Theory of two-electron photoemission from surfaces

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Abstract

A general theoretical approach to double photoemission from solid surfaces is formulated in terms of two-electron Green functions and two-electron states. By incorporating the screened Coulomb interaction between the two outgoing electrons in a dynamically screened effective one-electron potential, approximate expressions for the two-photoelectron current are derived, which essentially consist of elements well-known from one-electron photoemission theory. © 2000 Elsevier Science Ltd. All rights reserved.

Keywords: A. Surfaces and interfaces; C. Surface electron diffraction (LEED, RHEED); D. Electron–electron interactions; D. Electronic band structure; E. Photoelectron spectroscopies

1. Introduction

Traditionally, the basic conceptual framework for dealing with many-electron systems is the independent electron model. The electronic structure is described mostly by means of a self-consistent field, based on the Hartree–Fock or the Kohn–Sham equations. Although the effective-field approach has long served for the interpretation of photoemission spectra [1,2], its central assumption of a single-particle wave function is, in general, of limited applicability, e.g. it fails in narrow-band systems with strong correlation between valence electrons [3]. The basic quantity relevant to the many-body effects is the correlation energy which, within density functional theory, is thought to reach its exact value at the exact ground-state density. However, the main question—to what extent the motion of the electrons is interrelated—is to be addressed by means of many-particle wave functions rather than by static properties such as the correlation energy. On the experimental side, double photoelectron emission (DPE) from solids and surfaces [4] is perfectly suited for the study of the correlated dynamics. Detecting simultaneously two electrons after the absorption of one photon, this process is one of the few known that in principle cannot be described within the single-particle picture. If the initial-state and the final-state wave functions are taken as products of orthogonal one-electron wave functions, the transition-matrix element for double photoionization vanishes [5]. Thus, the inter-electronic correlation plays a major role in determining the characteristics of doubly excited states. In other words, quantities used for the theoretical formulation of the problem (wave functions, propagators, etc.) have to be of at least two-particle nature. On the other hand, realizing that all features of scattering within a crystal intrinsically complicate the problem, it would be essential to seek for an extension of the well-established one-step single-electron photoemission (SPE) framework [6–8] to the case of DPE. In the present Paper we follow both of these pathways.

In Section 2 we present a general formulation of the DPE in terms of two-particle states and Green functions. Section 3 deals with schemes for calculating correlated two-particle states in a solid. In particular, the pair interaction is formulated in terms of dynamical screening. This approximation is used in Section 4 to derive expressions for the DPE photo-current, which are directly connected with established SPE theory.

2. General expression for the two-electron photocurrent

We consider a process in which an incident photon with

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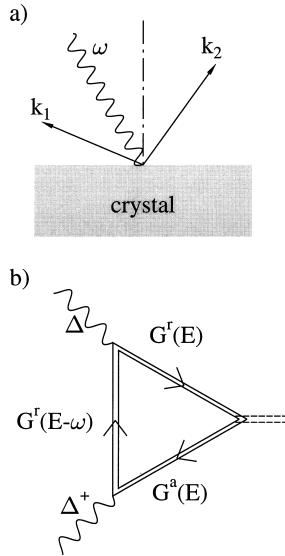 *E-mail address:* fom@mpi-halle.de (N. Fominykh).

Fig. 1. Two-electron photoemission. (a) Sketch of the experimental geometry. A photon with energy ω impinges onto the surface. Two outgoing electrons with momenta $\vec{k}_1$ and $\vec{k}_2$ are detected in coincidence. (b) Diagrammatic representation of the photocurrent expression (Eqs. (1) and (2)). Wavy lines represent the photon, double straight lines with arrows correspond to retarded and advanced two-electron Green functions G^r and G^a at the final and initial state energies E and $E - \omega$. The double dashed line symbolizes the emitted (and detected) electron pair.

energy ω knocks two electrons out of a semi-infinite solid with periodicity parallel to the surface.[1] The subsequent detection of both outgoing electrons in coincidence allows the simultaneous determination of their kinetic energies E_1 and E_2 as well as the surface-parallel wave-vector components $\vec{k}_1^{\parallel}$ and $\vec{k}_2^{\parallel}$ (cf. Fig. 1a). The plane waves at the detectors are fully described by their momentum $\vec{k}_j$, $j = 1, 2$, since the normal component $k_j^{\perp}$ is related to E_j by $k_j^{\perp} = \sqrt{2E_j - (\vec{k}_j^{\parallel})^2}$. Assuming the sudden approximation for the DPE process, the photon field affects only those degrees of freedom of the two electrons, which can be distinguished by the detection process. We restrict ourselves to the pair interaction between these two 'active' electrons, thus neglecting three-body and higher order terms as well as explicit many-body effects with or between the 'passive' (ground state) electrons.

In analogy to the well-known Green-function formulation of SPE by Caroli et al. [9], we express the DPE current in the dipole approximation in terms of the two-particle Green function G,

$$J(\vec{k}_1\vec{k}_2) = -\frac{1}{\pi}\langle\Psi|\Delta\mathrm{Im}\,G^r(E - \omega)\Delta^{\dagger}|\Psi\rangle, \qquad (1)$$

where $|\Psi\rangle$ can be viewed as a time-reversed LEED state for

two correlated electrons, e.g. it has the (experimentally set) boundary conditions of plane waves $|\vec{k}_1\rangle$ and $|\vec{k}_2\rangle$ taken at the detector positions and is propagated by the advanced Green function G^a from inside the solid towards the detectors,

$$|\Psi\rangle = G^a|\vec{k}_1\vec{k}_2\rangle. \qquad (2)$$

The kinetic energy of the outgoing electron pair is $E = E_1 + E_2$, its surface-parallel momentum $\vec{K}^{\parallel} = \vec{k}_1^{\parallel} + \vec{k}_2^{\parallel}$. In Eq. (1), Δ is the two-particle dipole operator, i.e. the sum of two single-particle dipole operators [5], and $-\mathrm{Im}\,G^r(E - \omega)/\pi$ is the non-local density of two-particle states.

Eq. (1) can be represented by the diagram in Fig. 1b, which is the two-particle analogue of the lowest order diagram of the SPE theory. Interactions between the 'active' electron pair and the other electrons of the solid are thus taken into account to the extent that they are incorporated in the on-the-total-energy-shell Green function G.

If the imaginary self-energy part is set to zero, e.g. assuming an infinite two-particle life-time, $G^r(E)$ in Eq. (1) can be written in terms of two-particle states $|\Phi_i\rangle$ with energies E_i and further quantum numbers denoted by the compound index i,

$$-\frac{1}{\pi}\,\mathrm{Im}\,G^r(E) = \sum_i |\Phi_i\rangle\delta(E - E_i)\langle\Phi_i|, \qquad (3)$$

where the summation over i is understood as integration in the case of continuous quantum numbers. Inserting Eq. (3) into the DPE expression (1) simplifies this to Fermi's 'golden rule',

$$J(\vec{k}_1\vec{k}_2) = \sum_i |\langle\Psi|\Delta|\Phi_i\rangle|^2\delta(E - \omega - E_i). \qquad (4)$$

The summation over unresolved quantum numbers contained in i accounts for all initial two-particle states that are compatible with energy conservation and symmetry requirements imposed by the dipole transition to the particular final state. As was shown in Ref. [5], conservation of the surface-parallel component of the momentum in the SPE translates in DPE into the same but for the two-particle momentum $\vec{K}^{\parallel}$. This means that the two-particle momenta are conserved modulo reciprocal surface-lattice vectors. In Eq. (1), G^r can be restricted to these values of $\vec{K}_i^{\parallel}$. Note that due to the Coulomb interaction, single-particle momenta are in general not 'good quantum numbers' in the DPE process.

In order to evaluate the above DPE current formulae, ways have to be found to actually calculate the two-particle Green function or the two-particle states involved. We address this problem in Section 3.

3. Two-electron states

The Hamiltonian H for two electrons inside the semi-infinite solid consists of the kinetic energy K, the electron–electron interaction U, and the crystal potential W, $H = K + U + W$. Due to the simultaneous occurrence

of two difficulties—the many-body and the scattering problem—we have to decide about the sequence of treating U and W. Paying tribute to the fact that DPE is due to the electron–electron interaction U, we assign the latter to the reference Hamiltonian $H_{int} = K + U$. In this way the crystal potential is kept as a perturbation. In the absence of W, the operator $G_{int}U$ promotes the uncorrelated two-particle state $|\Phi^0\rangle$, which is an eigenfunction of K, to the correlated one

$$|\Phi^1\rangle = (1 + G_{int}U)|\Phi^0\rangle, \tag{5}$$

the latter being an eigenfunction of H_{int}. G_{int}, the resolvent of H_{int}, is the propagator of the internal motion of the electron pair. The reference state $|\Phi^1\rangle$ is perturbed by the crystal potential W and evolves into the state

$$|\Phi\rangle = (1 + G_{int}T)|\Phi^1\rangle. \tag{6}$$

The transition operator T describes the dynamic response of the system upon the action of W and obeys the Lippmann–Schwinger equation $T = W + WG_{int}T$.

Despite the fact that $|\Phi^1\rangle$ in Eq. (5) is a quasi-single-particle subject to the scattering in the crystal, the internal and external motions are not separable due to the presence of G_{int} in Eq. (6). If U is negligible, the problem reduces to scattering of independent particles. If this is not the case, use of Eq. (6) in order to evaluate physically relevant quantities requires further approximations, e.g. application of the perturbation expansion of G_{int} with respect to U. This would allow for a systematic treatment of correlation effects. In the above formulation, our scheme is general and applicable for both initial and final two-particle states of the DPE process.

As an alternative to the above, we consider an approach for the calculation of the final two-particle state $|\Psi\rangle$, which uses single-particle scattering states of the semi-infinite system as reference states for the electron–electron interaction. These states are well-known from LEED and SPE theories and can be calculated by multiple-scattering methods (cf. e.g. Ref. [6]). Taking the Coulomb interaction U as a perturbation, $|\Psi\rangle$ then assumes the form

$$|\Psi\rangle = (1 + GU)|\psi_1\psi_2\rangle. \tag{7}$$

$|\psi_1\rangle$ and $|\psi_2\rangle$ are single-particle time-reversed LEED states which are plane waves $|\vec{k}_1\rangle$ and $|\vec{k}_2\rangle$, respectively, at the detectors.

A rigorous evaluation of Eq. (7) is however complicated. A computationally viable approximation has recently been proposed in the context of pair emission by electron impact, (e,2e) [10,11]. Taking U as a Thomas–Fermi-like screened Coulomb interaction, this two-particle potential was approximated by a sum of two single-particle potentials. This amounts to a dynamical screening. Each electron moves in an effective single-particle potential $\tilde{w}_j$, $j = 1, 2$, which is the usual quasi-particle potential w of LEED theory augmented by a dynamical screening term depending on the other electron. Denoting by g_j and $\tilde{g}_j$ the single-particle Green functions for electron j in the potentials w and $\tilde{w}_j$,

respectively, our approximation takes the operator form

$$(1 + GU)(1 + g_1w)(1 + g_2w) \approx (1 + \tilde{g}_1\tilde{w}_1)(1 + \tilde{g}_2\tilde{w}_2). \tag{8}$$

The time-reversed LEED states $|\tilde{\psi}_j\rangle$ can then be written as

$$|\tilde{\psi}_j\rangle = (1 + \tilde{g}_j^a\tilde{w}_j)g_j^0|\vec{k}_j\rangle = \tilde{g}_j^a|\vec{k}_j\rangle, \tag{9}$$

in analogy to Eq. (2). They can readily be calculated by employing $\tilde{w}_j$ in standard multiple-scattering computer codes. The two-particle final state is then simply an anti-symmetrized product of these single-particle states,

$$|\Psi\rangle = A(|\tilde{\psi}_1\rangle \otimes |\tilde{\psi}_2\rangle), \tag{10}$$

where operator A is antisymmetrizator.

4. Double photoemission from wide valence bands

In contrast to narrow-band systems, the ground state of metals with sp-valence bands consists in good approximation of independent quasi-electrons moving in an effective external potential. Hence, pair correlation can be neglected in our initial two-particle state. Since the screening of single electrons by the ground state electrons decreases with increasing energy, one can expect non-negligible pair correlation in the final state, which we approximate as described above.

In order to evaluate the general photocurrent expression Eq. (1) we first express the two-particle spectral density $-\text{Im } G^r/\pi$ in terms of retarded single-particle Green functions g^r. Straightforward calculation yields

$$\text{Im } G^r(12, 1'2'; E) = -\frac{1}{\pi} \int d E'(\text{Im } g^r(11'; E')$$

$$\times \text{Im } g^r(22'; E - E') - \text{Im } g^r(12'; E') \text{Im } g^r(21'; E - E')). \tag{11}$$

We thus have a convolution involving a direct product plus an exchange product, in which the co-ordinates $1'$ and $2'$ are interchanged. Note that by taking the trace of Eq. (1) the density of two-particle states N is obtained as a convolution of single-particle densities n,

$$N(E) = \int d E' n(E') n(E - E'). \tag{12}$$

We now substitute Eq. (11) and the final two-particle state, Eq. (10), into Eq. (1). Using the decomposition of the two-particle dipole operator into two single-particle operators, we eventually obtain the DPE current as

$$J(\vec{k}_1\vec{k}_2)\!\propto\!\frac{1}{\pi^2} \int_{E_{min}}^{E_F} d E'(I_d(E') - I_e(E')) \tag{13}$$

where $E_{min} = E - \omega - E_F$ is the lowest occupied single-particle level allowed by energy conservation. $I_d(E)$ is the
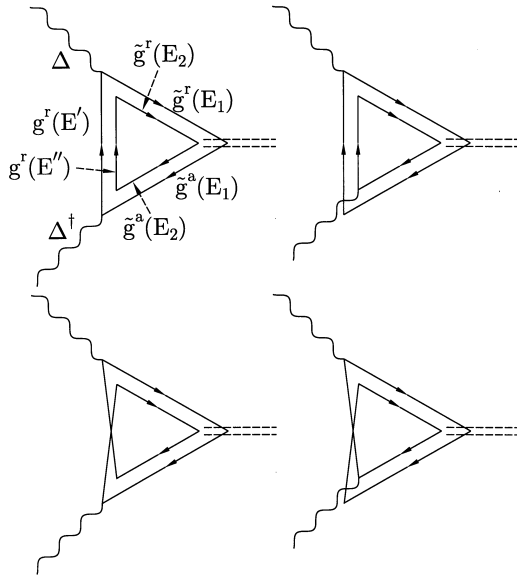
Fig. 2. Diagrammatic representation of the approximate two-electron photocurrent in terms of one-electron Green functions g and $\tilde{g}$. The upper (lower) two diagrams correspond to the first two direct (exchange) terms given in Eq. (14) (its analogue with $|\tilde{\psi}_1\rangle$ and $|\tilde{\psi}_2\rangle$ interchanged). The symbols are as in Fig. 1b except that single straight lines with arrows represent one-electron Green functions.
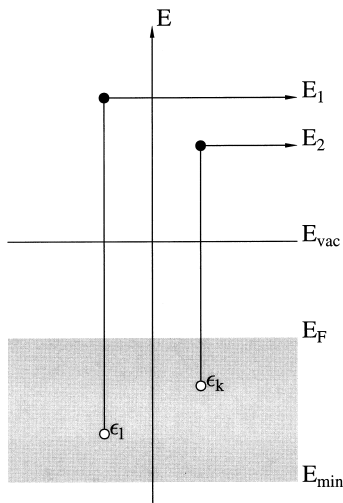

Fig. 3. Energy diagram of the approximate DPE process as depicted in Fig. 2. Initial states with energies ϵ_l and ϵ_k are excited to time-reversed LEED states with kinetic energies E_1 and E_2 (relative to the vacuum level E_{vac}), respectively. The energy region available for the initial states (grey area) is given by the Fermi energy E_F and E_{min} (see text).

direct intensity term defined as

$$I_d(E') = \langle \tilde{\psi}_1 | \Delta \mathrm{Im}\, g^r(E') \Delta^\dagger | \tilde{\psi}_1 \rangle \langle \tilde{\psi}_2 | \mathrm{Im}\, g^r(E'') | \tilde{\psi}_2 \rangle$$

$$+ \langle \tilde{\psi}_1 | \Delta \mathrm{Im}\, g^r(E') | \tilde{\psi}_1 \rangle \langle \tilde{\psi}_2 | \mathrm{Im}\, g^r(E'') \Delta^\dagger | \tilde{\psi}_2 \rangle$$

$$+ \langle \tilde{\psi}_1 | \mathrm{Im}\, g^r(E') \Delta^\dagger | \tilde{\psi}_1 \rangle \langle \tilde{\psi}_2 | \Delta \mathrm{Im}\, g^r(E'') | \tilde{\psi}_2 \rangle$$

$$+ \langle \tilde{\psi}_1 | \mathrm{Im}\, g^r(E') | \tilde{\psi}_1 \rangle \langle \tilde{\psi}_2 | \Delta \mathrm{Im}\, g^r(E'') \Delta^\dagger | \tilde{\psi}_2 \rangle \quad (14)$$

where $E'' = E - \omega - E'$. The exchange contribution I_e consists of four terms like those of I_d but in each term $|\tilde{\psi}_1\rangle\langle\tilde{\psi}_2|$ is exchanged by $|\tilde{\psi}_2\rangle\langle\tilde{\psi}_1|$.

Expressing the single-particle final states in terms of Green functions, cf. Eq. (9), the four individual parts of I_d and those of I_e can be represented by eight diagrams, four typical ones of which are shown in Fig. 2. The exchange terms in the lower row are seen to arise from the direct terms in the upper row by 'crossing' the two Green functions associated with the single-particle initial states.

In order to recover the 'golden rule' form of the DPE current, we assume infinite life-time of the particles and express the retarded Green functions g^r in terms of eigenstates of the single-particle Hamiltonian,

$$g^r(E') = \lim_{\eta \to 0^+} \sum_k \frac{|\phi_k\rangle\langle\phi_k|}{E' - \epsilon_k - i\eta}. \quad (15)$$

In other words, the two-particle initial states Φ_j with energies E_j are replaced by anti-symmetrized products of single-particle states ϕ_k and ϕ_l with energies $\epsilon_k + \epsilon_l = E_j$, cf. Eq. (11). Note that for a given E_j the energies ϵ_k and ϵ_l are not fixed but range from $E_{min} = E_j - E_F$ to the Fermi energy E_F. Eventually applying Dirac's identity, we arrive at

$$J(\vec{k}_1 \vec{k}_2) = \sum_{kl}^{occ} |M_{kl}^{(1)} + M_{kl}^{(2)} - M_{lk}^{(1)} - M_{lk}^{(2)}|^2 \delta(E - \omega - \epsilon_k - \epsilon_l),$$

$$(16)$$

where the matrix elements $M_{kl}^{(1)}$ and $M_{kl}^{(2)}$ are defined as

$$M_{kl}^{(1)} = \langle \tilde{\psi}_1 | \Delta | \phi_k \rangle \langle \tilde{\psi}_1 | \phi_l \rangle \quad (17)$$

$$M_{kl}^{(2)} = \langle \tilde{\psi}_2 | \Delta | \phi_k \rangle \langle \tilde{\psi}_1 | \phi_l \rangle. \quad (18)$$

The single-particle energy levels involved in Eq. (16) are illustrated by Fig. 3, in which the grey region depicts the initial state energy integration range contained in the k and l summations.

Each matrix element M is a product of a single-particle transition-matrix element and an overlap integral between 'the other' single-particle initial and final states. These overlap integrals do not vanish in general because the effective single-particle Hamiltonian is different for initial and final states due to the electron–electron interaction. This allows the following interpretation: when one electron absorbs the photon, the effective potential changes such that the 'shake-up' of the other one becomes possible. We further note that in the present approximation the individual surface-parallel

momenta are conserved, since when two electrons are uncoupled there is no longer a mechanism responsible for the momentum transfer within a pair.

From the above analytical expressions as well as from the diagrams it is evident that the two-particle photocurrent has been reduced to single-particle constituents. These can be evaluated using standard procedures of one-electron photo-emission theory with some modifications.

5. Conclusion

In conclusion, we have developed a multiple-scattering formalism for the treatment of correlated electron-pair emission from surfaces upon the absorption of a single VUV photon. By transforming the electron–electron interaction from position into momentum space the two-photoelectron current has been approximated in terms of single-electron Green functions and transition-matrix elements. Numerical evaluation of the formulae, which we derived in this work, is currently in progress.

Acknowledgements

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