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# Double photoemission from the surface state of Cu(1 1 1)

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## Abstract

We calculate the double photoemission spectra from the occupied surface state of Cu(1 1 1). We present and discuss the regularities in the angular and energy distributions of the process. For the emission from the d-band of Cu(1 1 1), the depth of generation of correlated photoelectron pairs is estimated. © 2002 Elsevier Science B.V. All rights reserved.

*Keywords:* Surface electronic phenomena (work function, surface potential, surface states, etc.); Photoelectron spectroscopy; Green's function methods; Many body and quasi-particle theories

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## 1. Introduction

Surface states (SS) of metals are recognized as an interesting candidate for the investigation of electronic correlations. Considerable attention is paid to the electron–electron interaction in the occupied and unoccupied SS [1,2], where the scattering happens between the SS electron and the ground state electrons of the system. In the present paper we discuss the application of the new type of correlation-accented techniques: the double photoemission (DPE). In this process the absorption of a single photon leads to the simultaneous excitation and emission of two photoelectrons. The distinct feature of DPE is that the spectra of the photoelectron pairs are strongly dependent on the interaction between these two excited particles [4]. In fact, the DPE process is merely inhibited in the independent-electron approximation.

DPE has been recently investigated experimentally [3]: photoelectrons were detected with energy and momentum resolution, the simultaneity of their creation was controlled by the time-of-flight technique. In previous works [7,8] we investigated the DPE from the conduction band of Cu and showed, in particular, that the density of the initial states has a profound influence in these kind of experiments. In the present work we envisage the application of the DPE technique for the investigation of the occupied surface state of Cu(1 1 1). Using the approximation for the two-particle photocurrent [5,8] we calculate the two-photoelectron emission spectra and compare them with the results of a simple model. In addition, to reveal the surface sensitivity of the DPE process, we calculate the layer-dependent DPE patterns from the d-band of the same face of copper in order to estimate the depth of generation of the photoelectron pairs.

## 2. Approximations and numerical realization

In single photoemission the single-particle Green function (IGF) is needed for the

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description of the ground and excited states of the surface. The ground states are provided adequately by the density functional theory within the local-density approximation whereas the treatment of excited states is a more involved task [9]. In DPE the two-particle Green function (2GF) [10] is required which is a much more complicated object than its one-particle counterpart. Our approach towards the derivation of a correlated two-particle Green function that can be implemented numerically can be summarized as follows (for the details cf. [5–8]): To a zero order approximation the 2GF is an antisymmetrized product of two 1GF, each of them describes the motion of the individual photoelectrons as moving independently in the crystal potential but obeying the Pauli exclusion principle. In the ladder approximation one goes beyond this zero order approximation by allowing the interaction between the photoelectrons. In this study we assume the coupling to be mediated by a Coulomb screened potential with the screening length  $\lambda$  being derived from a Thomas–Fermi type approach, i.e. it depends on the density of states at the Fermi level [11]. Evaluating the terms in the ladder approximation within a realistic model of electronic band structure of the surface is difficult numerically. Therefore we designed a method in which the screened interaction potential is incorporated in a non-perturbative way into the 1GF [5–8]). As a result, the 2GF becomes an antisymmetrized product of two ‘effective’ 1GFs. Each of the 1GFs depends dynamically on the properties of the two photoelectrons.

This procedure allows to express the two-electron photocurrent through certain types of single-particle matrix elements [5–8] that resemble formally the ones encountered in single photoemission. Finally, we utilize the ab initio computer code for electron spectroscopies [12] and extend it to end up with the DPE mode.

### 3. Single-particle properties

In general, the Coulomb interaction is accompanied by the energy and momentum transfer

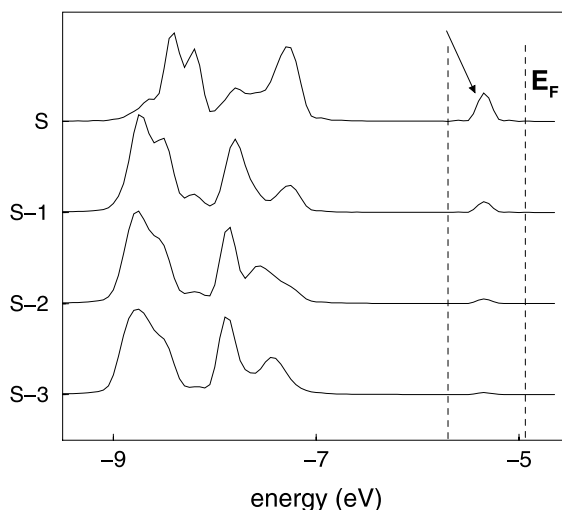


Fig. 1. Layer-resolved density of states (LDOS) of Cu(111) at  $\mathbf{k}^{\parallel} = 0$ . Dashed lines depict the integration range over the initial states for the DPE calculations (see text), arrow marks the position of the surface state.

within the photoelectron pair. Contrary to single photoemission process, individual surface-parallel momenta of the electrons  $\mathbf{k}_{1,2}^{\parallel}$  are not conserved in the DPE event. However, one of the consequences of the approximations of our model is that the final state surface-parallel momenta of emitted electrons remain good quantum numbers. Namely, only those initial states are participating in the optical transition, which are characterized by the same irreducible representation of the translation group, as the asymptotic final states. In particular, this means that  $\mathbf{k}^{\parallel}$ -resolved density of states is a meaningful quantity for the rough analysis of the calculated DPE spectra.

So, first, we ensure that SS on Cu(111) is reproduced correctly in our single-electron calculations. This is a Shockley-type state originating from the sp-band of copper and situated at  $\sim 0.4$  eV below the Fermi level [13]. Fig. 1 demonstrates the calculated Bloch spectral functions for the uppermost and few next layers of Cu(111), the SS is marked by the arrow. It decays at a depth of  $\sim 3$ –4 monolayers. The dispersion of the SS (Fig. 2), to a good approximation, shows a quadratic behaviour as a function of  $\mathbf{k}^{\parallel}$ .

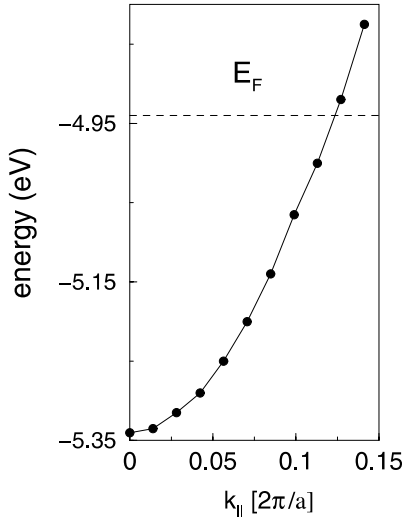


Fig. 2. Theoretical dispersion curve  $E(\mathbf{k}^{\parallel})$  for the surface state of Cu(111).

#### 4. DPE energy and angular spectra

Six independent variables (energies  $E_1$ ,  $E_2$ , and four angles of emission), characterizing asymptotic two-electron final state, can be combined in different ways to visualize the DPE process. Two particular situations will be considered here. At given energy and (linear) polarization of the photon DPE probability will be given: (i) as a function of the energy difference  $(E_1 - E_2)$  at fixed total energy  $(E_1 + E_2)$  and fixed angles  $(\theta_1, \phi_1)$ ,  $(\theta_2, \phi_2)$ , or (ii) as a function of  $(\theta_2, \phi_2)$  for fixed  $(\theta_1, \phi_1)$  and  $E_1, E_2$ .

First mode is referred to as energy sharing distribution (ESD). It shows, how favourable for photoemission is one or another partition of the total energy between two electrons. Fig. 3 shows the examples of the ESD's from the Cu(111) SS for the energies  $\hbar\omega = 41$  eV,  $E_1 + E_2 = 30$  eV, and light polarization in the plane of the surface along  $y$ -axis. In this case the initial state energies  $E_1^{\text{ini}}, E_2^{\text{ini}}$  are picked out of the narrow range of approximately 1 eV width around the location of the SS, according to the energy conservation

$$E_1 + E_2 = E_1^{\text{ini}} + E_2^{\text{ini}} + \hbar\omega. \quad (1)$$

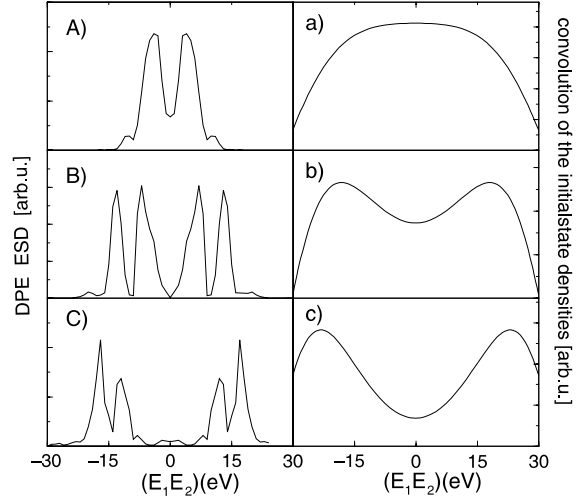


Fig. 3. (A)–(C), left column: DPE ESD from the surface state of Cu(111) for the energies  $\hbar\omega = 41$  eV,  $E_1 + E_2 = 30$  eV and angles  $\phi_1 = \phi_2 = 0$ ,  $\theta_1 = -\theta_2 = 30^\circ, 40^\circ, 50^\circ$ , respectively; (a)–(c), right column: corresponding convolution of the  $\mathbf{k}^{\parallel}$ -dependent densities of initial states of two electrons.

This energy range is boundaryed by the Fermi energy from above, and by  $E_{\text{min}} = E_1 + E_2 - E_F - \hbar\omega$  from below (shown by two dashed lines on Fig. 1). The DPE cross section is then obtained by the integration over this range. Directions of emission are set by the angles  $\phi_1 = \phi_2 = 0$ ,  $\theta_1 = -\theta_2 = 30^\circ, 40^\circ, 50^\circ$ . The final state energy sharing is formed, particularly, as a result of momentum transfer between electrons due to Coulomb interaction. ESD also reflects single-electron characteristics, namely, the momentum-resolved density of initial states. Finally, being the optically excited flux, it reflects the features of the dipole transition and contains a kinematical factor  $K \equiv \sqrt{E_1 \cdot E_2}$ . The latter leads to the zero value of the ESD at the edges, where  $E_1$  or  $E_2$  is equal to zero. So, each point of the ESD is related to certain  $E_1, E_2$ , corresponding  $\mathbf{k}_1^{\parallel}, \mathbf{k}_2^{\parallel}$  and  $\mathbf{k}^{\parallel}$ -resolved densities of initial states, and factor  $K$ . We compare our results with the auxiliary function  $B(\mathbf{k}_1^{\parallel}, \mathbf{k}_2^{\parallel})$  that simulate only the effect of the initial state single-particle densities. It is defined as a convolution of the corresponding  $\mathbf{k}^{\parallel}$ -resolved densities of initial states (let's denote them  $A(E_i^{\text{ini}}, \mathbf{k}_i^{\parallel}), i = 1, 2$ ):

$$B(\mathbf{k}_1^{\parallel}, \mathbf{k}_2^{\parallel}) = \int_{E_{\min}}^{E_F} A(E; \mathbf{k}_1^{\parallel}) \cdot A(E_1 + E_2 - E - \hbar\omega; \mathbf{k}_2^{\parallel}) dE. \quad (2)$$

For simplicity,  $A(E; \mathbf{k}_i^{\parallel})$  are simulated by Gaussians, whose position move towards lower energies as a function of  $\mathbf{k}_i^{\parallel}$  according to the dispersion curve, Fig. 2. Comparing the results, one can conclude (within the approximations made above), that the initial state densities shape the general profile of the ESD, while the fine structure should be attributed to another abovementioned aspects. For example, the minimum in the middle of ESDs, where the total energy is shared equally between the electrons, is due to the fact that the total asymptotic wave vector is then directed perpendicular to the vector of light polarization—in this situation the propensity rule [4] applies, which suppresses the dipole transition.

While ESDs are not straightforward in interpretation, DPE angular distributions (ADs) have more transparent appearance. Energies of emitted electrons are fixed there, the direction of emission of the first electron is fixed too. One should trace the DPE current as a function of emission direction of the second electron in the upper hemisphere above the surface. On the Fig. 4 we present the SPE and DPE ADs in the form of stereographic projections, where the direction perpendicular to the surface ( $z$ -axis) is a center of each circle. The energies are  $\hbar\omega = 45$  eV,  $E_1 = E_2 = 15$  eV, light is polarized along the normal to the surface. At these energies the range of integration over the initial states includes the region of the  $d$ -band, where the density of states is  $\sim 2.5$  times higher, than that of the SS (we do not illustrate this detailedly, but only mention that the DPE intensity from the SS is approximately factor 6 lower than that from the  $d$ -band). Black-to-white scale shows the normalized intensity from zero to one, respectively. Three pictures in the left column correspond to SPE, in the right column—to DPE ADs from 2, 3 and 10 monolayers of Cu(111). In DPE ADs the first electron is emitted normally to the surface plane. Two competing features determine the angular behaviour of the process: (i)

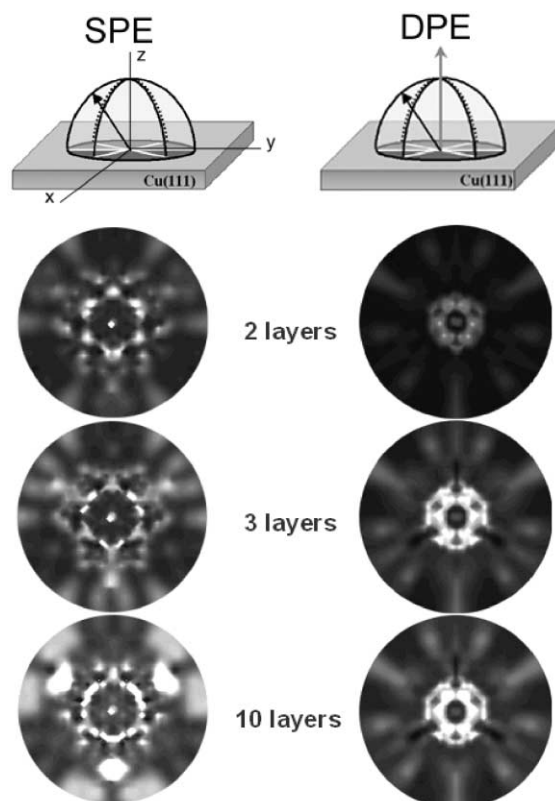


Fig. 4. Stereographically projected SPE and DPE angular patterns from the  $d$ -band of Cu(111). SPE (left column):  $\hbar\omega = 22.5$  eV,  $E_{\text{kin}} = 15$  eV; DPE (right column):  $\hbar\omega = 45$  eV,  $E_1 = E_2 = 15$  eV, the ‘fixed’ electron is emitted normally to the surface, photon polarization vector along  $z$ -axis.

Coulomb repulsion prevents the closely lying emission directions of two electrons, (ii) far-away directions are ‘suppressed’ by the fact that the interaction between electrons becomes small, and so does the DPE probability, which relies entirely on the strength of this interaction. So, in Fig. 4 one can observe the dark spot around the direction of emission of first electron, which is explained by the Coulomb repulsion. Then comes the ‘ring’ of high intensity, where actually the most of the DPE photocurrent occurs. Towards the boundaries the intensity falls down again. This general pattern is mixed with the diffraction effects due to scattering of the electrons from the lattice. In the given geometry (the photon polarization vector and the emission direction of the ‘fixed’ electron are normal

to the surface), the symmetry of the presented DPE ADs coincide with the symmetry of the copper face. However, this would be generally not true, if the emission direction of the ‘fixed’ electron would not coincide with the high-symmetry direction of the lattice point group (c.f. [8]). The mean angle with respect to the first electron, at which the second electron is preferentially emitted, depends on the value of the screening length  $\lambda$  and, hence, on the material. The larger is the screening length, the wider is the space where the electrons can interact and decline their trajectories, so the wider will be the ‘ring’ of high intensity. The depth of generation of correlated pairs as compared to the depth of generation of a photoelectron in SPE process is illustrated in Fig. 4. The rapidly decaying density of states of the SS does not effect much the depth of generation, since at these energies the contribution from the d-band is overwhelming. The photocurrent of both processes is calculated for different number of monolayers ( $n = 2, 3$  and 10). Intensities in SPE and DPE columns (normalized in the same way within each column) differ roughly by five orders of magnitude, which is in agreement with experimental observation [14], and is in line with the knowledge on double photoionization of atomic and molecular targets [15]. Within a simple model, the probability for two electrons to escape from the surface can be estimated as a square of the single-electron escape probability. The latter, being connected to the mean free path  $d$  by exponential law  $\exp(-z/d)$ , gives the effective two-electron mean free path equal to  $d/2$ . From Fig. 4 one can indeed see that the most of the DPE signal is formed up to the third monolayer, while in the case of SPE there is still no saturation at this depth.

## 5. Conclusions

We have presented the results of DPE calculations from the surface state and the d-band of Cu(111). The role of initial state densities, Cou-

lomb interaction, screening length, dipole transitions in the formation of angular and energy DPE spectra is illustrated and discussed. We perform calculations from the narrow energy band around the surface state and from the broader range, including the d-band. The nearly analytical behaviour of the SS dispersion allows to approximately single out the effect of the density of initial states on DPE energy sharing distributions. Emission from the d-band is used to illustrate the high surface sensitivity of DPE process: the depth of generation of correlated pairs is estimated to not exceed 3 monolayers.

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