

Dynamical screening in Auger processes near metal surfaces

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We develop a theory for Auger processes occurring when a slow ion interacts with a metal surface that includes dynamical screening. In particular, the theory contains the possibility that normal modes of the electron gas are excited in the Auger process. We perform a calculation of the Auger capture rate for a model system representing He^+ interacting with an Al surface and show that surface plasmons are indeed excited in this system. We also show that the inclusion of screening affects the exponential decrease of the Auger rate with increasing distance between ion and surface.

There is a growing interest in ion-surface scattering as a probe for obtaining information on both target and projectile. The exchange of electrons is due to several mechanisms depending mainly on the relative position of the electronic levels of ion and solid electrons. When resonant neutralization/ionization is not possible, the two-electron Auger mechanism is responsible for charge exchange between ion and solid. This is the case of slow He^+ ions interacting with metal surfaces of high work function.

The problem of Auger neutralization of ions at metal surfaces has been a long-standing one. Since Shekhter proposed the mechanism in 1937,¹ many workers have developed theoretical models of increasing sophistication to calculate Auger transition rates and electron emission spectra. But still there is no theory yielding satisfactory agreement with experiment. The main difficulties that arise when solving the problem are (i) in the close interaction of an ion with a surface, strong electronic hybridization and many-body effects happen, which would require us to solve a many-body problem including the ion potential. (ii) Besides, accounting for a dynamical screened interaction² is not an easy task.

Most of the work already done assumes that electronic states of ion and metal are not modified with respect to the situation in which they do not interact, except for the image-shift of the atomic energy level. One evident reason for this approximation is related to the difficulty of solving the problem stated in (i). Another reason is that, at present, a first-principles calculation of the Auger transition rate would be too demanding if one allows the ion to break the translational invariance of the surface. Relaxing this approximation requires the use of constant^{3,4} or approximate^{5,6} matrix elements or models such as the local model.^{7,8} Moreover, several approximations for the screened interaction have been made: bare Coulomb potential (unscreened interaction),^{5,9} Yukawa potential,¹⁰⁻¹² or screened potential in the semiclassical infinite barrier model.^{7,13} Then a self-consistent treatment of the dynamically screened interaction is still lacking.

In this paper, we develop a theory for the Auger process that includes dynamical screening within the above mentioned approximation of unperturbed states. In or-

der to show the new physics that we are including, we calculate the Auger capture rate for a simple system representing He^+ on Al. The Al surface is described by a step potential barrier and, within this assumption, our calculation is self-consistent. *We explicitly show that surface plasmons are excited in this system and that this phenomenon causes a much slower decrease of the Auger rate with increasing distance between ion and surface than predicted by essentially nonscreened calculations.* Recently, surface and bulk plasmons have been experimentally detected in the electron emission spectra of noble gas ions interacting with free-electron-like metal surfaces.¹⁴

The formula for the transition rate of an Auger process is going to be derived in first-order perturbation theory (atomic units $e = \hbar = m = 1$ will be used). Here we only work out the case in which the ion velocity is much smaller than the Fermi velocity of the metal electrons (that is $v_{\text{ion}} \approx 0$), but the theory can be easily generalized to the case of arbitrary velocity parallel to the surface. The derivation follows along the lines outlined in Refs. 15 and 16, for the bulk case.

The starting point is Fermi's golden rule

$$\frac{1}{\tau} = 2\pi \sum_{i,f} |\langle f|V|i\rangle|^2 \delta(E_f - E_i). \quad (1)$$

Due to the difficulties stated above, we will consider metallic and atomic states separately. For an Auger capture process we write for the initial state $|i\rangle$ and the final state $|f\rangle$

$$\begin{aligned} |i\rangle &= |0\rangle \otimes |\mathbf{k}_{or}\rangle \\ |f\rangle &= |n\rangle \otimes |a\rangle. \end{aligned} \quad (2)$$

In this equation $|0\rangle$ and $|n\rangle$ are the ground and an excited state of the many-body electron gas with energies E_0 and E_n , respectively; $|a\rangle$ is the final state of one electron in the atomic ion core with energy E_a ; and $|\mathbf{k}_{or}\rangle$ is a one-electron state representing the initial state of the electron that neutralizes the ion core. Since $|\mathbf{k}_{or}\rangle$ and $|a\rangle$ should be solutions of the same Hamiltonian, we take for $|\mathbf{k}_{or}\rangle$ a one-electron metallic state, $|\mathbf{k}\rangle$, orthogonalized to $|a\rangle$,^{9,15,16}

$$|\mathbf{k}_{or}\rangle = |\mathbf{k}\rangle - \langle a|\mathbf{k}\rangle|a\rangle. \quad (3)$$

The interaction Hamiltonian for the Auger transition is

$$V = \int d\mathbf{r}_1 \int d\mathbf{r}_2 \frac{\delta n(\mathbf{r}_1)\rho(\mathbf{r}_2)}{|\mathbf{r}_1 - \mathbf{r}_2|}, \quad (4)$$

where $\delta n(\mathbf{r}_1)$ is the density operator of the electron gas and $\rho(\mathbf{r}_2)$ is the density operator of the ion.

It is convenient to Fourier transform in the coordinates \mathbf{x} parallel to the surface as

$$\delta n(\mathbf{q}, z) = \int d\mathbf{x} \delta n(\mathbf{x}, z) e^{-i\mathbf{q}\cdot\mathbf{x}}. \quad (5)$$

Then, upon Fourier transforming the Coulomb potential, the matrix elements can be written as

$$\langle f|V|i\rangle = \int \frac{d\mathbf{q}}{(2\pi)^2} \int dz_1 \langle n|\delta n(\mathbf{q}, z_1)|0\rangle \Phi(\mathbf{k}; \mathbf{q}, z_1), \quad (6)$$

where we have defined

$$\Phi(\mathbf{k}; \mathbf{q}, z_1) = \frac{2\pi}{q} \langle a|e^{i\mathbf{q}\cdot\mathbf{x}_2} e^{-q|z_1 - z_2|} |\mathbf{k}_{or}\rangle. \quad (7)$$

Now, by substituting Eq. (6) into Eq. (1) and making use of the standard expression relating the imaginary part of the susceptibility $\chi(\omega, q; z, z')$ of the interacting electron gas to the density operators $\delta n(\mathbf{q}, z)$ and $\delta n(\mathbf{q}, z')$, the final expression for the Auger capture rate is obtained as

$$\begin{aligned} \frac{1}{\tau} = & 2 \sum_{\mathbf{k}(kf)} \int_0^\infty d\omega \int \frac{d\mathbf{q}}{(2\pi)^2} \int dz \int dz' \\ & \times [-\text{Im}\chi(\omega, q; z, z')] \\ & \times \Phi(\mathbf{k}; \mathbf{q}, z) \Phi^*(\mathbf{k}; \mathbf{q}, z') \delta(\omega + E_a - E_k). \end{aligned} \quad (8)$$

In Eq. (8), kf is the Fermi wave vector. The above derivation takes into account dynamical screening effects at the surface of the metal via the screened susceptibility χ . In the self-consistent field theory, the susceptibility for interacting electrons $\chi(\omega, q; z, z')$ is related to the susceptibility for noninteracting electrons $\chi_0(\omega, q; z, z')$ via the integral equation

$$\begin{aligned} \chi(\omega, q; z, z') = & \chi_0(\omega, q; z, z') + \frac{2\pi}{q} \int dz_1 \\ & \times \int dz_2 \chi_0(\omega, q; z, z_1) e^{-q|z_1 - z_2|} \\ & \times \chi(\omega, q; z_2, z'), \end{aligned} \quad (9)$$

and χ_0 is obtained from the one-electron wave functions and energies of the surface potential. Then, having specified the model for the surface potential, Eqs. (9), (3), and (7) provide a consistent framework for calculating the Auger rate of Eq. (8).

In order to gain insight into Eq. (8), it is convenient to work out the long distance limit of this formula. Let the metal occupy the half space $z < 0$. The ion is at a position z_0 outside the metal. We first notice that the susceptibility $\chi(\omega, q; z, z')$ goes very quickly to zero

when either z or z' is positive and greater than a typical length of the order of the inverse Fermi wave vector. On the other hand, the potential $\Phi(\mathbf{k}; \mathbf{q}, z)$ of Eq. (7) is the \mathbf{q} component of the Coulomb potential produced by the charge density $\rho_{\mathbf{k}}(\mathbf{r}) = \psi_a(\mathbf{r})\psi_{\mathbf{k}_{or}}(\mathbf{r})$. This charge distribution is localized near the ion and has zero total charge. Therefore, when the distance z_0 is such as $z \ll z_0$, $\Phi(\mathbf{k}; \mathbf{q}, z)$ approaches the dipole potential of $\rho_{\mathbf{k}}(\mathbf{r})$. Then in this limit, Eq. (8) reads

$$\begin{aligned} \frac{1}{\tau} = & 2 \sum_{\mathbf{k}(kf)} [\frac{1}{2}\vec{\mu}_{\parallel}(\mathbf{k})^2 + \mu_z(\mathbf{k})^2] \\ & \times \int_0^\infty dq q^2 e^{-2qz_0} \text{Im}g(q, \omega_k), \end{aligned} \quad (10)$$

where $\omega_k = E_k - E_a$ and $\vec{\mu}(\mathbf{k})$ is the dipole moment of $\rho_{\mathbf{k}}(\mathbf{r})$. The surface response function $g(q, \omega)$ (Ref. 17) represents the amplitude of the induced potential produced by a unit amplitude external potential. It has poles at the frequencies of the normal modes of the electron gas. Therefore $\text{Im}g(q, \omega)$ shows a peak at the frequency of a surface plasmon $\omega = \omega_{sp}(q)$. This structure is going to change the behavior of the Auger rate. The same effect was predicted in Ref. 18 for the deexcitation of multiply charged ions in front of metal surfaces.

Using the Lang-Kohn potential, Liebsch¹⁹ and Eguiluz²⁰ calculated χ for some values of ω and q . However in the problem of Auger neutralization, we need χ for all values of ω and q appearing in Eq. (8) and thus the computation of the rate is very time consuming. In order to show the importance of dynamical screening in the Auger process, we choose a simple model system simulating a low velocity He^+ ion interacting with an Al surface. Al is modeled by a jellium of $r_s = 2$ a.u. with a step potential barrier. The barrier height (Fermi energy plus work function) is 0.605 a.u. and the step barrier is 0.22 a.u. outside the jellium edge. The solution of the integral equation (9) is obtained by discretizing z and z' on a grid of points: Then we solved the resulting matrix equation by pivoting. This procedure gives converged results if q is not too small and ω is below the plasma frequency ω_p . It should be noticed that very small values of q contribute little to the q integral in Eq. (8) if the distance z_0 is not too large. For $\omega > \omega_p$, one has to allow for plasmons propagating strongly into the bulk and therefore special methods for solving Eq. (9) are required.²¹ We will avoid this problem of excitation of bulk plasmons by choosing for E_a a value such as the maximum value of the energy transfer, $E_f - E_a$, in Eq. (8) is ω_p . Then we raised the atomic energy level of He^+ by 4 eV, while keeping the atomic wave function for a 1s electron in the He atom. We think that our model ion is not far away from a real He^+ since an upward shift of 2 eV is found experimentally,²² for this ion, at the most probable distance of neutralization.

In order to discuss the results for the Auger transition rate it is convenient to write Eq. (8) as

$$\frac{1}{\tau} = \int_{\omega_{\min}}^{\omega_{\max}} d\omega \int_0^\infty dq \gamma_A(\omega, q), \quad (11)$$

with $\omega_{\min} = 0.25 \omega_p$ and $\omega_{\max} = \omega_p$ in our case. We will also refer to the function

$$\gamma_A(\omega) = \int_0^\infty dq \gamma_A(\omega, q). \quad (12)$$

In the following the distance z_0 , the ion location, is measured with respect to the step barrier. In Fig. 1, we show $\gamma_A(\omega, q)$, for $\omega = 0.78\omega_p$ and for two distances between ion and surface. In Fig. 1(a), $z_0 = 4$ a.u. and we notice the strong peak associated to the excitation of a surface plasmon with this energy and momentum $q \approx 0.2kf$. This peak gives almost the full contribution to the rate. Of course, it will be absent in calculations that do not screen the interaction dynamically. In Fig. 1(b), $z_0 = -1$ a.u. At this distance the surface plasmon is still excited together with a continuum of electron-hole pairs extending to high q . We find a similar behavior of $\gamma_A(\omega, q)$ for all frequencies above the frequency $\omega_{sp} = \omega_p/\sqrt{2}$.

The fact that the excitation of surface plasmons gives the main contribution to the Auger rate when the ion is outside the surface is more clearly seen when plotting the

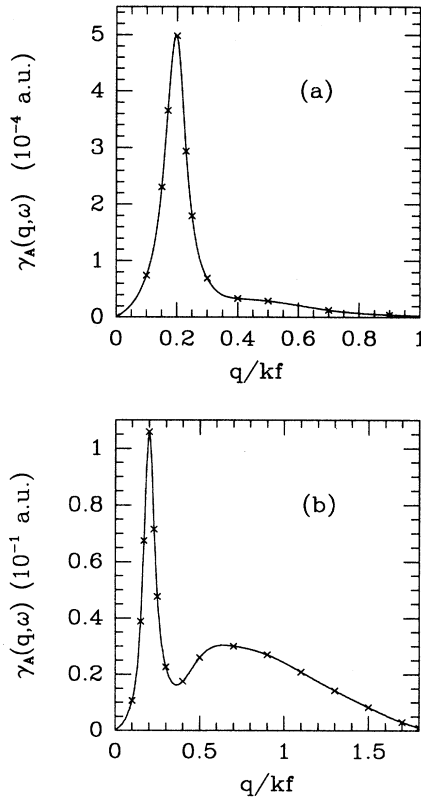


FIG. 1. The Auger rate vs parallel momentum transfer, for fixed value of the energy transfer $\omega = 0.78\omega_p$, for (a) $z_0 = 4$ a.u. and (b) $z_0 = -1$ a.u. Crosses are the calculated points and the solid line is the interpolation function used for the integration in q . The strong peak at $q \approx 0.2kf$ is the surface plasmon and it gives the main contribution to the rate in (a). In (b), the surface plasmon is still excited but the excitation of electron-hole pairs of higher momenta gives also an important contribution.

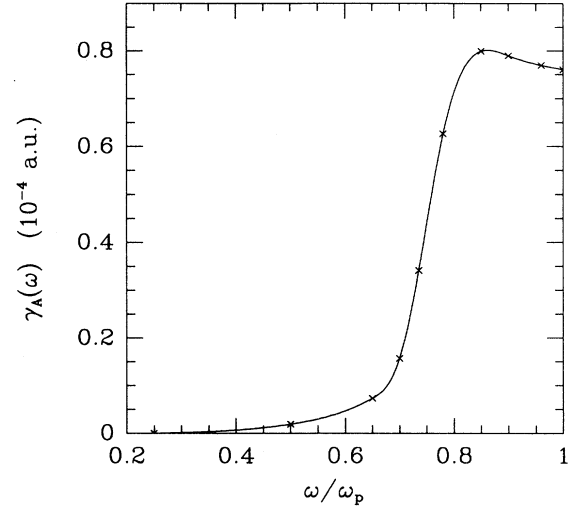


FIG. 2. The Auger rate as a function of the energy transfer for $z_0 = 4$ a.u. Crosses are the calculated points and the solid line is the interpolation function used for the integration in ω . The rapid increase of the rate above $\omega \approx 0.7\omega_p$ is due to the excitation of surface plasmons. The total rate is practically given by frequencies above ω_{sp} .

rate $\gamma_A(\omega)$ as a function of the energy transfer ω . This is done in Fig. 2 for $z_0 = 4$ a.u. It is remarkable the very rapid increase of γ_A after the frequency ω_{sp} is reached. Actually, the total Auger rate $1/\tau$ is given by the energies above ω_{sp} in the range of distances $z_0 \geq 3$ a.u. For smaller distances, we find that the relative contributions to the total rate of frequencies smaller and greater than ω_{sp} is not so striking, as it should, since we are entering the bulk.

Finally, we show in Fig. 3 the total Auger rate $1/\tau$ as

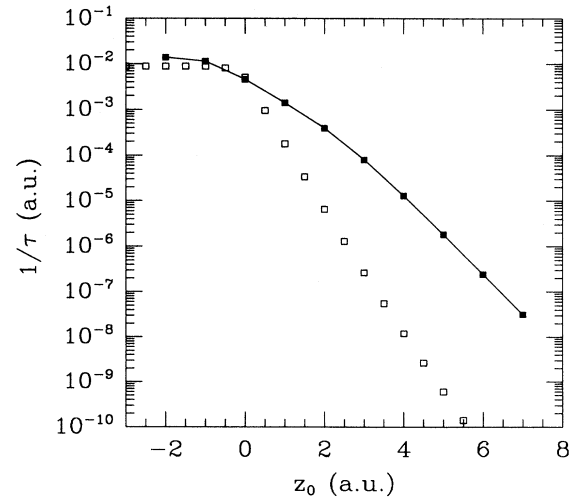


FIG. 3. The Auger rate as a function of distance. Open squares are the results of the local model of Ref. 7, which nearly reproduces the trend of an unscreened calculation. Full squares are the results of the screened calculation. The continuous line is a guide to the eye. Screening effects cause a much slower decrease of the rate.

a function of distance, compared with the results of the local model of Ref. 7 when, in this model, the density is calculated from the wave functions of the step potential barrier model. The local model predicts that the Auger rate decays as $n^2(z_0)$ [$n(z_0)$ is the electronic density evaluated at the ion position], while the calculations of Ref. 9 give a decay as $n^{1.8}(z_0)$ for $r_s = 2.07$ a.u. Thus, the comparison between both curves of Fig. 3 is intended to show how dynamical screening effects modify the behavior of the rate as a function of distance when surface plasmons are excited. We notice that to include screening amounts to a decrease in the exponent of the rate by roughly a factor of 2; that is, the Auger rate scales rather with the electronic density. This change will affect drastically the theoretical prediction for the distances where ions are most probably neutralized. Let us comment that all the existing calculations of the Auger rate for He^+ on Al, in the approximation of unperturbed atomic and metallic states, give a too rapid exponential decrease as compared with experimental estimates.

In summary, we present, to our knowledge, the first calculation of the Auger transition rate of a slow ion near a metal surface that includes dynamical screening effects in a self-consistent way. We think that to take into account these effects puts theory in a better agreement with experiment. Other processes entering in the problem of the Auger neutralization and not considered in this work are the shift in energy of the electronic levels of the ion and the lowering of the barrier felt by a metal electron as a consequence of the ion potential. With respect to the last process, it was shown in Ref. 7 that its effect on the Auger transition rate is also to decrease the exponent of the rate. Then, further theoretical effort is still necessary in order to produce a realistic description of the Auger capture process.

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