Approximate approach to metastable He deexcitation on metal surfaces

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Abstract
In this paper a simple approximate approach is used to reproduce the *ab initio* results for the deexcitation spectral profiles of a metastable helium atom at different distances from a surface. The main quantities of our method are the spin dependent local density of states (LDOS) around the excited helium atom. We show that the extension of the spherical volumes around the atom in which we evaluate the LDOS are the only relevant parameters in this approach and they do not depend on the atom–surface distance.

1. Introduction

When a slow excited rare gas atom approaches a substrate, the interaction with the surface causes the deexcitation of the atom, with the subsequent emission of an electron. Since the excited atoms do not penetrate into the bulk the kinetic energy distribution of the emitted electrons carries information about the electronic structure of the outermost surface layer of the substrate. This phenomenon is at the basis of metastable deexcitation spectroscopy (MDS), a useful experimental technique used to investigate the electronic structure of surfaces [1].

Although this spectroscopy provides the opportunity to study surface and adsorbate electronic structures with extreme surface specificity, the potential of this technique has not yet been fully realized. This is because the theoretical description of the deexcitation mechanism—which is essentially an Auger process—is quite complex since one needs to know not only the electronic structure of the surface but also the dynamics of the interaction between the excited atom and the substrate.

In a recent work [2] we presented an *ab initio* calculation of the Auger deexcitation lineshape of a slow metastable He atom in its triplet state on a Na jellium-like metal surface, in which the particle motion was treated within the adiabatic approximation. In contrast to previous approaches [3, 4] we treated the interacting metal–atom system in a fully consistent way within the density functional theory (DFT) framework. We showed that our results were able to reproduce quite well the shape of the emission spectrum. However, the *ab initio* approach is a very demanding task, even using a jellium model for the surface. Therefore it could be useful to find an approximate method, suitable to be applied to realistic substrates, to calculate the deexcitation lineshape.

In the present work we propose an approximate procedure to calculate the Auger deexcitation spectral profile of an excited He atom at any distance from the surface. We use a phenomenological expression which consists essentially in the convolution of two local densities of states calculated in spherical volumes around the excited atom. The radii of these spheres—the only free parameters in this approach—are calculated by fitting the *ab initio* Auger profiles, allowing one to reproduce the Auger profile at all He–surface distances.

This paper is organized as follows. In section 2 we describe the *ab initio* method we use to calculate the deexcitation mechanism of a metastable helium atom on a metal surface. In section 3 we present the details of our phenomenological approach. The results and their discussion are reported in section 4.

2. *Ab initio* method

The theoretical approach we use to calculate the deexcitation profile is discussed in detail in [2]; we briefly review it here. In order to calculate the Auger transition probability between an initial state i and a final state f, we use the Fermi golden rule (atomic units are used hereafter):

$$\mathcal{P}_{i \to f} = 2\pi \left| \langle \Psi^f | V | \Psi^i \rangle \right|^2 \delta(E^f - E^i), \tag{1}$$

where $V = \sum_{i>j} r_{ij}^{-1}$ is the Coulomb potential, and E^i and E^f are the energies of the initial and final state, respectively. The initial and final wavefunctions are built in the form of a Slater determinant using the eigenstates solution of the Kohn–Sham (KS) equation of DFT in the local spin density approximation [5]. Our method does not account for the sudden disappearance of the core hole in the final state of this Auger process, and both the initial and final wavefunctions are calculated from the initial excited state with a core hole in the 1s level (hereafter we assume that a spin down ($\downarrow$) electron has been removed from the 1s level). To solve the KS equation we use the Green function embedding approach [6, 7] and we perform an all-electron calculation using a linearized augmented plane-waves (LAPW) basis set. The use of the Green function allows us to naturally account for the continuous spectrum of the valence electronic states which play a key role in the spectral features.

The emitted Auger electron may have spin up or down with different probabilities even on a non-magnetic substrate; the total deexcitation rate at distance z from the jellium edge, as a function of the energy E of the emitted electron, is given by:

$$\mathcal{P}(E, z) = \mathcal{P}^{\uparrow}(E, z) + \mathcal{P}^{\downarrow}(E, z). \tag{2}$$

Exploiting the orthonormality of the orbitals, the transition probability $\mathcal{P}^{\sigma}(E, z)$ for the decay of the initial core hole, $1s_{\downarrow}$, becomes:

$$\mathcal{P}^{\uparrow}(E, z) = 2\pi \sum_{a,b} \int d\hat{k}_A \, |D|^2_{A\uparrow, 1s\downarrow, a\downarrow, b\uparrow} \delta(E + E_{1s\downarrow} - E_a - E_b), \tag{3}$$

$$\mathcal{P}^{\downarrow}(E, z) = \pi \sum_{a,b} \int d\hat{k}_A \, |D - E|^2_{A\downarrow, 1s\downarrow, a\downarrow, b\downarrow} \delta(E + E_{1s\downarrow} - E_a - E_b). \tag{4}$$
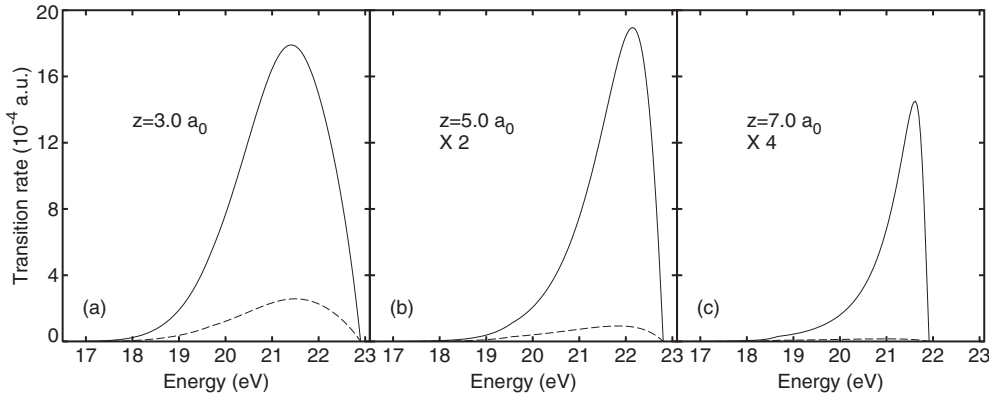
Figure 1. Probabilities for the emission of spin up (solid curve) and spin down (dashed curve) electrons. (a) He* at $z = 3.0\ a_0$ (a_0 being the Bohr radius), (b) He* at $z = 5.0\ a_0$, (c) He* at $z = 7.0\ a_0$.

We have summed over the final hole states involved in the transition, and the direct D and exchange E matrix elements are given by:

$$D_{A,1s\downarrow,\alpha,\beta} = E_{A,1s\downarrow,\beta,\alpha} = \int d\boldsymbol{r}_1\, d\boldsymbol{r}_2 \frac{\psi_\alpha^*(\boldsymbol{r}_1)\psi_{1s\downarrow}(\boldsymbol{r}_1)\psi_\beta^*(\boldsymbol{r}_2)\psi_A(\boldsymbol{r}_2)}{|\boldsymbol{r}_1 - \boldsymbol{r}_2|}, \qquad (5)$$

where $\alpha = (a, \sigma_a)$ and $\beta = (b, \sigma_b)$ are the quantum numbers (σ indicates the spin) of the two final valence state holes. Let us remark that, as is shown by equations (3) and (4), for a spin up emitted electron there is only one possible process, the direct one, while for a spin down emission the exchange process is also allowed. In figure 1 the probability for emission of spin up and spin down electrons for some helium–Na surface distances is shown. We can observe that the emission probability of spin down electrons is extremely small, especially when the atom is far from the surface. This is due to the partial cancellation of the direct and exchange terms in equation (4) and to the fact that the spin down population around the adatom becomes very small at large distances. In fact only such spin orientation may decay onto the spin down core hole. As described in [2], the final step of the method consists in using a simple rate equation to determine the survival probability of the excited He atom as a function of the distance from the surface and finally calculate the deexcitation spectrum.

We would like to remark that in our approach the interaction of the atom with the surface—which induces a modification of the substrate electronic structure involved in the deexcitation—is properly taken into account in our DFT framework. This is an improvement with respect to previous works [3, 4], where the metal surface and the atom were treated as non-interacting systems.

3. Phenomenological procedure

As shown in [2] the *ab initio* method we have developed is able to reproduce the experimental spectral profile of the deexcitation of slow metastable He atoms on a Na metal surface [8]. However the calculation of the matrix elements of the transition at various distances from the surface is a very demanding computational effort, even if the substrate is modelled as a jellium.

In recent works we have shown that a phenomenological approach is able to reproduce the *ab initio* results for the lineshape of CCV Auger spectra of adatoms or impurity in jellium [9] and that this procedure can be applied to realistic systems giving results in good agreement

with the experimental ones [10]. In that approach the CCV Auger transition probability is approximated with an expression based on the local density of states (LDOS) around the excited atom. The main parameter is the radius of the sphere in which the LDOS is calculated and it depends only on the atomic species regardless of the chemical environment of the atom.

Motivated by these results we try to approximate the deexcitation probability of an excited He atom making use of the LDOS around the He atom itself. This kind of approach is possible because, when states of the valence band are involved in the Auger decay, the probability that a particular energy level takes part in the transition is proportional to the valence band density of states at this energy $\rho(\epsilon)$. Therefore, for a CVV transition, which involves two such valence states, the observed electron energy distribution should reflect the self-convolution of the density of states in the valence band. Following this simple argument we propose using an expression of the form:

$$\mathcal{P}(E) = C \int_0^{E_F} \mathrm{d}\epsilon \, \rho_1^{\downarrow}(\epsilon) \rho_2^{\uparrow}(E + E_{1s\downarrow} - \epsilon), \tag{6}$$

where ρ_i is the local density of occupied states of the valence band in a sphere of radius $R_{\mathrm{cut},i}$ around the excited He atom and C is a constant. The density $\rho_1^{\downarrow}(\epsilon)$ is related to the decay process of an electron from the spin down population of the valence band to the 1s core hole of helium, while $\rho_2^{\uparrow}(\epsilon)$ instead accounts for the emission of a spin up electron from the valence band to the vacuum. We consider only the emission of spin up electrons since, as we have found, it represents the main contribution to the deexcitation probability.

It is interesting to compare equation (6) with the commonly used phenomenological expression. The MDS spectra are often analysed by means of the LDOS of the unperturbed substrate $\rho_0(\epsilon)$ [1, 11]. On high work function metal surfaces the energy distribution of the emitted electrons is supposed to be proportional to the self-convolution of the unperturbed surface LDOS. This is due to the fact that the deexcitation mechanism is described by the resonant ionization + Auger neutralization (RI + AN) model. In this two step model the excited He atom first undergoes a ionization process through tunnelling of the 2s electron of He into an unoccupied metal state and then a CVV Auger transition takes place. Such CVV Auger decay is responsible for the spectral lineshape and can be roughly described by equation (6) substituting $\rho^{\downarrow(\uparrow)}(\epsilon)$ by $\frac{1}{2}\rho_0(\epsilon)$. On low work function metal surface or on insulating substrates the experimental profile is supposed to be proportional to the unperturbed surface LDOS. In this case a direct Auger deexcitation (AD) is believed to occur: an electron of the valence band of the metal fills the 1s core hole of He and the 2s electron is emitted. Equation (6) can describe this process if $\rho^{\downarrow}(\epsilon)$ is replaced with $\frac{1}{2}\rho_0(\epsilon)$ and $\rho^{\uparrow}(\epsilon)$ with $\delta(\epsilon - E_{2s\uparrow})$.

Our purpose is to use equation (6) in which we consider the LDOS of the interacting metal–atom system. This in some way allows us to take into account the modification induced by the presence of the excited He atom on the surface electronic structure, which plays a key role in MDS [12].

The procedure to reproduce the *ab initio* results is the following. We employ equation (6) in which instead of $\rho_1^{\downarrow}(\epsilon)$ we use only its *s* component. This is justified since the main contribution of the matrix elements comes from the *s* component of the valence wavefunction because of the presence of the 1s He core wavefunction. Then we treat $R_{\mathrm{cut},1}$ and $R_{\mathrm{cut},2}$, the radii of the spheres in which we calculate the LDOS, as free parameters. These two parameters are determined by fitting the *ab initio* results with our simplified formula. The quality of the fit is tested with a statistical variable R-square method.

Finally, it is worth noting that the use of the *s* component of $\rho_1^{\downarrow}(\epsilon)$ can be seen as a quite rough way to introduce a weight on the various angular components of the LDOS. Of course, one could think of a more sophisticated phenomenological expression to treat the *l* components
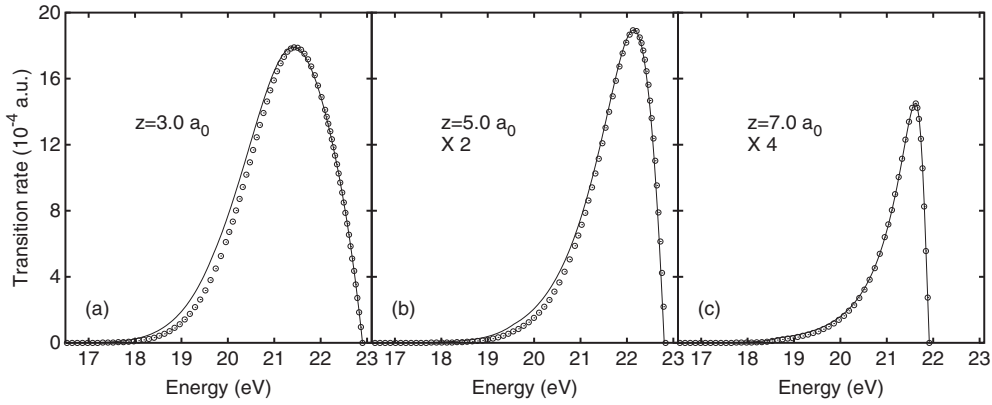
Figure 2. Solid curves: as in figure 1. Circles: results from equation (6).
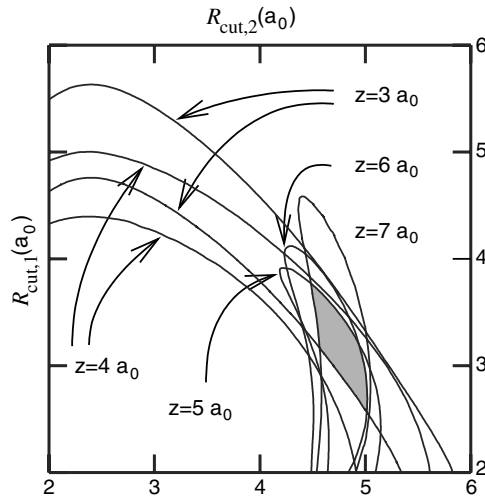

Figure 3. Best fit regions for five different atom–surface distances.

of the LDOS, as, for example, we have done for CCV Auger transitions [9]. However, this would increase the number of parameters needed to describe the process and furthermore it seems not to be necessary because we have already obtained a good agreement in reproducing *ab initio* results by using only two parameters.

4. Results and conclusion

In figure 2 we present the spectral profiles calculated *ab initio* (solid curve) and those obtained via equation (6) (circles) for the same choice of distances as in figure 1. The agreement is fairly good even if in the low energy region the phenomenological expression always underestimates the *ab initio* result.

In figure 3 we report the best fit regions for several values of the atom–surface distance z in the $\{R_{cut,1}, R_{cut,2}\}$ space. The shape of this region significantly depends on the distance of the atom from the surface. For large distances ($z = 5, 6$ and $7 \, a_0$) these regions are located in

the right lower corner while at small separations ($z = 3$ and 4 a_0) they extend also towards the left upper corner. The behaviour at small distances is explained by the fact that in this case the atom–surface interaction becomes stronger and induces a decrease of the spin polarization of the adatom [13]. Therefore ρ_1 and ρ_2 become very similar and it is possible to exchange them without significant effect.

The most interesting result of this procedure is represented by the existence of a region (grey shaded in figure 3) in which all the $\mathcal{P}(E, z)$ are well fitted. This means that there is a couple of R_{cut} values which can be used to reproduce the *ab initio* spectral profiles at any atom–surface distance. The values we determined are $R_{\text{cut},1} \sim 3.0$ a_0 and $R_{\text{cut},2} \sim 4.8$ a_0. Another relevant result is that the proportionality constant C in equation (6) turns out to be independent of z. This indicates that the deexcitation probabilities calculated via the LDOS follow the same trend as a function of z as the *ab initio* results and this is an important point when one has to determine the total deexcitation spectrum summing the various contributions at different distances (see [2, 3]).

In conclusion, we have shown a procedure to calculate the deexcitation profiles of an excited He atom at different distances from the surface. This approach allows us to avoid the extremely demanding calculation of the matrix elements of the Auger transition. One simply needs a standard *ab initio* calculation of the electronic properties, in particular of the LDOS in two well defined regions, of the helium atom in its triplet state interacting with the metal surface. Then, equation (6) can be used to find out the transition probability at any atom–surface distance. Work is in progress to test this procedure for the deexcitation of He* on other metal surfaces.

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