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Theory of metastable deexcitation spectroscopy on simple metals

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In this work we investigate the Auger deexcitation process of a slow metastable helium atom (He*) in its triplet state on a Na surface. The electronic properties and the Auger rates of the interacting atom-metal system are calculated self-consistently at any distance of He* from the surface in the framework of the local spin-density approximation using the embedding Green's function method. The energy distribution of the emitted electrons is obtained by integrating the Auger rates along the classical trajectory in the adiabatic approximation. The analysis of the spin-resolved local density of states shows that the excited atomic states broaden into resonances already at large atom-surface distances. The calculated atom deexcitation rates are in good agreement with experimental results.

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I. INTRODUCTION

Metastable deexcitation spectroscopy (MDS), sometimes also denoted as metastable impact (or atom) electron spectroscopy, is a useful experimental technique developed to investigate the electronic structure of solid surfaces.[1] Recent developments comprise adsorbate coverage dependent MDS profiles[2,3] and studies on the energy transfer in metastable adatom-surface interactions.[4]

In the MDS technique a beam of excited atoms is focussed on a substrate and electrons are ejected as a consequence of the deexcitation of the impinging atoms. It is well established that this phenomenon is essentially an Auger process and that the kinetic-energy distribution of the emitted electrons contains information on the electronic structure of the surface.[5,6] Unlike photons or electrons used in ordinary electron spectroscopies, metastable atoms do not penetrate the bulk of the solid and so MDS gives the opportunity to probe the outermost surface layer selectively. However, it is usually quite difficult to obtain information on the surface electronic structure from an experimental spectrum since the energy distribution of the emitted electrons depends not only on the electronic density of states of the surface, but also on the dynamics of the interaction between the excited atom and the substrate. Therefore any theoretical description of the emission spectra should properly account for the metal-atom interaction, which can lead to a modification of the unperturbed electronic structure of the probe and the target, and also consider the process of the electron emission along the trajectory of the approaching atom. Although some attempts have been made to reproduce the experimental results,[7,8] also within a density-functional theory (DFT) framework,[9] an *ab initio* approach to treat the interacting metal-atom system in a fully consistent way is still lacking. For this reason relevant problems, such as the deexcitation rates or the most likely distance from the solid at which the atom deexcites, still present open questions. We believe that only a detailed comparison between experimental spectra and theoretical ones could allow one to extract a great deal of information and to realize the full potentiality of this spectroscopy.

In this work we shall concentrate on the Auger deexcitation of a slow metastable helium atom (He*) in its triplet state on a jelliumlike Na metal substrate. It is quite interesting to investigate the deexcitation process on such a low work-function metal since it is reasonable to expect that an Auger transition directly causes the deexcitation event on this substrate and no other processes are in competition with this one.[1] Moreover, we can compare the experimental results[10] with our theoretical ones to test our approach.

In previous works[11,12] we investigated the Auger deexcitation of atoms chemisorbed on a simple metal surface within a DFT approach. It is clear that a further challenging difficulty of the MD process with respect to standard Auger spectroscopy is the presence of an additional degree of freedom, the He trajectory. To make such a problem manageable, the energy distribution of the ejected electrons is determined neglecting the effect of the motion of the atom on the deexcitation rate (adiabatic approximation). In this approximation, we can extend the theory we have developed,[11] and calculate the Auger deexcitation probability of the excited He atom at different distances from the surface. Then, using a simple rate equation, we can work out the survival probability of the excited species as a function of the distance, and finally calculate the total deexcitation spectrum.

This paper is organized as follows. In Sec. II we describe the main features of the deexcitation mechanism of a metastable helium atom on a metal surface. In Sec. III we present the details of our theoretical approach. The results and their discussion are reported in Sec. IV. The last section is devoted to the conclusions.

II. DEEXCITATION MECHANISM

It is usual to classify the deexcitation processes at a metal surface according to the values of the work function Φ of the metal and of the ionization potential of the excited atom. In

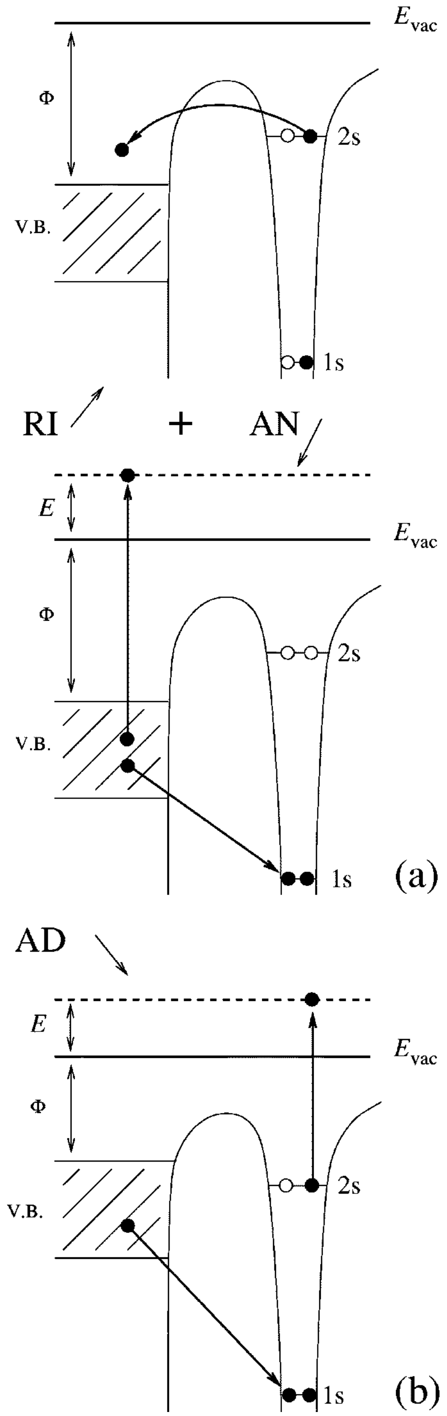

FIG. 1. Deexcitation mechanisms: (a) (upper panel) resonant ionization (RI) + (lower panel) Auger neutralization (AN), (b) Auger Deexcitation (AD).

Fig. 1 we schematically illustrate the two main processes that may occur.[1]

In each energy level diagram a metallic surface is shown on the left with a conduction band filled up to the Fermi energy, while the localized well of a closely approaching excited atom is shown on the right. If the work function of the surface is comparable to or larger than the ionization potential of the excited atom, the incident particle can undergo resonant ionization (RI) through tunneling of the electron in the excited state into an unfilled level above the Fermi energy in the metal [Fig. 1(a), upper panel]. The resulting ion continues toward the surface where it is neutralized by a conduction electron from the metal. The released energy is imparted to a second (Auger) electron of the metal, which may be ejected from the surface if the energy transferred is sufficiently large. This second step of the deexcitation, which is essentially a core-valence-valence (CVV) Auger transition, is called Auger neutralization (AN) [Fig. 1(a), lower panel]. The second deexcitation mechanism, called Auger deexcitation (AD) or Penning ionization, is illustrated in Fig. 1(b). This occurs if the incident excited atom ionization potential is greater than the work function of the metal. In this case, the RI process is suppressed because there are no empty levels of appropriate energy within the metal. A common and simplified explanation of this deexcitation process is that an electron of the conduction band of the metal fills the deeply lying hole of the probe atom. Hence the energy produced in this transition is transferred to the electron bound in the excited state of the atom which is therefore ejected. According to this interpretation, this type of interaction yields an energy distribution of emitted electrons which is a direct image of the occupied states of the valence band (if the ejection probability is the same for all electron states). This suggests a correlation between MD spectra and those obtained with ultraviolet photoemission spectroscopy (UPS), and, in fact, the spectral features of MD spectra are usually identified by a comparison with UPS data.[1,10]

This explanation of the AD process is somewhat oversimplified. In fact, the atom and the substrate retain their individual electronic structure when they are widely separated. However, this is no longer true when the atom is close enough to the solid so that its wave function begins to overlap the metal surface ones. In this case it is no more strictly meaningful to speak of purely atom's or metal's states in the energy range of the conduction band of the solid whose electron wave functions overlap with the atomic excited state of the approaching atom. Consequently, the sharp atomic level broadens into a resonance. It is therefore clear that the deexcitation spectrum may significantly depend on the metal-atom interaction which can lead to a modification of the unperturbed local electronic structure. The purpose of this work is to calculate the energy distribution of the emitted electron when a 2^3S He is scattered off a low-work-function metal surface, by calculating the atom-metal electronic properties in a consistent picture.

III. THEORETICAL FRAMEWORK

In this section we illustrate the theoretical model we use to calculate the Auger deexcitation probability of a slow metastable 2^3S helium atom that interacts with a metal surface described by the jellium model following Ref. 7.

The total probability (number) of electrons produced at energy E when an excited atom with a hole in its $1s$ shell impinges on a metal surface is given by

$$N(E)=\int_{-\infty}^{\infty} dt\, P(E,t)n(t). \tag{1}$$

Here, $P(E,t)$ is the rate per unit energy at which Auger electrons of either spin are produced at energy E by the core ionized atom that deexcites at time t, and $n(t)$ is the probability that the initially (at $t=-\infty$) empty $1s$ state is still empty at time t. To determine the quantity $n(t)$ we use the simple rate equation

$$\frac{dn(t)}{dt}=-R(t)n(t), \tag{2}$$

with the condition that $n(t=-\infty)=1$. In this equation R is the total rate at which the Auger electrons of either spin are produced at time t:

$$R(t)=\int_{-\infty}^{\infty} dE\, P(E,t). \tag{3}$$

We assume that a given metastable atom, in view of its large mass compared to the electron one, follows a classical motion and we only consider the z dependence of the trajectory, with the z axis normal to the surface and pointing outside the metal (the origin of the z axis is taken at the positive background edge of jellium). Thus we call $z(t)$ the coordinate of the atom at time t. Of course, in this scattering problem we have $z(t=-\infty)=\infty$. Due to the low kinetic energy of the approaching atom [tens of meV (Refs. 1 and 10)], we also assume that it is possible to neglect the time dependence of the interaction potential between atom and surface (adiabatic approximation). In this way the deexcitation probability P does not depend on time but only on the coordinate z of the atom and we can evaluate P at a certain distance from the surface as if the atom were fixed in that position. Thus we can express the total deexcitation probability from Eq. (1) as

$$N(E)=\int_{\gamma}\frac{dz}{v(z)}P(E,z)n(z), \tag{4}$$

where γ is the round trip path on the z axis followed by the atom in the scattering process, $v[z(t)]=dz(t)/dt$ is the z component of the velocity of the atom, and the quantities P and n are now expressed in terms of the coordinate z. The rate equation in Eq. (2) becomes

$$\frac{dn}{dz}=-\frac{R(z)}{v(z)}n(z), \tag{5}$$

where R is the total deexcitation rate when the atom is located at a distance z from the surface either before or after the impact with the metal. This equation has the solution

$$n[z(t)]=\exp\left[-\int_{\gamma[z(t)]} dz'\frac{R(z')}{v(z')}\right], \tag{6}$$

where $\gamma[z(t)]$ indicates the path (possibly considering a round trip part) on the z axis which goes from $z(-\infty)=\infty$ to the position $z(t)$ of the particle at time t. Thus the knowledge of the rate at which Auger electron are produced, $P(E,z)$, allows one to obtain the number of Auger electrons, $N(E)$, per unit energy created at energy E, by an excited He atom incident on a metal surface [see Eq. (1)].

It is worth noting that in this treatment we have implicitly assumed that the Auger deexcitation event is the only deexcitation process that takes place. If other processes were involved, in competition with the Auger one, these could affect the survival probability of the excited atom, $n(z)$, and consequently the total probability of emitted electrons per unit energy, $N(E)$, and should therefore be taken into account.

Under the previous hypothesis of a normal scattering energy conservation process, we can calculate the velocity $v(z)$ of the atom using the following equation:

$$\frac{1}{2}M_{\mathrm{He}}v(z)^2+U(z)=E^{i}_{\mathrm{kin}}, \tag{7}$$

where M_{He} is the mass of helium, $U(z)$ is the interaction potential between atom and substrate, and E^{i}_{kin} is the initial kinetic energy of the atom.

In order to derive the deexcitation rate, $P(E,z)$, at different distances from the surface we extend the approach we used in previous works[11,12] to treat spin polarized systems and CVV Auger transitions. Using the Fermi golden rule, we can write the transition probabilities for the emission of spin up ($\uparrow$), $\mathcal{P}^{\uparrow}(E,z)$, and spin down ($\downarrow$), $\mathcal{P}^{\downarrow}(E,z)$, electrons at energy E, when an excited He atom is at position z from the jellium edge (atomic units are used). The atom has a hole in the $1s$ shell, and we shall assume from now on that a spin down ($\downarrow$) electron has been removed. Then, integrating over the Auger wave function solid angle, we obtain[13]

$$\mathcal{P}^{\uparrow}(E,z)=2\pi\sum_{\alpha,\beta}\int d\hat{k}|D_{A\uparrow,C\downarrow,\alpha\downarrow,\beta\uparrow}|^2\delta(E+E_C-E_\alpha-E_\beta), \tag{8}$$

$$\mathcal{P}^{\downarrow}(E,z)=\pi\sum_{\alpha,\beta}\int d\hat{k}|D_{A\downarrow,C\downarrow,\alpha\downarrow,\beta\downarrow} - E_{A\downarrow,C\downarrow,\alpha\downarrow,\beta\downarrow}|^2\delta(E+E_C-E_\alpha-E_\beta). \tag{9}$$

The sum of these two contributions gives the deexcitation rate

$$P(E,z)=\mathcal{P}^{\uparrow}(E,z)+\mathcal{P}^{\downarrow}(E,z). \tag{10}$$

In Eqs. (8) and (9) the direct $D_{A,C,\alpha,\beta}$ and exchange $E_{A,C,\alpha,\beta}$ matrix elements are given by

$$D_{A,C,\alpha,\beta}=\int d\mathbf{r}_1 d\mathbf{r}_2\psi^*_\alpha(\mathbf{r}_1)\psi_C(\mathbf{r}_1)\frac{1}{|\mathbf{r}_1-\mathbf{r}_2|}\psi^*_\beta(\mathbf{r}_2)\psi_A(\mathbf{r}_2) \tag{11}$$

and

$$E_{A,C,\alpha,\beta}=\int d\mathbf{r}_1 d\mathbf{r}_2\psi^*_\alpha(\mathbf{r}_1)\psi_A(\mathbf{r}_1)\frac{1}{|\mathbf{r}_1-\mathbf{r}_2|}\psi^*_\beta(\mathbf{r}_2)\psi_C(\mathbf{r}_2), \tag{12}$$

where ψ_A is the Auger electron wave function, ψ_C is the orbital of the initial core hole, and ψ_α and ψ_β are the final valence state hole wave functions (we dropped the spin index

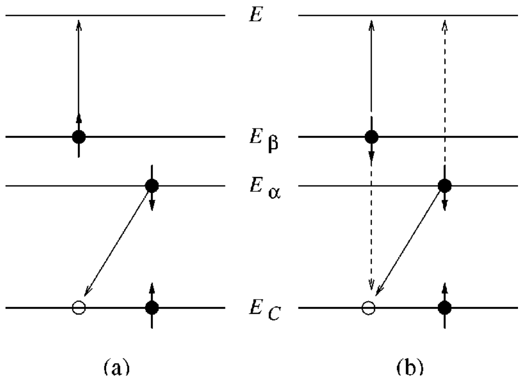

FIG. 2. (a) shows the emission of spin-up electrons and (b) the emission of spin-down electrons. The full lines indicate the direct process and the dashed lines the exchange one. The full circles represent the electrons.

for simplicity). All such wave functions are evaluated solving the Kohn and Sham (KS) equations of DFT in the local spin-density approximation (LSDA) by the Green's function embedding approach.[14] Note that Eqs. (8) and (9) show that the emitted Auger electron may have spin up or spin down with different probabilities, also for a nonmagnetic substrate. For a spin-up emitted electron there is only one possible process, the direct one [Fig. 2(a)], but for a spin-down one there are two possible processes, the direct and the exchange one [Fig. 2(b)]. To obtain the initial state with a core hole the KS equations are solved self-consistently with the constraint that the occupation number of the spin-down $1s$ core state is zero. The details about the orbitals and the method we use to treat the sums over the valence states are described in the Appendix.

The same theoretical treatment has been previously used to calculate the deexcitation spectra of metastable He atoms on Ni[7] and on Cu.[8] In these works, however, the interaction of the atom with the surface has not be taken into account and the deexcitation process was treated using wave functions for both, metal and atomic states, which were calculated independently. The metal-atom interaction can lead to a modification of the unperturbed surface electronic structure, and to take care of this it is necessary to perform a self-consistent calculation of the interacting metal-atom system. However, the need to account for the metal-atom interaction opens a relevant question about the dynamical effect related to the sudden disappearance of the core hole in the final state of a CVV Auger process.[15,16] In this work we do not consider this final state effect and we calculate the Auger transition probability using the electron wave functions of the initial excited state.

IV. RESULTS

In this section we present the results for the deexcitation process of a metastable 2^3S helium atom (He*) interacting with a Na metal surface. This substrate is described by a jellium with $r_s = 3.93a_0$. Differently from our previous calculations,[11,12] in this case we make use of the LSDA and solve the Kohn-Sham equation in a sphere of radius $s = 9.0a_0$.

First of all, in order to test the possibility of describing the metastable helium atom in its triplet state by using the DFT and the LSDA, we have studied the free atom case. The self-consistent solution obtained when the atom is constrained to have only a spin-up electron in the $1s$ level is the triplet state, with two parallel spin-up electrons, one occupying the $1s$ atomic state and the other electron the $2s$ state. Our calculated excitation energy of this system, i.e., the difference between the total energy of the excited atom, $E(\mathrm{He}^*)$, and that of the atom in its ground state, $E(\mathrm{He})$, is given by

$$E(\mathrm{He}^*) - E(\mathrm{He}) = (-58.24 + 78.10)\ \mathrm{eV} = 19.86\ \mathrm{eV}. \tag{13}$$

This value is in good agreement with the experimental result of 19.82 eV.[1]

Now we investigate how the induced density of states (IDOS) of both spin populations varies with the adatom distance from the metal surface. In the different panels of Fig. 3 we present the IDOS's for He* at distances $z = 7.0a_0$, $z = 5.0a_0$, and $z = 3.0a_0$ from the jellium edge. Note that the $1s$ Helium level always lies below the valence band and it is not shown in the figures. When the atom is far from the surface, at $z = 7.0a_0$ [panel (a)], the IDOS of the spin-up population (solid line) displays a narrow peak just below the Fermi level which is due to the occupied $2s$ state and a more pronounced peak at about 1.0 eV above E_F due to the empty $2p$ resonance. Observe how the metal-atom interaction broadens the atomic levels into resonances. It is also worth noting that from the values of the ionization potential of a free metastable He atom (about 4.7 eV) and of the work function of the Na substrate (about 2.7 eV), one may expect the $2s$ resonance to be peaked at a lower energy. In our LSDA calculation such resonance is quite close to the Fermi level and not completely occupied, indicating a small charge transfer to the substrate. For this reason the $2s$ electron is partially delocalized in the metal and the deexcitation phenomenon also comprises a contribution that can be considered as a RI+AN process. Another point that we can observe is that the spin-down population (dashed line) has no occupied states on the atom, since in this case both, the $2s$ and $2p$, resonances lie much above the Fermi level. As the atom approaches the surface closer and closer [see Figs. 3(b) and 3(c)], the spin-up $2s$ resonance broadens and becomes smoother as a consequence of a stronger interaction with the electronic charge of the metal, and slightly shifts to lower energies. Observe that the interaction with the substrate causes also a partial occupation of the spin-down states.

In Fig. 4 we present the Auger deexcitation spectra of the excited He* atom located at various distances from the surface. In the figure all energies are referred to the bottom of the valence band. The maximum energy of each Auger spectrum lies at $E = 2E_F - E_C$, where E_C is the eigenvalue of the empty $1s$ state of He* at a given distance from the substrate. So the different energy maxima of the Auger spectra obtained with the atom at various distances are the consequence of the variation of E_C with the metal-atom separation.

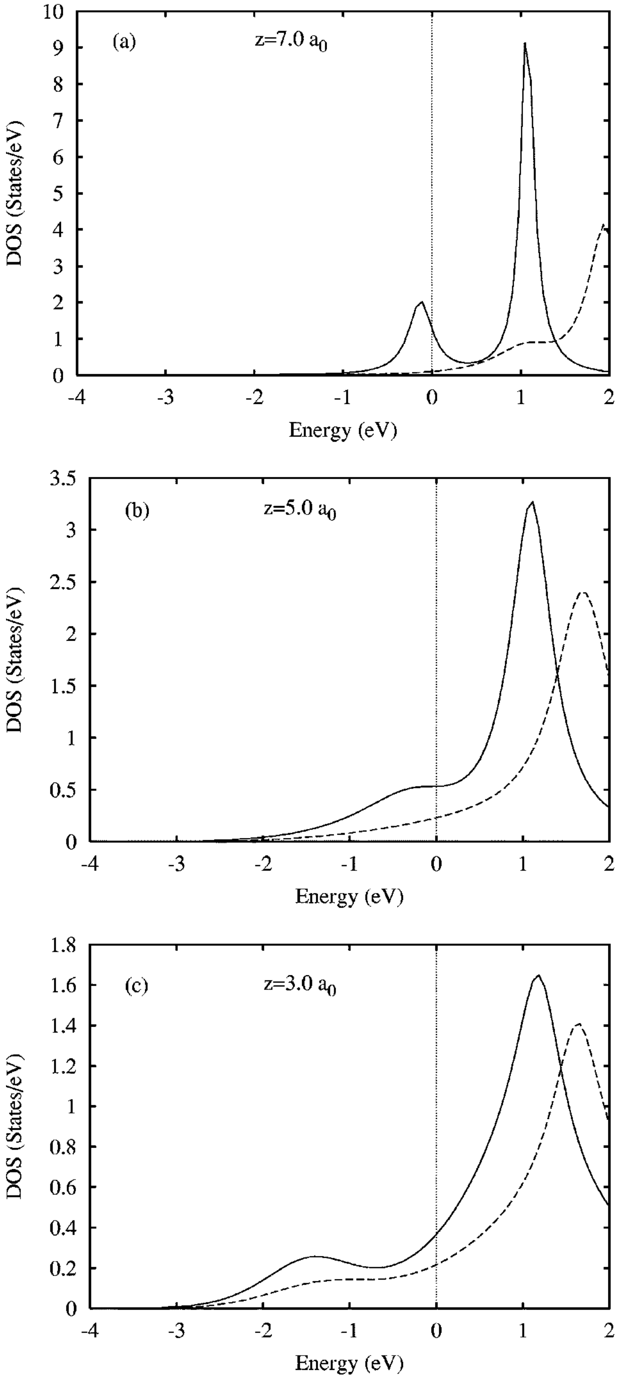

FIG. 3. He* atom at different distances from the Na surface. IDOS's for both spin-up (solid line) and spin-down (dashed line) populations at $z=7.0a_0$ (a), $z=5.0a_0$ (b), and $z=3.0a_0$ (c). The dotted line is the Fermi level.

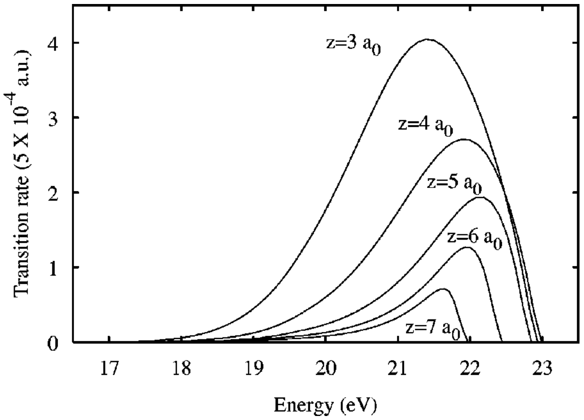

FIG. 4. Auger transition rates for the atom at $z=7.0a_0$, $6.0a_0$, $5.0a_0$, $4.0a_0$, and $3.0a_0$.

As is well known, the eigenvalues obtained by solving the KS equation do not allow one to determine the correct kinetic energy of the Auger electron. However, we assume that they can provide a reasonable description of the variation with distance of the binding energy of the core level and so of the energy position of the Auger spectra. The comparison of the line shapes clearly shows a significant dependence of the Auger transition probability on the distance of the atom from the substrate. In particular, when the atom approaches the surface the deexcitation rate increases as a consequence of the increasing overlap between atom and metal wave functions. We also observe that the width of these curves rises as the metal-atom separation decreases. This is essentially due to the broadening of the $2s$ resonance (Fig. 3).

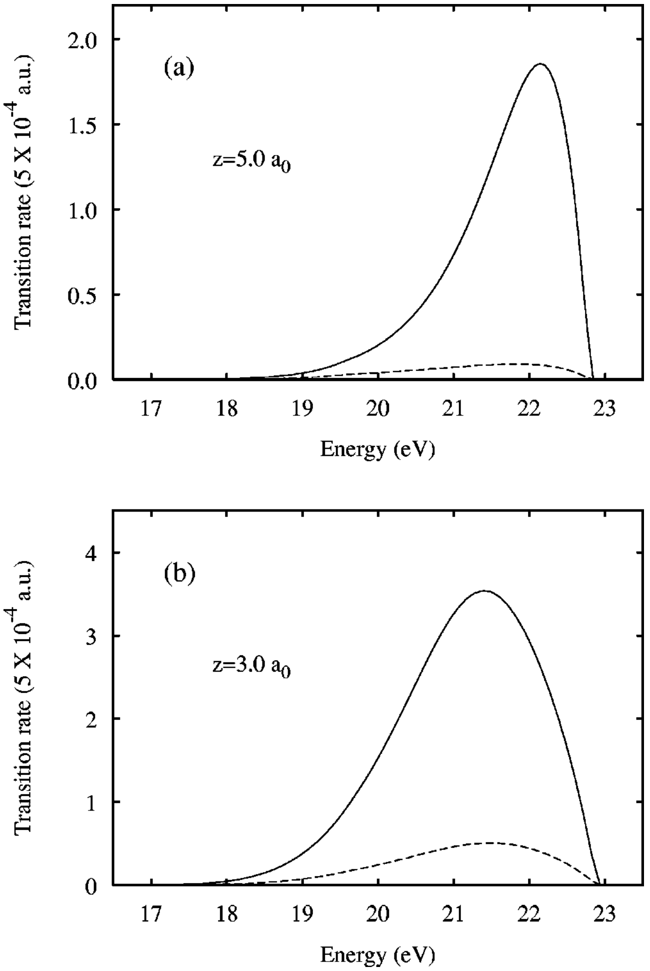

FIG. 5. Auger transition probabilities for the emission of spin-up (solid line) and spin-down (dashed line) electrons. (a) He* at $z=5.0a_0$, (b) He* at $z=3.0a_0$.

In Fig. 5 we display the Auger transition probabilities for the emission of spin-up and spin-down electrons. In particular, we present the results for the atom located at two different distances from the surface, namely, at $z=5.0a_0$ [panel (a)] and at $z=3.0a_0$ [panel (b)]. Our results show a strong polarization of the produced Auger electrons. In particular, we find that the probability for the emission of spin-up electrons is always significantly greater than that for spin-down electrons. Such a polarization effect is determined by two contributions. First, the Auger transition probabilities for the emission of spin-up and spin-down electrons are determined by distinct matrix elements. Second, the polarization effect is significantly affected by the difference in the local DOS's between the two spin populations on the metastable He atom.

In order to calculate the total deexcitation probability $N(E)$ [see Eq. (4)], we have to determine the velocity $v(z)$ of the metastable He* atom and its survival probability as a function of z, $n(z)$. To evaluate the velocity of the atom using the energy conservation law (7), we have to provide an expression for the interaction potential $U(z)$ between the atom and the metal surface. Since at present we are not able to calculate the total energy of an excited atom near the surface, we estimate such an interaction potential using the effective medium theory.[17] In particular, we have calculated by LSDA the total energy of a metastable He* atom embedded in bulk jellium of different electronic densities to simulate the different atom-surface separations.[18] We have fitted the effective medium theory results by the Morse potential

$$U_m(z)=a\{1-\exp[-c(z-z_0)]\}^2-a, \tag{14}$$

where the parameters a, c, and z_0 represent the depth of the well, its width, and the position of the minimum, respectively. The fitted values are $a=60$ meV, $c=0.55a_0^{-1}$, $z_0=5.2a_0$. The minimum of the potential energy is in agreement with previous estimates.[19] To calculate the velocity we consider an initial kinetic energy of the metastable atom of $E^i_{\mathrm{kin}}=60$ meV.[10] In this way the turning point of the trajectory of the atom is $z_{tp}=3.6a_0$.

To compute the survival probability (5) we also have to determine the quantity $R(z)$. This is done using Eq. (3), i.e., integrating in energy the spectra, $P(E,z)$, at the various distances. Since we have calculated these spectra for a limited number of positions in the range of distances between $3.0a_0$ and $7.0a_0$, we need to interpolate our results in this range and to continue these for distances above $7.0a_0$. The continuation is performed using an exponential law

$$R(z)=A\exp(-Bz), \tag{15}$$

where the parameters A and B are obtained by fitting to the tail of the calculated $R(z)$ at large z. This exponential law at large distances follows from the decrease of the Auger matrix element with increasing atom-metal separation which is essentially governed by the exponential decay of the wave function of the metal valence electron involved in the transition.[5,20,21]

In Fig. 6 we present the probability $n(z)$ that a He* atom is still in its excited state at a distance z from the jellium edge [Eq. (5)]. In particular, the solid line refers to the survival probability when the atom is approaching the surface, while the dashed line is that for the atom which is moving away from the jellium edge after the scattering process, for normal incidence. Observe that the deexcitation events occur essentially in a limited range of distances between $z=3.6a_0$ (the turning point) and $z\approx 8a_0$. Our result also shows that the probability that an atom is reflected without deexcitation is ≈ 0.5.

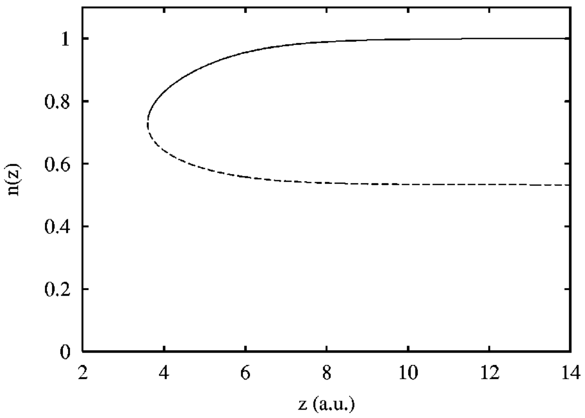

FIG. 6. Survival probability $n(z)$ of the excited He* atom. The solid (dashed) line indicates the survival probability of He* before (after) the impact with the metal.

There are reasons to believe that our calculated value does overestimate the exact one.[1,3] First of all, as previously observed, in our calculation the metastable helium atom is partially ionized even at large distance from the surface. The result of this is that the fraction of the $2s$ wave function which is delocalized in the substrate does not participate in the described decay process and cannot contribute to the emission probability. A second point that we want to stress is that our results are obtained under the hypothesis of normal scattering: a different angle of incidence should increase the time spent by the atom near the surface and so decrease the survival probability. We have also to consider that the lack of charge neutrality[17] in the embedding region may be relevant if the embedding sphere is not large enough to contain the region of space mainly perturbed by the presence of the He atom on the surface. In our calculation a small deficit of electronic charge is present even using a sphere of radius $s=9.0a_0$. Taking a much larger embedding region the accuracy (and the computational effort) of the calculation increases and we find that while the shape of the Auger spectra is essentially unaffected, the survival probability slightly decreases. Finally, another source of inaccuracy in our calculation could be the estimate of the interaction potential between atom and surface. Indeed, the effective medium theory usually gives a reasonable description of the main features of the atom-surface potential, but the quantitative agreement with the result of a more accurate analysis is not always satisfactory. For example, small variations of the classical turning point can change significantly the final survival probability $n(z=+\infty)$.

At this point we can calculate the total Auger electron energy distribution using Eq. (4) and compare it with the experimental result.[10] To make such a comparison we have

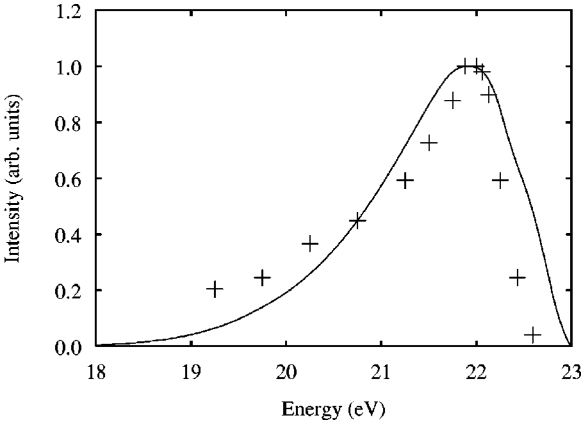

FIG. 7. 2^3S He*-deexcitation spectral profile of a Na surface. The solid line is the theoretical result. The crosses indicate the experimental data.(Ref. 10) The energies are referred to the bottom of the valence band.

to take into account the broadening contributions due to the limited instrumental resolution [full width at half maximum $=0.15$ eV][10] and to the finite lifetimes of both initial and final states. In this case the latter contribution can be neglected. Indeed, assuming that the Auger decay is the most important deexcitation process, the lifetime of the initial state is determined by the transition rate $R(z)$. So the energy width is less than 0.01 eV (Ref. 22) (in the range of distances we considered) and does not affect the line shape. Besides, since the finite lifetime of the final state is due to the holes in the valence band, one expects negligible effects at the top of the emission band and significant broadening in the low-energy region. However such an effect at lower energies is difficult to observe in the experimental curves because it is largely obscured by secondary electrons.

In Fig. 7 we report the comparison between the theoretical and the experimental results. The energy is referred to the bottom of the valence band and the experimental data have been shifted in order to align the maxima of the two spectra. The experimental profile shows a pronounced peak near the top of the emission band, while the tail at low kinetic energy is essentially the background contribution due to secondary electrons.[10] Our theoretical result predicts quite well the shape of the emission band, but somewhat overestimates the width of the peak at high energy.

V. CONCLUSIONS

In this paper we have presented a full *ab initio* calculation of the Auger deexcitation line shape of a slow metastable He atom on a Na metal surface, in which the particle motion is treated in the adiabatic approximation. Our theoretical result reproduces quite well the characteristic asymmetric shape of the experimental data.[23]

We wish to stress that differently from previous approaches[7,8,24] which studied deexcitation or neutralization events of atoms at surfaces, we calculate self-consistently the electronic properties of the interacting atom-metal system within the DFT framework. This allows for a better description of the electronic structure than that provided by methods that determine the wave functions of both, metal and atomic, states independently or treat the effects of the presence of the atom on the surface perturbatively. On the other hand, our approach does not account for several many-body phenomena such as the sudden disappearance of the initial core hole in the CVV Auger process or the interaction of two core holes in the valence band.

Finally, we point out that we calculate the Auger transition matrix elements without approximations, starting from a single Slater determinant description of the wave functions of the interacting He*-metal system. These rates are instead often derived from the knowledge of the local DOS of the system weighted by suitable terms (more recently also in a DFT framework).[9] The validity of this approximation has been discussed since long in the more general realm of CCV and CVV Auger transitions.[16,23,25] For example, we recall that it is well accepted that CCV spectra probe the local DOS of a screened ionized core hole. Since there is a core hole in the initial and final states, either initial or final state wave function may be used in calculating the Auger rates with no appreciable difference.[11] For a CVV transition, one expects to get (final state) information on the local DOS around a neutral atom. However, the effect of the initial ionized core cannot be neglected, since it crucially affects the Auger rates entering the golden rule expression. Such a contribution, which can only be included phenomenologically by expressions that use the crystal DOS, is correctly accounted for by our approach of the MDS process.

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APPENDIX

The wave functions of the core state and of the Auger electron involved in the transition are

$$\psi_C(\mathbf{r})=R_{l_c,\downarrow}(E_c,r)Y_{l_c,m_c}(\Omega), \tag{A1}$$

$$\psi_A(\mathbf{r})=\sum_l \sum_{m=-l}^{l} R_{l,\sigma_A}(k,r)Y_{l,m}(\Omega)Y^*_{l,m}(\hat{k}), \tag{A2}$$

where $Y_{l,m}(\Omega)$ are spherical harmonics and σ_A is the spin index. For the Auger electrons we assume a free-particle energy–wave-vector ($\mathbf{k}$) relation, $E=k^2/2$, the energy of the emitted electron being determined by the δ-function energy conservation in Eqs. (9) and (8). More details on the radial parts of these wave functions are in Ref. 11.

In the calculation of the transition probabilities we have to evaluate the sum over the continuum of all valence states. This can be performed using the following relationship with the Green's function, $G(\mathbf{r},\mathbf{r}';E)$, of the system[26] (hereafter $E=E'+i\delta$, with E' the energy belonging to the continuous spectrum of the system and δ a positive, infinitesimal quantity):

$$\sum_v \delta(E-E_v)\psi_v(\mathbf{r})\psi_v^*(\mathbf{r}')=\frac{1}{2\pi i}[G(\mathbf{r},\mathbf{r}';E)-G^*(\mathbf{r}',\mathbf{r};E)]. \tag{A3}$$

In this case we need the Green's functions for both the spin-up and the spin-down populations. In our calculation, each of them is expanded on the linearized augmented plane wave (LAPW) basis set:[14]

$$G^\sigma(\mathbf{r},\mathbf{r}',E)=\sum_{\mu\mu'}\mathcal{G}^\sigma_{\mu\mu'}(E)\chi^\sigma_\mu(\mathbf{r})[\chi^\sigma_{\mu'}(\mathbf{r}')]^*, \quad \sigma=\downarrow,\uparrow. \tag{A4}$$

Using the identity

$$\delta(E+E_c-E_a-E_b)=\int d\epsilon\,\delta(\epsilon-E_a)\,\delta(E+E_c-E_b-\epsilon), \tag{A5}$$

one can exploit the relationship of Eq. (A3) and integrating Eqs. (8) and (9) over the full solid angle we obtain the following expressions for $\mathcal{P}^\uparrow(E,z)$ and $\mathcal{P}^\downarrow(E,z)$:

$$\begin{aligned}\mathcal{P}^\uparrow(E,z)=8\sum_{I,I'}\sum_{N,N'}\sum_{L_A} C^*_{L_i',L_n',L_A}C_{L_i,L_n,L_A}\\ \times\frac{1}{(2l_i+1)(2l_i'+1)}S^\uparrow_{I,I';N,N'}(E)\\ \times M(i',n',l_A,l_i',l_n',\uparrow)M(i,n,l_A,l_i,l_n,\uparrow),\end{aligned} \tag{A6}$$

$$\begin{aligned}\mathcal{P}^\downarrow(E,z)=8\Bigg\{\sum_{I,I'}\sum_{N,N'}\sum_{L_A} C^*_{L_i',L_n',L_A}C_{L_i,L_n,L_A}\\ \times\Bigg[\frac{1}{(2l_i+1)(2l_i'+1)}S^\downarrow_{I,I';N,N'}(E)\\ \times M(i',n',l_A,l_i',l_n',\downarrow)\;\; M(i,n,l_A,l_i,l_n,\downarrow)\\ -\frac{1}{(2l_n+1)(2l_i'+1)}\mathrm{Re}S^\downarrow_{I,I';N,N'}(E)\\ \times M(i',n',l_A,l_i',l_n',\downarrow)M(n,i,l_A,l_n,l_i,\downarrow)\Bigg]\Bigg\},\end{aligned} \tag{A7}$$

where $I=(i,L_i)$, $N=(n,L_n)$, $L_i=l_i,m_i$, $L_n=l_n,m_n$, and $L_A=l_A,m_A$. The terms M and S are given by

$$\begin{aligned}M(i,n,l_A,l_i,l_n,\sigma)\\ =\int drdr'r^2r'^2f^\downarrow_{i,l_i}(r)R_{l_c,\downarrow}(E_c,r)\\ \times\frac{r_<^{l_i}}{r_>^{l_i+1}}f^\sigma_{n,l_n}(r')R_{l_A,\sigma}(k_A,r'),\end{aligned} \tag{A8}$$

$$\begin{aligned}S^\sigma_{I,I';N,N'}(E)=\int_0^{E_F}d\epsilon\Delta\mathcal{G}^\downarrow_{I,I'}(\epsilon)\Delta\mathcal{G}^\sigma_{N,N'}(E+E_c-\epsilon)\\ \times\Theta(E_F-E-E_c+\epsilon),\end{aligned} \tag{A9}$$

where

$$\Delta\mathcal{G}^\sigma_{n,n',L_n,L_n'}(E)=\frac{1}{2i}\{\mathcal{G}^\sigma_{n,n',L_n,L_n'}(E)-[\mathcal{G}^\sigma_{n',n,L_n',L_n}(E)]^*\} \tag{A10}$$

and $\sigma=\uparrow,\downarrow$. In Eq. (A9) the range of integration and the $T=0$ K Fermi factor Θ account for the fact that in Eqs. (8) and (9) one has to sum over the occupied states in the valence band.

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