaks to higher velocities as its value increases and their disappearance as velocity is lowered (as $V/\gamma v$ is increased).

The energy difference $\varepsilon_a - \varepsilon_c$ also reduces the oscillations, what can be explained if we remember that, in the two level case, the interference responsible for the oscillatory behavior is more intense for larger values of $V/|\varepsilon_a - \varepsilon_c|$. The intensity of charge transfer is reduced since the atomic state couples preferentially with states far from the center of the band, where the interaction strength $\Delta_R(\varepsilon)$ is small. The effects of $\varepsilon_a - \varepsilon_c$ and Λ_0 are important only at low and intermediate velocities.

4. Conclusion

In conclusion, we have presented a model that allows us to deal simultaneously with quasi-resonant and Auger processes in charge transfer between ions and surfaces. We have reported an analytically soluble model, which permits the elucidation of the roles played by characteristic parameters of the problem, related to the atom velocity, energy levels positions, interaction potentials and bands structures. In another paper, we investigate the influence of the occupation of the band and of the time dependence of the atomic energy level and make comparison with experiments [15].

References

[1] P.W. Anderson, Phys. Rev. 124 (1969) 41.
[2] D.M. Newns, Phys. Rev. 178 (1969) 1123.
[3] A. Blandin, A. Nourtier, D.W. Hone, J. Phys. (Paris) 37 (1976) 369.
[4] R. Brako, D. Newns, Rep. Prog. Phys. 52 (1989) 655.
[5] Y. Muda, D. Newns, Phys. Rev. B 37 (1988) 7048.
[6] Y. Muda, T. Hanawa, Surf. Sci. 97 (1980) 283.
[7] E.A. Garcia, E.C. Goldberg, M. Passeggi, Surf. Sci. 325 (1995) 311.
[8] J. Merino, N. Lorente, M.Yu. Gusev, F. Flores, M. Maazouz, L. Guillemot, V.A. Esaulov, Phys. Rev. B 57 (1998) 1947.
[9] W. Bloss, D. Hone, Surf. Sci. 72 (1978) 277.
[10] H. Shao, D.C. Langreth, P. Nordlander, Phys. Rev. B 49 (1994) 13929.
[11] J.B. Marston, D.R. Anderson, E.H. Behringer, B.H. Cooper, C.A. DiRubio, G.A. Kimmel, C. Richardson, Phys. Rev. B 48 (1993) 7809.
[12] M.A.V. Alvarez, V.H. Ponce, E. Goldberg, Phys. Rev. B 57 (1998) 14919.
[13] E.A. García, R. Monreal, Phys. Rev. B 61 (2000) 13565.
[14] Y.N. Demkov, Sov. Phys.-JETP 18 (1964) 138.
[15] R.T. Pepino, G.G. Kleiman, unpublished.

[16] L.V. Keldysh, Sov. Phys.-JETP 20 (1965) 1018.
[17] G.G. Kleiman, Appl. Surf. Sci. 11/12 (1981) 730.
[18] A.T. Dorsey, K.W. Jacobsen, Z.H. Levine, J.W. Wilkins, Phys. Rev. B 40 (1989) 3417.
[19] E.C. Goldberg, R. Monreal, F. Flores, H.H. Brongersma, P. Bauer, Surf. Sci. 440 (1999) L875.
[20] J.B. Hasted, Adv. At. Mol. Phys. 15 (1979) 205.