Dynamic screening and electron–electron scattering in low-dimensional metallic systems

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Abstract

The modification of dynamic screening in the electron–electron interaction in systems with reduced dimensionality and tunable one-particle electronic structure is studied. Two examples of such systems are considered, namely, the adsorbate-induced quantum well states at the Na adlayer covered Cu[111] surface, and metal clusters of sizes up to few nanometers. The dependence of the electron–electron decay rates on the Na coverage in the former case and on the cluster size in the latter is investigated. The role played by the dynamical screened interaction in such processes is addressed as well.

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1. Introduction

Electronic excitations in metallic media can decay through various mechanisms, the most important of them being electron–electron (e–e) and electron–phonon (e–ph) scattering. Over the last years, a large amount of theoretical and experimental work has been devoted to understand and predict the lifetime of these excitations in solids [1–5] and at surfaces [6–10]. Focusing on the e–e scattering process, one of the key quantities that determine the rate at which the electronic excitations can decay is the dynamic screening among the medium electrons. However, the screening properties of metallic systems are profoundly affected by their dimensionality. Confinement and surface effects are, among others, two features that can drastically change the electronic screening and thus the lifetime of electronic excitations as compared with the bulk case. The modification at wish of the electronic properties of metallic systems and the subsequent change in the lifetime of electronic excitations is not a question of purely academic interest, but has important implications for many technological applications.

In present work, we analyze two cases in which the reduction of dimensionality leads to significant modifications in the electron–electron interaction. First, we study the case of quantum well states formed under the deposition of alkali atoms on metal surfaces [11,12]. Whereas the number of adsorbed alkali atoms is small, and they can be considered as independent, the picture of almost total transition of s valence electron from the alkali atom to the substrate is appropriate. However, when the coverage reaches rates of around 1 monolayer (ML) [13] an adsorbate-induced electron band which forms a quasi two-dimensional electron gas confined between the vacuum barrier and the metal substrate [14,15] (called a quantum well state (QWS)), unoccupied for low coverage, starts to fill [16]. A prominent example of this is the case of Na adsorption on Cu[111], for that the properties of this QWS have been intensively studied. Thus, the dynamics of holes created at wave vector \(k_{||} = 0\) has been studied for this system, both experimentally and theoretically.
In this study it was proven that e–e and the e–ph contributions are equally important for the hole decay for 1 ML coverage. Very recently a joint experimental and theoretical investigation of electron dynamics for Cs and Na adlayers on Cu(1 1 1) was performed as well [18]. Here, we investigate the energy dependence of the e–e contribution for several positions of the QWS band relative to the Fermi level $E_F$, which, in turn, depends on the Na coverage. For the sake of comparison with the experiment, a reasonable assumption could be that the e–ph contribution should not change significantly for such small variation of the QWS energy.

As a second case study, we analyze dynamic screening properties in metal clusters. In clusters and nanoparticles, chemical, optical, and electronic properties can be tuned by varying the size and/or the shape of the system. Besides its fundamental interest, tailoring the electronic properties can be of vast importance for many processes of technological interest, such as photochemical reactivity. Over the last years, the advent of femtosecond lasers has fueled the experimental study of electron relaxation processes. Particular attention has been paid to the dependence on size of the electron–electron interaction processes [19–21]. We will show that the interplay between screening effects and space localization of the initial excitation makes the lifetime of the excitation vary with respect to the bulk equivalent.

2. Theoretical methods

In very recent years, improvements in experimental methods, in particular in the field of ultrafast laser spectroscopies, are making it possible to study electronic excitations at time scales below the femtosecond [22,23]. In this time scale, the screening of excited electrons in condensed matter can be incomplete and the description of the electronic excitations as quasiparticles is questionable [24]. However, most standard experimental techniques provide information on time scales for which the screening of excited electrons can be approximated as instantaneous in practice. In this case, the description of the many-body electronic excitation can be simplified by means of the quasiparticle picture. In the following, we focus into this situation.

The scattering rate of an excited electron or hole due to inelastic e–e scattering can be evaluated by means of many-body calculations based on the electronic self-energy [25,26]. In this approach the lifetime broadening of a quasi-particle in a quantum state characterized by an energy $E_0$ and wave function $\psi_0$ is obtained as the projection of the imaginary part of the self-energy $\Sigma(\mathbf{r},\mathbf{r}',E_0)$ onto the state itself (atomic units are used throughout, i.e., $\hbar = e^2 = m_e = 1$, unless otherwise is stated)

$$\Gamma_{e-e} = \tau_{e-e}^{-1} = 2\int d\mathbf{r} d\mathbf{r}' \psi_0^*(\mathbf{r}) \text{Im} \Sigma(\mathbf{r},\mathbf{r}',E_0) \psi_0(\mathbf{r}).$$

Frequently the self-energy $\Sigma$ is represented by the so-called $GW$ approximation [25], which is the first term in a series expansion of $\Sigma$ in terms of the screened Coulomb interaction $W$. Usually, the non-interacting Green function $G^0$ is used to replace the full one-electron Green function $G$. In the following we provide a brief description of the numerical methods used in the calculation of scattering rates in the two examples considered in this work, namely, quantum well states at metal surfaces and metal clusters. A more detailed account can be found elsewhere [26,27].

2.1. Quantum well states

In the case of Na adlayers on the Cu(1 1 1) surface, we assume that the charge density and the one-electron potential only vary along the z-direction perpendicular to the surface and are constant in the $(x, y)$ plane parallel to the surface. This assumption is valid for Na induced QWS’s at coverage rates close to 1 ML, since the wave functions lie mainly in the Na layer and in the vacuum side, i.e., in a region with little potential variation in the direction parallel to the surface [28]. This leads to significant simplification of Eq. (1), which now takes a form

$$\Gamma_{e-e} = \tau_{e-e}^{-1} = \sum_i \frac{d q_i}{(2\pi)^2} \int d z d' z' \phi_0(z) \phi_i(z') \times \text{Im}[-W(z, z', q_i, E_0 - E_i)] \phi_0(z') \phi_i(z),$$

where the summation is performed over all available final states $i$, $W(z, z', q_i, \omega)$ is the two-dimensional Fourier transform of the screened Coulomb interaction, and $\phi_i(z)$ is the $z$-dependent component of the wave function $\psi_i(\mathbf{r})$:

$$\psi_i(\mathbf{r}) = \frac{1}{\sqrt{S}} e^{i q_i \mathbf{r}} \phi_i(z)$$

with $S$ being a normalization area. To describe the Cu(1 1 1) surface covered by Na adlayers, we employ a slab containing 31 atomic layers of Cu together with a region corresponding to Na and a vacuum region corresponding to 20 Cu interlayer spacings. For the description of the surface electronic structure, the model potential of Ref. [17], based on the model potential of the bare Cu(1 1 1) surface [29], has been employed. This potential reproduces the QWS energy position of $E_{T/QWS} = -0.127$ eV at the surface Brillouin zone center for 1 ML Na coverage [30]. To investigate the linewidth dependence on the QWS energy position relative to the Fermi level and demonstrate the dramatic change of the screening upon the QWS band shrink below $E_F$, we evaluate $\Gamma_{e-e}$ for the cases with QWS energies $E_{T/QWS} = 0$ eV and $E_{T/QWS} = -0.042$ eV. We assume that the small variation of the QWS binding energy at the scale of 0.1 eV does not significantly affect the QWS wave function, and therefore use the same set of wave functions obtained for the $E_{T/QWS} = -0.127$ eV case, just shifting the QWS band to the corresponding energy positions. We also assume here that

1 As the QWS energy position at the $T$ point is gradually moved down with increasing Na coverage [16] this energy position should roughly correspond to $\theta \approx 0.9$.\n
\[2\]
the QWS wave functions do not change along the QWS energy band, although this can have a significant effect on the excited electron linewidth in some cases [31,32]. For the QWS energy dispersion curve vs the two-dimensional wave vector \( \mathbf{k}_\parallel \), we use a parabolic form \( E_{\text{QWS}}(\mathbf{k}_\parallel) = E_{\text{QWS}}^0 + k^2/2m^*_{\text{QWS}} \), taking as effective mass the experimental value \( m^*_{\text{QWS}} = 0.7 \) [30]. Further calculation details on the evaluation of the screened Coulomb interaction \( W(z', z, q_0, \omega) \) can be found in Refs. [33,34].

2.2. Metal clusters

The spherical jellium model [35,36] is used to represent metal clusters of variable size. The average one-electron radius \( r_s \) in the cluster can be defined from \( r_s = R/N^{1/3} \), where \( R \) is the radius of the cluster and \( N \) the number of electrons in it. If the cluster is neutral, the equality \( 1/n^2_e = 4\pi r_s^3/3 \) holds as well, with \( n^2_e \) being the constant background positive charge of the cluster.

We restrict our discussion to neutral clusters in closed-shell configurations. The ground state properties of the cluster are described using density functional theory (DFT) and Kohn–Sham (KS) equations [37]. The exchange-correlation potential is calculated in the local density approximation (LDA) with the parametrization of Ref. [38]. The KS wave functions \( \psi(r) \) are calculated numerically after expansion in the spherical harmonic basis set \( Y_{lm}(\Omega) \). The set of KS equations are solved self-consistently using an iterative procedure.

In real space, when the exact Green function \( G \) is replaced by the independent-elecrtons Green function \( G^0 \) in Eq. (1), one can show that

\[
\Gamma_{e-e} = -2 \sum_f \int \frac{d\mathbf{r}d\mathbf{r}' \omega}{(2\pi)^2} \psi^*_f(\mathbf{r}) \psi_f(\mathbf{r}') W(\mathbf{r}, \mathbf{r}', \omega) \psi^*_f(\mathbf{r}) \psi_f(\mathbf{r}),
\]

where \( \psi_f(\mathbf{r}) \) is a KS wave function with eigenvalue \( E_f, \omega = E_0 - E_f \), and the sum over \( f \) runs over all unoccupied KS states of eigenvalues \( E_f < E_0 \). Hence we are approximating the energy levels and wave functions in the decay by the eigenvalues and wave functions of unoccupied KS levels. This is a reasonable first-order approximation [39].

In practice, the spherical symmetry of the problem simplifies the calculation [27]. All quantities in Eq. (4) are expanded in the spherical harmonics basis set. The screened interaction \( W(\mathbf{r}, \mathbf{r}', \omega) \) is calculated from the response function of the system \( \chi(\mathbf{r}, \mathbf{r}', \omega) \) obtained in the random phase approximation (RPA) [40,41]. The latter is built in a similar way to that of Ref. [42]: one-electron Green functions are built from the KS wave functions for every \( \omega \). These Green functions are used to calculate the multipole components of the independent-electrons response function \( \chi^0(\mathbf{r}, \mathbf{r}', \omega) \), and the RPA integral equation is solved in real space after matrix inversion for every polar component. Finally, the decay rate \( \Gamma_{e-e} \) is calculated as a sum over the independent contributions of each of the available final states [27].

3. Calculation results and discussion

3.1. Quantum well states

In Fig. 1, the calculated dependence of the linewidth \( \Gamma_{e-e} \) on the excited energy is presented for three Na QWS energy positions. A large variation of the linewidth as a function of coverage is observed. A particularly strong enhancement of \( \Gamma_{e-e} \) for small excitation energies and for the two systems with partially occupied QWS band is observed, with respect to the case of unoccupied QWS. Additionally, one can note the different behavior between the two occupied QWS cases. For small energies, \( \Gamma_{e-e} \) for \( E^\text{QWS}_T = -0.042 \text{ eV} \) is larger than \( \Gamma_{e-e} \) for \( E^\text{QWS}_T = 0.127 \text{ eV} \). Indeed, the two curves cross around \( E = 0.25 \text{ eV} \), and the linewidth for \( E^\text{QWS}_T = -0.127 \text{ eV} \) starts to be the largest for higher energies. This finding is rather difficult to understand in simple terms such as phase space available for the quasiparticle decay, since this phase space is the same for all three systems as is seen in Fig. 2. Note that these intraband transitions within the QWS band itself are the main source for excited electron decay in all systems under study. Thus, for small energies this contribution accounts for almost 10% of the total decay rate. With the increase of the excitation energy the contribution from interband transitions to the empty bulk electronic states increases faster than that from intraband transitions. Nevertheless, even for energies around \( 2 \text{ eV} \) the intraband contribution accounts for more than 90% of the total \( \Gamma_{e-e} \). Hence, the two-dimensional effects in Na/Cu(111) systems are much stronger than in the case of surface states at clean metal surfaces [8,43]. This fact can be explained by the larger decoupling of the QWS state wave functions from the bulk electron system [17].

To understand the behavior of \( \Gamma_{e-e} \) as a function of the QWS energy position let us see Eq. (2), where the double integration in \( z \) and \( z' \) is performed. As mentioned above,
the QWS wave functions $\phi_0(z)$ and the bulk electronic structure for all the three different QWS energy positions have been held the same in the present calculation. In addition to the above-mentioned similarity of the available phase space for decay, the remaining difference between these calculations is the screened Coulomb interaction $W(z,z',q||,\omega)$ originated from different QWS energy positions. We perform calculation of $W(z,z',q||,\omega)$ for all the three systems and analyze them below. First of all, we note a strong variation of Im $W$ as a function of all its variables $z$, $q||$, and $\omega$. To give a general idea of it in Fig. 3, we present Im $W(z,z',q||,\omega)$ as a function of $z$ and $\omega$ for the $E^{\text{QWS}}_T = -0.127$ eV and $E^{\text{QWS}}_T = -0.042$ eV cases for two-dimensional momentum value $q_|| = 0.05$ a.u.$^{-1}$. The use of Im $W(z,z',q||,\omega)$ as an example is reasonable as inside the solid and near the surface Im $W(z,z',q||,\omega)$ has the maximum magnitude at $z = z'$ and only far from the surface into the vacuum the maximum of this quantity occurs at $z \neq z'$ [44]. In Fig. 3 one can observe a strong enhancement of Im $W(z,z',q||,\omega)$ for $z \geq 0$ and energies $\omega \leq 0.25$ eV and $\omega \leq 0.18$ eV, respectively. Comparing both figures one can see that the amplitude of Im $W$ in low left corner for the $E^{\text{QWS}}_T = -0.042$ eV case is much larger than for the $E^{\text{QWS}}_T = -0.127$ eV case. Therefore, although the phase space in the former case is smaller as one can appreciate in Fig. 5, this Im $W$ enhancement leads to a larger linewidth for the $E^{\text{QWS}}_T = -0.042$ eV case for small energies. When the energy increases, the relative role of this enhanced region of Im $W$ decreases leading to a smaller linewidth for the $E^{\text{QWS}}_T = -0.127$ eV one. In Fig. 4, Im $W(z,z,q||,\omega)$ for $E^{\text{QWS}}_T = -0.127$ eV and $E^{\text{QWS}}_T = 0$ are presented for two values of $q||$, demonstrating that, at the surface, the amplitude of Im $W$ is two orders of magnitude larger than in the former case, whereas the latter is very similar to the clean Cu(111) case [44].

Furthermore, in Fig. 3, one can see additional peaks at the maximum energy for QWS intraband e–h excitations which correspond to the collective electronic excitations similar to the acoustic surface plasmon (ASP) at the clean metal surfaces [33,34]. Their dispersions closely follow the upper edge of regions for e–h excitations within the QWS bands and are shown in Fig. 5. The origin of this collective mode is the coexistence at the surface of both the QWS and bulk electrons. More detailed analysis of its properties will be given elsewhere. From Fig. 5, it is clear that the ASP contributes to the total linewidth $\Gamma_{\text{e–c}}$. Nevertheless, it is difficult to separate this contribution from the very efficient decay channel due to intraband QWS e–h excitations.

3.2. Metal clusters

One of the most appealing features of low-dimensional systems such as clusters is that their properties can often
be tuned by varying the size and thus they can be different from the bulk case. For this reason and in the following, we focus into clusters of variable size and fixed average electronic density ($r_s = 4$, that represents for instance sodium clusters). In this respect, the difference between the dynamics of hot electrons in clusters and in bulk has been discussed bringing up two different effects. First, the electron lifetime can be enhanced in the cluster because of the discretization of levels that reduces the number of final states to which the electronic excitation can decay. Then again, the electron lifetime can decrease in the cluster because of the reduction of dynamic screening in the proximity of the cluster surface. We show in the following that the screening in clusters is not only modified due to the presence of the surface but also due to the different mobility of the cluster electrons with respect to those in bulk. The dynamically screened interaction between the cluster electrons is affected by this factor, in particular for low excitation energies.

In Fig. 6, we show the linewidth $\Gamma_{e-e}$ of electron excitations with energy $E_0 \approx 1$ eV measured from the Fermi level of the cluster. Due to the discretization of levels in the cluster, the initial energy of the excitation cannot be fixed exactly to 1 eV, but the eigenvalue closest in energy is chosen. In any case, the variation with respect to the reference value is never larger than 10%. We come back to this...
point below. $\Gamma_{e-e}$ is plotted as a function of the cluster radius $R$. For small cluster sizes, the discretization of levels is clearly observable in the large oscillations found. For clusters of nanometer size, however, these oscillations are damped and the value of the linewidth is $\Gamma_{e-e} \sim 150$ meV. Let us also mention that an RPA calculation of the electron lifetime in a homogeneous electron gas, with the same parameters that we fix in our calculation ($E_0 = 1$ eV and $r_s = 4$) gives a value $\Gamma_{e-e} = 60$ meV [45], smaller than the ones obtained for these big clusters.

One of the reasons not often discussed in the literature for the difference between the value of $\Gamma_{e-e}$ in bulk and in nanometer-sized clusters is the difference in the electron–electron screened interaction $W(r, r', \omega)$ between an infinite electron gas and a finite jellium system, even for values of $r$ and $r'$ far from the cluster surface. In Fig. 7, we quantify this statement by showing the imaginary part of $\text{Im} W(r, r', \omega)$ for a value of $r$ near the cluster center ($r = 0.31$) and as a function of $r'$. The dimension of the chosen is sufficiently big ($R = 38.8$ a.u.) to consider that no surface effects are relevant. $\text{Im} W$ is plotted for two different values of the energy, namely $\omega = 0.815$ meV and $\omega = 54.4$ eV. The former is representative of actual values of $\omega$ that enter the calculation of $\Gamma_{e-e}$ in clusters. Fig. 7 shows that $\text{Im} W(0, r', \omega = 0.815$ eV) is clearly different in a cluster as compared to the bulk counterpart. The dynamic screening between electrons is thus modified due to the different mobility of electrons in a confined system.

However, for higher values of $\omega$, the response of the system is similar to that calculated in the independent-electron approximation $\gamma^0$ and finite-size effects are not relevant.

Confinement effects are also relevant in the choice of the initial state in the decay process. The discretization of levels in the cluster makes it impossible to exactly define the same initial energy $E_0$ for all the cluster sizes considered. An estimate of the variation that this feature can introduce in the linewidth value is also shown in Fig. 6. For a cluster size of $R = 31$ a.u., the value of $\Gamma_{e-e}$ for two initial states very close in energy is plotted. One of them is the first $l = 13$ state with $E_0 = 1$ eV, and the second one is a $l = 4$ state with $E_0 = 0.99$ eV. In spite of the proximity of the two energy levels, the value of $\Gamma_{e-e}$ varies as much as $\approx 35\%$. The main reason for that is the different coupling between the initial state wave function and the available final states for the decay. In Fig. 8, we show the normalized radial distribution of the KS wave functions $r R_{l,E_0}(r)$, where $\psi_0(r) = R_{l,E_0}(r) Y_{lm}(\Omega_r)$, for the two cases considered. The integrated radial distributions

$$Q(r) = \int_0^r dr' r'^2 |R_{l,E_0}(r')|^2$$

are plotted in Fig. 8 as well. While the $l = 13$ wave function does not have any nodes, oscillations in the $l = 4$ wave function are conspicuous. A proper definition of the initial excitation in the decay process can thus be crucial when calculating the linewidth.
4. Summary and conclusions

Low-dimensional systems bear electronic properties that can be very different from those well studied in bulk systems. Here, we have shown that the modification of the dynamic screening in the electron–electron interaction and the change in the structure of energy levels in these systems can combine to drastically modify the linewidth of electronic excitations as compared to the bulk reference. In particular, we have analyzed the screened interaction between electrons and the phase space availability for the decay in two different cases: quantum well states in overlayers of Na over Cu(111) and gas-phase metal clusters of sizes up to few nanometers. In the former case, the amount of alkali atoms coverage on the metal surface leads to a shift of the QWS energy band, that produces an appreciable change in the linewidth. In the latter case, the variation in size of the cluster is responsible for modifications in the decay rate. Our detailed analysis of these properties shows that a proper choice of the system characteristics can allow to tune the excitation linewidths due to electron–electron scattering processes.

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