Van der Waals contribution to the inelastic atom-surface scattering

M. Machado¹ and D. Sánchez-Portal²

¹ Departamento de Física de Materiales, Facultad de Química, UPV-EHU
Apdo. 1072, 20080 Donostia, Spain

² Centro Mixto CSIC-UPV-EHU and Donostia International Physics Center (DIPC)
Paseo Manuel de Lardizabal, 4, 20018 Donostia, Spain

Abstract

A calculation of the inelastic scattering rate of Xe atoms on Cu(111) is presented. We focus in the regimes of low and intermediate velocities, where the energy loss is mainly associated to the excitation electron-hole pairs in the substrate. We consider trajectories parallel to the surface and restrict ourselves to the Van der Waals contribution. The decay rate is calculated within a self-energy formulation. The effect of the response function of the substrate is studied by comparing the results obtained with two different approaches: the Specular Reflection Model and the Random Phase Approximation. In the latter, the surface is described by a finite slab and the wave functions are obtained from a one-dimensional model potential that describes the main features of the surface electronic structure while correctly retains the image-like asymptotic behaviour. We have also studied the influence of the surface state on the calculation, finding that it represents around 50% of the total probability of electron-hole pairs excitation.

¹ Electronic address: wabmagam@sc.ehu.es; Fax: +34-943015600
An incident particle scattering with a solid metal surface losses energy mainly through two channels: excitation of phonons and electronic excitations (electron-hole pairs, plasmons, etc). At low energies, creation of phonons and electron-hole pairs becomes the main available channel. Understanding the different mechanisms for energy loss is a difficult task that has attracted both experimental and theoretical work. In an early experiment, Amirav and Cardillo [1] reported a method for measuring directly the electron-hole (e-h) pair excitation in the scattering of Xe atoms on a semiconducting surface. More recently, it has been possible to measure the e-h pairs created by adsorption of hydrogen and deuterium [2–4] on transition metal surfaces.

In the theoretical side, e-h pair creation probabilities due to moving atoms have been calculated with the use of several models. The most simple calculations were carried out within the Specular Reflection Model (SRM) [3], in which the surface potential is replaced by an infinite barrier [6]. This implies that the electronic density vanishes at the surface, so the surface polarizability is not well described and energy losses are underestimated. More realistic calculations were performed by using the jellium model [7–11] but surface states, which represent an important channel of electron-hole pair creation, are not included in this description. Very few calculations of the energy loss to date incorporate most of the complexity of the surface. One example, however, is the very recent ab initio calculation of the e-h pair creation by hydrogen scattering on Cu(111) performed by Trail et al. [12]. There is also a large amount of theoretical calculations of energy loss of charged particles, ranging from very simplified models for the response function [14–18] to more accurate self-consistent jellium calculations [19,20].

In this paper, we calculate the contribution of the long-range van der Waals term to the probability of excitation of e-h pairs by an incident atom interacting with a metal surface. This problem was also studied by Annett and Echenique [21], in an attempt to explain the experimental results of Amirav and Cardillo. They used a self-energy formalism, with the response function described within the SRM, and obtained a probability four orders of magnitude less than the experimental one. Several reasons might explain this large difference. On the one hand, the use of the simple SRM model for the response function. On the other hand, several other contributions to the scattering process were not taken into account, like those related to the atom-surface overlap (shorter-range effects), interaction between the static dipole generated in the atom by the surface proximity and the substrate, and non-adiabatic effects. We also focus on the van der Waals term, leaving the exploration of the other terms to a future publication, and try to study the influence of the model used for the response function, the semiclassical SRM or the more realistic Random Phase Approximation (RPA). RPA provides a more correct description of the electron density at the surface region and permits to investigate the importance of the surface state band in the electron-hole pair excitation.

Unless otherwise is stated, atomic units are used throughout, i.e., \( m = e^2 = \hbar = 1 \).

We consider neutral atoms moving parallel to a metal surface with a constant, non-relativistic velocity \( v \), at a distance \( z_0 \) from the substrate, which occupies the \( z < 0 \) half-space. We will start from the Born-Oppenheimer wave function for the atom, \( |\alpha> = \phi_\alpha(R)\psi_\alpha(r_1, r_2, ..., R) \), where the \( r_i \) are the electronic coordinates and \( R \) the nuclear ones. Ground state wave functions of the solid will be denoted by \( |\beta> \), and \( |\beta'> \) will be the excited states. Neglecting coupling between the atom and the substrate, the many-body
wave function of the system can be written as the product of the respective wave functions of the atom and the solid.

The contribution to the energy loss due to the long-range van der Waals coupling between the surface and the atom can be obtained by defining a self-energy, whose real part represents the van der Waals energy, and its imaginary part is related with the inelastic scattering rate, \( \Gamma \), so that \( \Gamma = -2Im(\Sigma) \). The transition rate of the incident atom by excitation of electrons from the Fermi sea to unoccupied levels can be calculated by introducing the Coulomb operator, \( \hat{V} \), as the coupling between atom and substrate in Fermi’s golden rule. Therefore, the self-energy will be given by:

\[
\Sigma_{\alpha\beta} = -\sum_{\alpha',\beta'} \frac{|\langle \alpha' \beta' | \hat{V} | \alpha \beta \rangle|^2}{\epsilon_{\alpha'} + \epsilon_{\beta'} - \epsilon_\alpha - \epsilon_\beta - i\delta}
\]  

(1)

Where the \( \epsilon \) are the corresponding energies of the states of the incoming atoms and the substrate. We can simplify eq. (1) by introducing the response function of the metal and the two-dimensional Fourier transform of the Coulomb potential, obtaining:

\[
\Sigma_\alpha = -\sum_\omega \int_0^\infty \frac{d\omega}{\pi} \frac{1}{\omega + \epsilon_\alpha - \epsilon_\beta - i\delta} \int d\mathbf{r}_\parallel d\mathbf{r}_\parallel' dz d\bar{z} d\bar{z}' d\bar{z}'' Im[\chi(q_\parallel; \omega; \bar{z}', \bar{z}'')|e^{i\mathbf{q}_\parallel (\mathbf{r}_\parallel - \mathbf{r}_\parallel')} e^{-q_\parallel |z-z'|} e^{-q_\parallel |z''-z'''|}] < \alpha |\hat{\rho}_\alpha(\mathbf{r})|\alpha' > < \alpha' |\hat{\rho}_\alpha(\mathbf{r}'')|\alpha >
\]

(2)

Where \( \omega \) is the transferred energy, and \( \hat{\rho}_\alpha(\mathbf{r}) \) is the charge-density operator for the atom. Eq. (2) is valid for arbitrary trajectories. Now we focus on trajectories parallel to the surface, replace the density operator by \( \hat{\rho}_\alpha(\mathbf{r}) = Z\delta(\mathbf{r} - \mathbf{R}) - \sum_i \delta(\mathbf{r} - \mathbf{r}_i) \), where \( Z \) is the nuclear charge, and take nuclear wavefunctions as,

\[
\phi_\alpha(\mathbf{R}) = \frac{1}{(2\pi)^2} e^{i(Mv_\parallel |\mathbf{r}|)} \delta(z - z_0)
\]

(3)

Assuming the atom is far from the surface, we can make a multipole expansion in which we take the dipole term as the leading contribution, because for neutral atoms there is no monopole contribution. This term introduces the dipole oscillator strengths, corresponding to transitions from electronic state 0 to \( n \), \( f_{n0} = 2\omega_{n0} < n|\mathbf{r}|0 > |^2/3 \) where \( \omega_{n0} \) are the frequencies of the dipolar transitions. These transformations in eq. (2) lead to the following expression of the scattering rate:

\[
\Gamma = -\sum_n \frac{f_{n0}}{\omega_{n0}} \int_0^\infty d\omega \int d^2\mathbf{q}_\parallel \int dz' \int dz'' Im[\chi(q_\parallel; \omega; z', z'') e^{-q_\parallel |z_0 - z'|} e^{-q_\parallel |z_0 - z'''|} (1 + sig(z_0 - z') sig(z_0 - z'')) \delta(\omega + \omega_{n0} - \mathbf{q}_\parallel \cdot \mathbf{v}_\parallel + q^2/2M)]
\]

(4)

Where \( sig(z-z') \) stands for the sign function. Once the energy transfer is fixed by Dirac’s delta, maximum and minimum momentum transfers are given by \( q^\pm_\parallel = M(v cos \theta \pm \sqrt{v^2 cos^2 \theta - 2\omega_{n0}/M}) \). \( \theta \) is the angle between the parallel momentum and the initial velocity. \( M \) is the mass of the atom, which for Xe atoms is of the order of \( 10^4 \) a.u. Energies above the 9 eV threshold, corresponding to the first available dipole transition in the Xe atom, are needed so that e-h pair excitation is feasible. Therefore, it is the gap in the atomic
levels which determines the need of a minimum momentum transfer different from zero. \( q^+ \) corresponds to the transfer of the whole initial energy.

We have used two different models for the response function. In the SRM the surface potential is replaced by an infinite barrier and it is assumed that the electrons are specularly reflected at the surface, with no interference terms. Therefore, the surface response function is strictly zero beyond the jellium edge. In the more realistic RPA model \[23–25\], electrons respond as a non-interacting gas to the total potential, and the response function is obtained solving a self-consistent equation on the induced potential. We model the metal by a slab, such that one-particle wave functions in the directions parallel to the surface are plane waves, while in the perpendicular direction they are the solutions of a one-dimensional model potential \[26\]. This potential reproduces the width and position of the band gap, as well as the binding energies of the surface and image states. Close to the Fermi level, the resulting wave functions are comparable to those obtained with an ab initio calculation \[24\]. The potential has also been proved to accurately predict the broadening of surface and image states on metal surfaces \[27–30\].

For the RPA calculations we have used a supercell geometry where the Cu(111) surface is represented by a 30-layers slab, and the vacuum region is equivalent to 20 atomic layers. In the SRM model \[5\], the surface response is directly obtained from Mermin’s dielectric function \[22\]. We have used the values 2.67 and 0.013 a.u. for \( r_s \) and the damping parameter \( \gamma \) respectively. Our results exhibit only a slight dependence on \( \gamma \). This is a clear indication that, for the moderate projectile velocities considered here, the main contribution to the inelastic scattering rate \( \Gamma \) comes from the creation of e-h pairs. Therefore, from a practical point of view, it is justified to consider \( \Gamma \) as equivalent to the probability of e-h pair creation, and we will make no distinction in what follows. The energies and oscillator strengths of the electronic transition of the Xe atom were taken from Ref. \[13\].

Fig. 1 depicts \( \Gamma \) for trajectories parallel to the metal surface with different incident velocities as a function of the impact parameter \( z_0 \) (measured from the jellium edge) calculated using a) the SRM and, b) our model RPA surface response. The e-h pair creation probability obtained within the SRM approximation is roughly three times smaller, and decays much faster with \( z_0 \) than the one calculated using the RPA model response. These results indicate that the polarizability of the copper surface is seriously underestimated in the simplified SRM model due to the presence of a fictitious infinite barrier at the surface. In fact, the induced electronic charge becomes strictly zero beyond the jellium edge. This is in contrast with the model RPA response, which peaks at the surface and penetrates some atomic units into the vacuum (see Fig. 3), allowing for higher scattering rates for larger impact parameters. Our data also point out that, in order to obtain a reliable description of the inelastic scattering at low and intermediate velocities, it is necessary to explicitly include a relatively accurate description of the electronic structure in the vicinity of the Fermi level. This is specially true for the surface band, as will become clearer below.

In Fig. 2 we show the scattering rate for both SRM and RPA response functions as a function of the velocity of the incident atom, for two different impact parameters close to the surface. At very low \( v \), no creation processes are possible because the initial energy must at least equal the energy of the first allowed transition in the incoming atom (\( \sim 9 \) eV for Xe). When \( v \) increases, this threshold can be overcome, but there is a simultaneous requirement of small energy and relatively large momentum transfer to the target that severely reduces
the phase space of the allowed electronic excitations in the substrate. Increasing $v$ the e-h pair creation probability increases until it reaches a maximum for $v$ around 2 a.u.. The position of this maximum is only slightly dependent on the impact parameter. By further increasing $v$, $\Gamma$ starts to decrease since, as the energy transfer gets larger, the low $q_\parallel$ region available in phase space becomes smaller, and the surface response tends to decrease for large values of $q_\parallel$. Finally, in the limit of very high $v$ (not reached here) only the plasmon contribution becomes important.

The surface state in Cu(111) crosses the Fermi level, so it is a partially occupied band. This, in addition to the larger weight of this state in the surface region, makes reasonable the expectation that a large fraction of the electrons excited by incoming Xe atoms will be originated from inter and mainly intraband transitions in this band. We will study the effect of the surface band in the following. Fig.3 shows the imaginary part of the RPA response function for our slab model $\text{Im} \chi^{RPA}(q_\parallel, \omega; z, z' = z)$ for $q_\parallel=0.3$ a.u., $\omega=1$ eV, as a function of $z$ (coordinate normal to the surface), with and without the surface state contribution. The imaginary part of the RPA response function gives the number of available electronic transitions in the substrate. While the removal of the surface state does not affect the response in the bulk region, the number of excitations (e-h pairs in this energy range) generated at the surface decreases dramatically.

Fig.4 shows $\Gamma$ versus the impact parameter with and without the surface state, for an incident velocity of 2 a.u. Close to the surface, the result without the surface state is reduced to a 50% of what we get with all the states. This reduction, however, gets somewhat lower as the atom is farther away from the surface.

In summary, we have reported calculations of the inelastic scattering rate of neutral atoms with moderate velocities by metal surfaces. We have restricted here to the long-range van der Waals term. Results for other contributions to the total inelastic rate will be presented elsewhere. We have found that the introduction of a more realistic model of the surface, which explicitly includes the electronic structure of the surface near the Fermi energy and where the response function is calculated within RPA approximation, increases the scattering rate given by the semiclassical SRM model by approximately a factor of three. These differences are enhanced at low and intermediate velocities. By removing the contribution of the surface state in the calculation of the RPA response function, we have seen that this band is the main source electronic excitations in the surface region. we conclude then that surface bands have to be correctly described in order to achieve a complete description of surface-atom scattering events.

Acknowledgments

The authors gratefully acknowledge P.M. Echenique, J. García de Abajo and A. García-Lekue for useful discussions. This work has been partially funded by the University of the Basque Country under Grant UPV/EHU (9/UPV 00206.215-13639/2001) and Spanish MCyT under Grant (MAT2001-0946). D.S.P acknowledges support from Spanish CSIC and MCyT under the "Ramón y Cajal" programme.
REFERENCES

[1] A. Amirav, M. J. Cardillo, Phys. Rev. Lett. 57, (1986) 2299
[2] H. Nienhaus, H. S. Bergh, B. Gergen, A. Majumdar, W. H. Weinberg, E. W. McFarland, Phys. Rev. Lett. 82 (1999) 446
[3] B. Gergen, H. Nienhaus, W. H. Weinberg, E. W. McFarland, Science 294 (2001) 2521
[4] H. Nienhaus, Surf. Sci. Rep. 45 (2002) 1
[5] R. H. Ritchie, A. L. Marusak, Surf. Sci 4 (1966) 234
[6] B. N. J. Persson and M. Persson, Surf. Sci. 3 (1980) 609
[7] P. J. Feibelman, Phys. Rev. B 22 (1980) 3654; 12 (1975) 1319; 14 (1976) 762; 9 (1974) 5077
[8] B. N. J. Persson, N. D. Lang, Phys. Rev. B 26 (1982) 5409
[9] B. N. J. Persson, E. Zaremba, Phys. Rev. B 31 (1985) 1863
[10] A. G. Eguíluz, Phys. Rev. Lett. 51 (1983) 1907
[11] A. Liebsch, Phys. Rev. B 55 (1997) 13263
[12] J. R. Trail, M. C. Graham, D. M. Bird, M. Persson, S. Holloway, Phys. Rev. Lett. 88 (2002) 166802
[13] W. F. Chan, G. Cooper, X. Guo, C. E. Brion, Phys. Rev. A 46 (1992) 149
[14] P. M. Echenique, J. B. Pendry, J. Phys. C 8 (1975) 2936
[15] R. Nuñez, P. M. Echenique, R. H. Ritchie, J. Phys. C 13 (1980) 4229
[16] N. Zabala, P. M. Echenique, Ultramicroscopy 32 (1990) 327
[17] J. I. Juaristi, F. J. García de Abajo, P. M. Echenique, Phys. Rev. B 53 (1996) 4980
[18] T. Nagatomi, R. Shimizu, R. H. Ritchie, Surf. Sci. 419 (1999) 158
[19] M. A. Cazalilla, F. J. García de Abajo, Nucl. Instrum. Methods Phys. Res. B 125 (1997) 106
[20] A. García-Lekue, J. M. Pitarke, Phys. Rev. B 64 (2001) 035423
[21] J. F. Annett, P. M. Echenique, Phys. Rev. B 36 (1987) 8986
[22] N. D. Mermin, Phys. Rev. B 1 (1970) 2362
[23] J. Lindhard, K. Dan. Vidensk. Selsk. Mat.-Fys. Medd 28, No. 8 (1954)
[24] P. M. Echenique, J. M. Pitarke, E. V. Chulkov, A. Rubio, Chem. Phys. 251 (2000) 1
[25] A. Eguíluz, Phys. Rev. B 31 (1985) 3303
[26] E.V. Chulkov, V. M. Silkin, P. M. Echenique, Surf. Sci. 437 (1999) 30
[27] E.V. Chulkov, I. Sarria, V. M. Silkin, J. M. Pitarke, P. M. Echenique, Phys. Rev. Lett. 80 (1998) 4947
[28] J. Kliewer, R. Berndt, E. V. Chulkov, V. M. Silkin, P. M. Echenique, S. Crampin, Science 288 (2000) 1399
[29] E. V. Chulkov, V. M. Silkin, M. Machado, Surf. Sci. 482-485 (2001) 693
[30] P. M. Echenique, J. Osma, M. Machado, V. M. Silkin, E. V. Chulkov, J. M Pitarke, Prog. Surf. Sci. 67 (2001) 271
FIGURES

FIG. 1. Inelastic scattering rate for Xe atoms moving parallel to a Cu(111) surface as a function of the impact parameter. The incident velocity is $v=1$ a.u. (dot-dashed line), 2 a.u. (dashed) and $v=3$ a.u. (solid). a) results for the SRM surface response function, and b) for a model RPA response.

FIG. 2. Inelastic scattering rate for Xe atoms moving parallel to a Cu(111) surface as a function of the incident velocity. The impact parameter $z_0$ is 1 a.u. (solid lines) and 2 a.u. (dashed). a) results for the SRM surface response function, and b) for a model RPA response.

FIG. 3. Imaginary part of our model RPA response function for $q_\parallel=0.3$ a.u. and $\omega=1$ eV, as a function of $z$ (coordinate normal to the surface), for $z = z'$ with (solid line), and without (dashed line) the surface state contribution.

FIG. 4. Inelastic scattering rate for Xe atoms moving parallel to a Cu(111) surface as a function of the impact parameter. The model RPA surface response function was used with (solid lines) and, without (dashed) the contribution of the surface state.
q = 0.3 a.u.
ω = 1 eV

\[ \text{Im}[\chi(q_{\parallel}, \omega; z=z')] \text{ (a.u.)} \]

- With surface state
- Without surface state
$v=2$ a.u.

- With ss contrib.
- Without ss contrib.