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Multielectron neutralization channels in ion-surface scattering

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The neutralization of an ion impinging on a metal surface via capture in a low-lying level is studied. A self-consistent local density approximation calculation of the capture rate in the ground state of helium in front of an aluminum surface is reported. This calculation allows us to study the different multielectron channels involved. Using this knowledge about the possible neutralization channels, different systems are analyzed. This leads to a revision of the neutralization probabilities of ions in front of metal surfaces.

The study of ion-surface collision reveals the structure of both projectile and target. The information that can be obtained during the interaction has been long sought for the analysis of surfaces.[1] The collision determines the final charge of the different ionic species, the amount of electron emission, and the sputtered particles from the solid.[2–4] Thus, the many existing experimental techniques yield structural information on ion and solid, together with information on the complicated dynamical aspects of the collision. But, the interest of ion-surface collisions transcends the frame of surface and atomic physics. The different ionic species available nowadays[3] have led to the study of hollow atom collisions with surfaces. Hollow atoms imply an energetic inverted population that can be used for laser emission, for directing impurities onto a surface with a potential for high information storage, and for controlling macromolecule desorption from surfaces. Yet, few first-principles calculations exist.

The metal surface brings about many difficulties in any computation. Most of the existing models simply assume that a surface is an infinite reservoir of electrons, which at best are modeled via one-electron Schrödinger equations. Then, the many-body aspects of the problem are usually shunned. The usage of parameters fitted from experiments or from atomic physics is a common practice that reveals the difficulty of surface many-body calculations.

Among the neutralization channels existing in ion-surface collisions, only one is currently well described. This is the resonance neutralization channel.[5] A high-lying level of the ion at conduction-band energies is neutralized by one metal electron. Thus, a one-electron description is reliable because the metal relaxation effects are small. However, the rest of the existing channels involve several electrons. These are what have been termed *multielectron neutralization channels*. Low-lying levels will not be resonantly neutralized, since there are no single electron transfers that can preserve the energy of the system. One of the available neutralization channels in this case is the Auger neutralization.[1] As is described in Ref. 1, an electron from the metal surface makes the transition to a low-lying level of the incident ion, and the potential energy of the transition is transferred to a second electron within the metal, which is ejected. But there are other multielectron channels that, even though assumed to be important,[6] have not been properly taken into account,[7] as is the case of electron capture plus some surface collective excitation. The way of treating these multielectron channels is easily pictured: an electron is captured by the ion and the energy released in the process is absorbed by some surface excitation. So in this zero-order picture, we only have to weigh the one-electron transition term by the surface structure factor.[8] The complexity in the calculation of these multielectron channels is given by the difficulty of the evaluation of the surface structure factor.

In this paper, we present the general formalism for treating multielectron neutralization of ions in front of a metal surface. We will apply this formalism to He^+ scattered off a jellium surface of electron density given by $r_s=2.00a_0$. To our knowledge, this is the first self-consistent local density approximation (LDA) calculation of its kind. In this system the excitation of surface plasmons is an open channel for the ion neutralization, as will be shown. As the ion-surface system changes, new channels open and close. For example, the H^+-aluminum system does not include collective oscillation channels,[7] but we will show that the electron-hole channels change when the electron-electron interaction in the metal is kept, leading to a big discrepancy with common unscreened treatments. Other systems, such as those with hollow atoms, may capture electrons directly from the surface in deep core holes, with such a high energy transfer that unscreened calculations remain realistic.

The model presented here is the generalization of the theory of core-hole neutralization in bulk of Refs. 9,10 to the surface system. Due to the presence of the surface, the explicit dependence in the coordinate perpendicular to the surface, z, is maintained, while the translational invariance along the surface allows us to perform a two-dimensional Fourier transform. That is to say, the electron-electron interaction in atomic units ($\hbar=m=e=1$) is written as

$$\frac{1}{|\mathbf{r}-\mathbf{r}'|}=\int\frac{d^2q_\parallel}{(2\pi)^2}\frac{2\pi}{q_\parallel}e^{-q_\parallel|z-z'|}e^{i\mathbf{q}_\parallel\cdot(\mathbf{r}_\parallel-\mathbf{r}'_\parallel)}.$$

And the surface structure factor, proportional to the imaginary part of the surface dielectric susceptibility, $\mathrm{Im}\chi(q_\parallel,\omega,z,z')$, is coupled to the one-electron matrix element giving the electron capture:

$$\frac{2\pi}{q_\parallel}\langle s|e^{-q_\parallel|z-z'|}e^{i\mathbf{q}_\parallel\cdot\mathbf{r}_\parallel}|\mathbf{k}\rangle,$$

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where $|s\rangle$ is the core-hole state, and $|\mathbf{k}\rangle$ is a one-electron metal state, orthogonalized to the core state.[9,10] Then the neutralization rate of Refs. 9,10 becomes

$$\frac{1}{\tau}=2\sum_{\mathbf{k}}\int_0^\infty d\omega\int d^2q_\parallel\int_{-\infty}^{\infty}dz'\int_{-\infty}^{\infty}dz''\frac{1}{q_\parallel^2}\times[-\mathrm{Im}\chi(q_\parallel,\omega,z',z'')]\langle s|e^{-q_\parallel|z-z'|}e^{i\mathbf{q}_\parallel\cdot\mathbf{r}_\parallel}|\mathbf{k}\rangle\times\langle\mathbf{k}|e^{-q_\parallel|z-z''|}e^{-i\mathbf{q}_\parallel\cdot\mathbf{r}_\parallel}|s\rangle\,\delta(\omega-(E_k-E_s)),\qquad(1)$$

where the one-electron energies of the metal and the core electrons are E_k and E_s, respectively. The energy transferred in the process is ω, as written in the energy conservation δ. Here we are disregarding velocity effects, which is a good approximation as long as the ion speed is much smaller than the electron Fermi velocity. This is the case of He^+ at 1 keV.

Equation (1) includes all possible multielectron final channels. This can be traced back to the origin of the surface susceptibility, since it appears as the sum of the charge fluctuations over all possible excited states of the metal. The appearance of fluctuation operators instead of the full density operators comes from removing the elastic channel, $\omega=0$, so that we do not include one-electron transitions and concentrate on multielectron channels.

The difficulty of Eq. (1) is the computation of $\chi(q_\parallel,\omega,z,z')$ for as many values as required to perform the multidimensional integrations. The theory in which the susceptibility is formally defined for jellium surfaces is the time-dependent density functional theory (TDDFT).[11] In the case of a surface, the TDDFT susceptibility is defined as

$$\chi(q_\parallel,\omega,z,z')=\chi_0(q_\parallel,\omega,z,z')+\int_{-\infty}^{\infty}\int_{-\infty}^{\infty}dz_1dz_2\times\chi_0(q_\parallel,\omega,z,z_1)R(q_\parallel,\omega,z_1,z_2)\times\chi(q_\parallel,\omega,z_2,z'),\qquad(2)$$

where χ_0 is the susceptibility of noninteracting particles, which is calculated for the considered jellium surface. And, the effective interaction is the corresponding Fourier transforms of

$$R(\mathbf{r}_1,\mathbf{r}_2,t_1,t_2)=\frac{\delta(t_1-t_2)}{|\mathbf{r}_1-\mathbf{r}_2|}+\left.\frac{\delta v_{\mathrm{xc}}[\rho](\mathbf{r}_1,t_1)}{\delta\rho(\mathbf{r}_2,t_2)}\right|_{\rho_0},$$

where ρ_0 is the ground-state electron density of the metal, $v_{\mathrm{xc}}[\rho]$ is the exchange and correlation functional of the Kohn and Sham time-dependent formalism.[11] As in density functional theory, the approximations are introduced in the exchange and correlation functional. We are going to use the LDA Lang and Kohn surface, so that we are consistently using the local exchange and correlation potential. We are going to introduce the already standard LDA approximation for the susceptibility, disregarding the time dependence in the effective interaction.[11–15]

This procedure has the appealing feature of self-consistency. Self-consistency is important in order to conserve the surface response sum rules.[14] Calculations in electron energy loss[15] and photoemission[16] have yielded excellent agreement with experiment. Hence we expect that the locality and time independence of the exchange and correlation potential are minor problems in the theory. In addition to this, the large amount of existing literature provides a good starting basis for the complicated numerical calculations.[15]

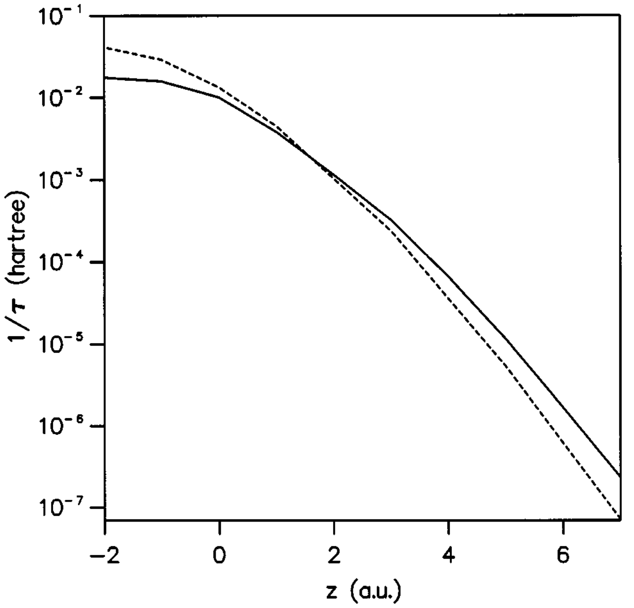

FIG. 1. Neutralization rates of He^+ in front of an LDA $r_s=2.0a_0$ surface. The full line corresponds to the multielectron neutralization rate, calculated in LDA. The dashed line is the rate of the Auger channel of noninteracting electrons. This unscreened calculation overestimates the Auger neutralization channel, and thus the long-range effect of the plasmon channels in the multielectron calculation leads to an increase of the neutralization rate only a factor 3 bigger at 5 a.u. from the jellium edge. At the jellium edge, the Auger channel dominates, therefore the unscreened calculation is bigger.

In Fig. 1 we find the results for the neutralization of He^+ on a jellium surface of $r_s=2.00a_0$. The full line is the multielectron neutralization rate. The dashed line is a plot of the Auger neutralization of noninteracting electrons.[17] We performed the calculation depicted by the dashed line by replacing the interacting susceptibility χ by the noninteracting χ_0 in Eq. (1).

The discrepancies in the two calculations shown are due to conceptual differences. In the dashed line, the Coulomb interaction among the metal electrons is neglected, while it is treated within the self-consistent field approximation[14] in the plotted full line. Thus this last calculation includes all possible surface excitation channels: single-particle and collective excitations.

Although we find that the calculated rates do not differ very much, we emphasize that the physical picture is qualitatively different. The apparent agreement (only a factor 3 bigger at 5 a.u. from the jellium edge) is due to the overestimation of the Auger channel by the noninteracting electrons. This can be seen in Fig. 2. We have represented here the ω dependence of the neutralization rate, $1/\tau(\omega)$, which is the probability per unit energy of exciting the metal when one particle is captured by the ion. The area under the plotted line is the neutralization rate at $z=5$ a.u. from the jellium edge. The smooth curve (squares) is the noninteracting-electron calculation. It is the probability per unit energy of

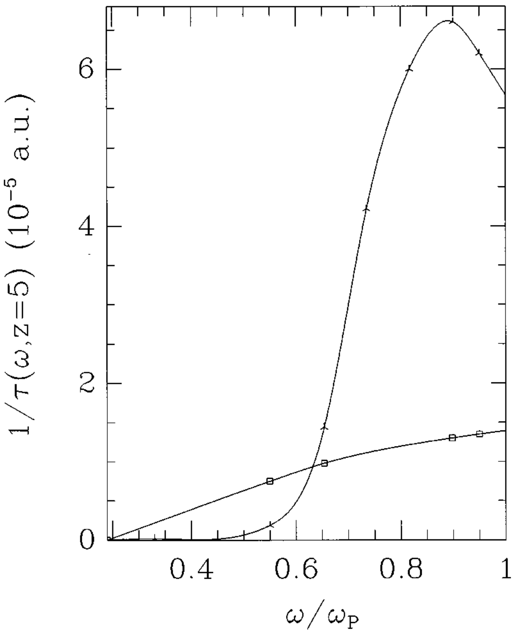

FIG. 2. Neutralization rate per unit of transferred energy at 5 a.u. from the jellium edge. The smooth, almost constant curve is the unscreened Auger calculation (squares). The sharp rising curve at $0.65\omega_P$ (crosses), where ω_P is the plasma frequency, is the multielectron channel calculation. Clearly, the overestimation of the Auger channel by the noninteracting calculation reduces the numerical differences in the total rates, despite the fact that both calculations are qualitatively very different. However, in systems where the multielectron channels are not available, that is, for energy transfers much smaller than the metal plasma frequency, the Auger channel rates calculated with noninteracting approaches will be overestimated (like the case of H^+ neutralized on aluminum). In systems where the transfer energy region corresponds to the surface plasmon region (such as Ar^+ scattered off magnesium) the unscreened (noninteracting) calculation underestimates the neutralization rate, while at big energy transfers the noninteracting calculation approaches the many-body calculation (such as in highly charged ion-surface scattering).

exciting an electron over the Fermi energy, when one particle is captured by the ion. The curve strongly rising at 0.65 ω_P, where ω_P is the plasma frequency, is the interacting-electron calculation (crosses). Here we see that in the region where only interacting electron-hole pairs can be excited (below $0.7\omega_P$) the neutralization is small; it can be up to one order of magnitude smaller than the noninteracting calculation. When the surface plasmon channel opens, the calculation with interacting electrons is a factor 4 bigger than the noninteracting calculation.

Two things become clear. First, despite the fact that our calculation includes all possible neutralization channels, *the determining neutralization channel at distances greater than 3 a.u. from the surface is the monopole surface plasmon channel.*[15] Second, as we approach the bulk, electron-hole pairs become increasingly important. The overestimation of the single particle-hole channel (Auger neutralization) by a noninteracting type of calculation leads us to find a higher neutralization probability in bulk than in the multielectron calculation.

The experimental data of Ref. 18 show a slope in the neutralization rate that has not been explained by the existing calculations.[17,19] Our theory shows a clear increase in the slope due to the long range of the plasmon channels, improving the agreement with experiment. The exponential fit to the experimental data gives a distance of decay of 1.3 a.u. for the experiment,[18] while our results give a decay of 0.92 a.u. (full line, Fig. 1) in the region between the jellium edge and 3 a.u. This decay is 0.75 a.u. in the same region for the unscreened results (dashed line). The differences between theory and experiment may be overcome by the proper inclusion of the ion potential in the one-electron Hamiltonian of the collision states.[19] In this paper we focus on many-body aspects of the electron capture by an ion at a metal surface. In Ref. 19 it was shown that the effect of the ion potential on the one-electron Hamiltonian of the collision states tends to improve the agreement with experimental estimations. However, a proper calculation of this effect still has to be performed.

Extrapolating the above discussion to other systems, we can conclude that a noninteracting calculation for Auger neutralization of protons on aluminum will overestimate the neutralization rate by about one order of magnitude in the region near the suface. This is due to the energy range of this neutralization process, which is under $0.57\omega_P$ in Fig. 2. There are systems in which the energy range will fall in the surface plasmon frequency region. This is the case of Ar^+ scattered off magnesium, in which the energy range spans the interval going from $0.46\omega_P$ to $1.1\omega_P$. In this case we expect the interacting calculation to give a factor of 5 or bigger in the noninteracting calculation at 5 a.u. from the jellium edge.

On the other hand, high-energy transfers ($\omega \gg \omega_P$) will leave the collective mode channels closed, and the dominant Auger channel can be perfectly calculated with free particles. For hollow ions aproaching a metal surface, the Auger channel can be well described in this way.

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