Double photo-ionization of He near a polarizable surface

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We calculate the differential cross-section of the direct double photo-ionization of He physisorbed on a polarizable surface. By including the influence of the surface potential in the correlated two-electron final state wavefunction, we show that the differential cross-section carries detailed information on the electronic correlations at the surface. In particular, photo-emission along opposite directions, which is prohibited in the free space, is allowed if the surface potential is long-ranged.

The simultaneous photo-emission of two electrons $e_1$ and $e_2$ (direct double photo-ionization, DPI) is a straightforward manifestation of electronic correlations in the initial and/or final state. Despite this fundamental aspect, the experimental determination of the differential cross-section (DCS) of this process and quantitative agreement with theoretical calculations are relatively recent achievements even in the simplest atomic systems. Stimulated by the present availability of bright synchrotron radiation sources, it has now become of interest to look at the DPI process also in solid-state systems, in order to investigate electronic correlations in the material, particularly near the surface.

As a step in this direction, in this paper we study the angular distribution of photo-electrons in a DPI process in the simplest two-electron atomic system, an He atom, adjacent to a polarizable surface. By virtue of the dipole interaction with the surface, at low temperature an He atom weakly adheres to the surface (physisorption) at a rather large distance $d$ from the surface edge. The He (correlated) ground state is only slightly distorted by the weak atom-surface interaction; therefore, possible effects due to the surface should primarily be regarded as final state effects. In fact, we shall demonstrate that the DCS of the DPI process from physisorbed He is affected by the nearby surface and, in particular, atomic selection rules are relaxed in a way that depends on the surface potential. Therefore, the measurement of the DPI cross-section from physisorbed He might give detailed informations on the surface potential, in analogy with the angle-resolved spectroscopy of image states.

In the velocity gauge, the DCS of the DPI process is

$$d\sigma \propto \left| \langle \Psi_i | \hat{\mathbf{e}} \cdot (\mathbf{p}_1 + \mathbf{p}_2) | \Psi_f \rangle \right|^2,$$

where $\hat{\mathbf{e}}$ is the light polarization vector, $\mathbf{p}_i$ is the momentum operator for $e_i$, and $\Psi_i$ and $\Psi_f$ are the two-electron initial and final state, respectively. $\Omega$ denotes the solid angle at which $e_i$ is detected with energy $E_i$, and $E = E_1 + E_2$.

We next consider the case of equal energy sharing, $E_1 = E_2 = E/2$, between the photo-electrons. In this case, the selection rules apply for free He, i.e., photo-electrons cannot be emitted either in the same or in opposite directions and with the same energy. Equation (2a) derives from the form of the operator $\mathbf{p}_1 + \mathbf{p}_2$: the DCS is zero if the final state corresponds to a channel with the photo-electrons emitted with zero center-of-mass momentum. This is easily seen if $|\Psi_i\rangle$ is taken as the uncorrelated product of two plane waves with wavevectors $\mathbf{k}_1\mathbf{,} \mathbf{k}_2$, but Eq. (2a) holds also when more realistic final states are used, with the $e_1\mathbf{-} e_2$ repulsion correctly taken into account; it is such repulsion which leads to the second selection rule, Eq. (2b).

Eqs. (2a) and (2b) have been experimentally confirmed for free He.

Obviously, a surface breaks the translational invariance in one direction and we may argue that the DCS has a different shape in this case. The system we are mainly interested in is the surface of a metal, treated here within the jellium model. We shall demonstrate by explicit calculations that for physisorbed He i) the selection rule (2a) is relaxed when the long-ranged potential outside the jellium surface is taken into account; ii) if, on the other hand, the surface potential is characterized by a screening length $l_0$, atomic selection rules are recovered if $l_0$ is comparable to or smaller than the physisorption distance $d$; in this regime, on the other hand, the DCS becomes peaked along particular directions.

In proximity of a polarizable surface, the Coulomb interaction between two charges is renormalized with respect to vacuum and, in general, it is also dependent on the dynamical state — energy and momentum — of the interacting particles. This renormalization affects both the $e_1\mathbf{-} e_2$ interaction, $V_{12}$, and the electron-ion core interaction, $V_{\text{ion}}$; in addition, the renormalization of the Coulomb interaction gives rise to a single-particle potential (surface potential) $\Sigma_i(z_i)$ for $e_i$; outside a metallic surface, $\Sigma_i(z_i)$ is long-ranged, and coincides with the classical image potential $-1/4z_i$ at large $z_i$ (we consider...
a surface filling the half-space $z < 0$; energy is measured with respect to vacuum; hartree atomic units are used throughout), while it converges to the inner potential inside the metal (see inset of Fig. 1). The final state two-electron Hamiltonian $H_f$ can be written as

$$H_f = H_1 + H_2 + V_{12},$$

$$H_i = -\frac{1}{2} p_i^2 + \Sigma_i + V_{ion,i},$$

where the single-particle Hamiltonian $H_i$ acts on the coordinates $r_i$ of $e_i$. Because of the large ionic mass, $V_{ion,i}$ is simply the potential of a dipole comprising the ion core and its classical image charge and, therefore, it is short-ranged. Accordingly, we neglect $V_{ion,i}$ with respect to $\Sigma_i$, and we define an approximate single-particle Hamiltonian $H_i = -\frac{1}{2} p_i^2 + \Sigma_i$ as the limit of $H_i$ at large distances from the surface.

To calculate the two-electron eigenstates of the approximate final state Hamiltonian $H_f = H_1 + H_2 + V_{12}$ we consider wavefunctions of the form

$$\langle r_1, r_2 | \psi_f \rangle = \psi_{\alpha_1}(r_1) \psi_{\alpha_2}(r_2) M_{\alpha_1 \alpha_2}(r).$$

The function $M_{E_1 K_1 E_2 K_2}(r)$ is the solution of

$$\left\{-\nabla_R^2 - \frac{\partial^2}{\partial z^2} - i \left[K \cdot \nabla_R + F(z_1, z_2) \frac{\partial}{\partial z}\right] + V_{12}(R, z)\right\} M_{E_1 K_1 E_2 K_2}(R, z) = 0,$$

where $K = K_1 - K_2$, and we have defined $F(z_1, z_2) = f(\phi_{\alpha_1, z_1}) - f(\phi_{\alpha_2, z_2})$, with $f(\phi_{\alpha, z}) = \phi_{\alpha, z}^{-1} \partial \phi_{\alpha, z} / \partial z$. Note that, due to the presence of the surface potential, $M(R, z)$ depends parametrically on the center of mass of the two electrons through the function $F(z_1, z_2)$; in the following we take $F(z_1, z_2) = -i(k_{z_1} - k_{z_2})$, with $k_{z_i} = \sqrt{2(E_i - K_i^2/2)}$; this is the value of $F(z_1, z_2)$ if $\phi_{E_i K_i}(z_i)$ is a plane-wave with wavevector $k_{z_i}$. The full (i.e., energy and momentum dependent) calculation of $V_{12}$ is a complicated task which, to our knowledge, has not been undertaken so far. In this work we take the $e_1-e_2$ interaction $V_{12}$ as the bare Coulomb interaction. Note that the above approximations correspond to calculate the two-electron function $M(R, z)$ in the free space; the influence of the surface, however, is still present in the complete wavefunction through the single-electron functions $\psi_{\alpha_i}(r_i)$ in Eq. (7).

We take $\Sigma_i(z_i)$ in a static approximation $V(z_i)$, with

$$V(z) = \begin{cases} -U_0/(4z^2) + 1 & z < 0 \\ (4z)^{-\frac{1}{2}} e^{-\zeta/\ell_0} \{1 - e^{-\zeta/\ell_0}\} & z > 0 \end{cases},$$

which is the analytical form proposed in Ref. with the inclusion of an exponential factor $e^{-\zeta/\ell_0}$ characterized by a screening length $\ell_0$. When $\ell_0 \to \infty$, $V(z)$ decays as the image potential at large $z$ (see inset in Fig. 1); inside the metal, $V(z)$ converges to the inner potential $U_0$. As mentioned above, we assume that the initial state is the unperturbed ground state of the He atom, which we describe by the variational wavefunction

$$\langle r_1, r_2 | \psi_i \rangle = e^{-\sum_i r_i} \left[1 + \frac{e^{-\alpha r}}{2}\right] \sum_i \frac{\sinh \beta r_i}{\beta r_i},$$

with variational parameters $\beta = 1.08\text{a.u.}$, $\alpha = 0.15\text{a.u.}$.

Figure 1 shows a polar representation of the calculated DCS with $\ell_0 = \infty$. In order to better single out the effect of the surface, we have chosen a configuration in which one electron is emitted at a large polar angle with respect to the normal to the surface; then, we plot the DCS with the other electron emitted with a polar angle in the range $(-\pi/2, \pi/2)$ and in a coplanar geometry; the condition $k_1 + k_2 = 0$ is approximately met when both electrons are emitted in the $z > 0$ half-space at large polar angles. We consider linearly polarized light with the electric field parallel (s-polarization) or perpendicular (p-polarization) to the surface.

For comparison, we show in Fig. 1 the DCS calculated both with the surface potential given by Eq. (8) and with $V(z) = 0$ everywhere; note that the latter case, with no surface potential present, is not fully equivalent to previous calculations of the DCS for the free He, because the electron-ion interaction is neglected in our calculation. Nonetheless, the shape of our calculated DCS is in general agreement with those reported in Refs. In particular, the atomic selection rules (2a) and (2b) are strictly obeyed.
In the s-polarization the selection rules which apply in the atomic case, which inhibit simultaneous emission of \( e_1 \) and \( e_2 \) in the same as well as in opposite directions, are still strictly obeyed in presence of the surface. In general, there is very little difference between the full calculation and the \( V(z) = 0 \) case. This is at difference with the p-polarization; in this case, in fact, the surface changes the DCS and shifts photo-emission towards larger polar angles; note, in particular, that the emission in opposite directions is allowed, in sharp contrast with the atomic case.

The relaxation of the atomic selection rules in the physisorbed system is due to the long-range nature of the surface potential. In Fig. 2 we show the calculated DCS for selected values of \( l_0 \), from infinity to \( l_0 \) comparable to or smaller than \( d = 6.5a.u. \). The different curves are similar to each other (and to the \( V(z) = 0 \) case) in the s-polarization. For p-polarization, instead, the photo-electron distribution is narrower for small values of \( l_0 \). Moreover, the atomic selection rule \( \mathbf{k}_1 + \mathbf{k}_2 \neq \mathbf{0} \) is relaxed only as long as \( l_0 \gg d \); the DCS at large polar angles, in fact, drops rapidly when \( l_0 \) becomes comparable to the physisorption distance; at the same time, for the lowest values of \( l_0 \) the DCS develops modulations, and becomes peaked along selected directions, corresponding to interference between electrons emitted directly in the free space and those which reach the vacuum after a reflection due to the surface potential.

In conclusion, we have analyzed the modifications induced on the DPI of He by a polarizable surface. We have shown that the DCS depends on the screening properties of the surface; in particular, the presence of a long-ranged surface potential is associated with a substantial relaxation of the atomic selections rules. On the other hand, the precise angular distribution of the photoelectrons depends on the details of the surface, such as the precise shape of the potential or the physisorption distance. Therefore, DPI from metals promises to become an interesting tool in assessing the screening properties of the surfaces.

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1 O. Schwarzkopf, B. Krässig, J. Elminger, and V. Schmidt, Phys. Rev. Lett. 70, 3008 (1993); R. Dörner et al., Phys. Rev. A 57, 1074 (1998).
2 J. Berakdar, Phys. Rev. B 58, 9808 (1998).
3 For a recent review, see R. M. Osgood and X. Wang, Solid State Physics, 51, 1 (1997).
4 For atomic He, previous calculations have shown that for equal energy sharing the DCS calculated with the velocity and the length gauge give very similar results (while the absolute cross-section may differ). Moreover, the velocity gauge gives better agreement with experiments when the two gauges differ quantitatively, such as for unequal energy sharing.
5 These selection rules do not hold if \( E_1 \neq E_2 \).
6 H. G. Eriksson, B. R. Karlsson, and K. A. I. L. Wijewardena, Phys. Rev. B 31, 843 (1985).
7 F. J. García de Abajo and P. M. Echenique, Phys. Rev. B 46, 2663 (1992).
8 We can make a comparison with the so-called 3C wave-
functions used in three-body scattering problems [C. R. Garibotti and J. Miraglia, Phys. Rev. A 21, 572 (1980); M. Brauner, J. S. Briggs, and H. Klar, J. Phys. B 22, 2265 (1989); F. D. Colavecchia, G. Gasaneo, and C. R. Garibotti, Phys. Rev. A 57, 1018 (1998)] and, in particular, in the calculation of the DPI cross-section of atoms (see Ref. 9); here, $\psi_{\alpha i}(r_i)$ is determined by the single-particle surface potential $V(z_i)$ rather than by the ion core Coulomb potential, as in the above mentioned calculations.

9 F. Maulbetsch and J. S. Briggs, Phys. Rev. Lett. 68, 2004 (1992); L. R. Andersson and J. Burgdörfer, ibid. 71, 50 (1993); Y. Qiu, J.-Z. Tang, J. Burgdörfer, and J. Wang, Phys. Rev. A 57, R1489 (1998).

10 This is in analogy to what is usually done in the calculation of the DPI cross-section of atoms, where the two-electron distortion factor $M^*(r)$ is calculated neglecting terms which arise from the bare electron-ion interaction. See also note 8.

11 R. O. Jones, P. J. Jennings, and O. Jepsen, Phys. Rev. B 29, 6473 (1984); P. J. Jennings, R. O. Jones, and M. Weinert, ibid. 37, 6113 (1988).

12 The matching conditions for $V(z)$ and $dV(z)/dz$ at $z = 0$ give the constants $A = 4U_0/\lambda - 1$, $B = (\lambda/2+1/l_0)(4U_0/\lambda A)$.

13 C. Le Sech, G. Hadinger, and M. Aubert-Frécon, Z. Phys. D 32, 219 (1994).

14 F. Maulbetsch and J. S. Briggs, J. Phys. B: At. Mol. Opt. Phys. 27, 4095 (1994)