Relativistic photoemission theory for general nonlocal potentials

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Abstract

An improved formulation of the one-step model of photoemission from crystal surfaces is proposed which overcomes different limitations of the original theory. Considering the results of an electronic-structure calculation, the electronic (one-particle) potential and the (many-body) self-energy, as given quantities, we derive explicit expressions for the dipole transition-matrix elements. The theory is formulated within a spin-polarized, relativistic framework for general nonspherical and space-filling one-particle potentials and general nonlocal, complex and energy-dependent self-energies. It applies to semi-infinite lattices with perfect lateral translational invariance and arbitrary number of atoms per unit cell.

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1 Introduction

The spectrum of one-particle excitations of a metallic system of correlated electrons in a solid is a fundamental question in condensed-matter physics. Experimentally, the interesting valence-band region around the Fermi energy is accessible by means of ultraviolet photoemission spectroscopy (PES) [1] and inverse photoemission spectroscopy (IPE) [2].

The theoretical understanding of the excitation spectrum poses a long-standing and not yet generally solved problem. Within the independent-electron approximation the spectrum is simply given in terms of the one-particle (Hartree-Fock) eigenenergies of the Hamiltonian. Analogously, it is widely accepted to interpret a measured photoemission spectrum by referring to the results of band-structure calculations that are based on density functional theory (DFT) and the local density approximation (LDA) [3, 4]. Despite a sometimes convincing success in practice [5, 6, 7], such an interpretation is questionable since there is actually no known correspondence between the Kohn-Sham eigenenergies and the one-particle excitations of the system [4, 8]. For an in principle correct description of the excitation energies, the local LDA exchange-correlation potential has to be supplemented by the nonlocal, complex and energy-dependent self-energy which leads to the Dyson equation [4, 9] instead of the Schrödinger-type equation in the Kohn-Sham scheme.

Provided that the self-energy is known, one can deduce a PES/IPE “raw spectrum” from the solution of the Dyson equation. To achieve a reliable interpretation of experiments, however, it is inevitable to deal with so-called “secondary effects” which considerably modify and distort the raw spectrum. Above all, the wave-vector and energy dependence of the transition-matrix elements has to be accounted for. These dependencies are known to be important and actually cannot be neglected. They result from strong multiple-scattering processes which dominate the electron dynamics in the low-energy regime of typically 1-100 eV [10]. The transition-matrix elements also include the effects of selection rules which are not accounted for in the raw spectrum. Strictly speaking, it can be stated that the main task of a theory of photoemission is to close the gap between the raw spectrum obtained by (many-body) electronic-structure calculations and the experiment.

It turns out, however, that the calculation of the transition-matrix elements is by no means a trivial task. Probably, the most successful theoretical approach is the so-called one-step model of photoemission as originally proposed by Pendry and co-workers [10, 11, 12]. A review on the recent developments and refinements [13] of the approach can be found in Ref. [7]. The main idea of the one-step model is to describe the actual excitation process, the transport of the photoelectron to the crystal surface as well as the escape into the vacuum [14] as a single quantum-mechanically coherent process including all multiple-scattering events.

The main disadvantage of the conventional formulation of the one-step model consists in the fact that it is intrinsically based on a local potential. This is sufficient if the calculation starts from the self-consistent LDA potential. The inclusion of the nonlocal self-energy which is needed for an in principle correct description of the one-particle
excitations, however, is not possible. In a preceding study we were able to show that one can overcome this difficulty and that the nonlocal self-energy term can be included within an alternative formulation of the one-step model.

The purpose of the present paper is to generalize the results of Ref. in different respects: (i) The two-component formalism is replaced by a four-component, relativistic framework necessary for the study of high-$Z$ materials or for spin-polarized photoemission from nonmagnetic samples excited by circularly polarized radiation, for example. (ii) For ferromagnetic systems, the exchange splitting and the spin-orbit splitting are treated on equal footing. This allows to investigate e.g. magnetic dichroic effects. (iii) The theory is no longer based on the muffin-tin approximation for the input LDA potential. Instead, the general case of space-filling, nonspherical potentials is considered which becomes important for more open crystal structures. (iv) To cover the case of complex geometries (ordered compounds, multilayers), we also generalize to more than one atom per unit cell. (v) The Korringa-Kohn-Rostocker (KKR) multiple-scattering formalism is used for both, the final as well as the initial states. This internal consistency of the formalism represents another improvement compared with Ref. where a muffin-tin-orbitals basis was used with respect to the initial states.

As in Ref. we keep the basic structure of the one-step model. Starting from Pendry’s formula for the photocurrent, analytical expressions for the matrix elements are derived referring to a crystal surface with perfect lateral translational invariance. For the solution of the (atomic) Dirac equation we use the phase-functional ansatz of Calogero generalized to the nonspherical case. The initial state is treated within the relativistic version of KKR theory for space-filling potentials but adapted for a slab geometry, and the final state is constructed using a full-potential relativistic layer-KKR method. The new formalism is developed up to the point where the numerical evaluation has to start.

The LDA potential and the self-energy are assumed to be given (input) quantities that must be obtained from a preceding electronic-structure calculation. The related many-body problem is beyond the scope of the present paper. In particular, one must be aware of a possible double counting of interactions, once on a mean-field level in the LDA and once explicitly in the self-energy. While there are pragmatic ways to circumvent this problem, it generally remains unsolved. Whether or not the self-energy is calculated within a relativistic framework is not decisive for the applicability of the presented approach. A two-component, nonrelativistic self-energy as it is usually provided (see e.g.) can be used as an input quantity in the relativistic formulation.

2 One-step model of photoemission

Photoemission (PES) and inverse photoemission (IPE) are complemental spectroscopies. We concentrate on PES in the following since IPE can simply be treated analogously by taking into account geometrical factors that regard the respective experimental setups. We start our considerations by a discussion of Pendry’s formula for the photocurrent.
which defines the one-step model of PES [11]:

\[
P_{\text{PES}} \propto \text{Im} \left( \langle \epsilon_f, k_\parallel | G_2^+ \Delta G_1^+ \Delta_1 G_2^- | \epsilon_f, k_\parallel \rangle \right). \tag{1}
\]

The expression can be derived from Fermi’s golden rule for the transition probability per unit time [8]. Consequently, \( P_{\text{PES}} \) denotes the elastic part of the photocurrent. Vertex renormalizations are neglected. This excludes inelastic energy losses and corresponding quantum-mechanical interference terms [8, 11, 29]. Furthermore, the interaction of the outgoing photoelectron with the rest system is not taken into account. This “sudden approximation” is expected to be justified for not too small photon energies.

We consider an energy-, angle- and spin-resolved photoemission experiment. The state of the photoelectron at the detector is written as \( |\epsilon_f, k_\parallel \rangle \), where \( k_\parallel \) is the component of the wave vector parallel to the surface, and \( \epsilon_f \) is the kinetic energy of the photoelectron. The spin state of the photoelectron is implicit in \( |\epsilon_f, k_\parallel \rangle \) which is understood as a four-component Dirac spinor. The advanced Green function \( G_2^- \) in Eq. (1) characterizes the scattering properties of the material at the final-state energy \( E_2 \equiv \epsilon_f \). Via \( |f\rangle = G_2^- |\epsilon_f, k_\parallel \rangle \) all multiple-scattering corrections are formally included. Using standard Korringa-Kohn-Rostocker (KKR) multiple scattering techniques [22], we can calculate the final state \( |f\rangle \) as a (time-reversed) relativistic LEED state (see Sec. 4).

As far as concerns the final state, many-body effects are included only phenomenologically in the LEED calculation, i.e. by using a parametrized, weakly energy-dependent and complex inner potential \( V_0(E_2) = V_0(E_2) + iV_0(E_2) \) as usual [10]. This generalized inner potential also includes the (imaginary) optical potential, which takes into account inelastic corrections to the elastic photocurrent [8] as well as the actual (real) inner potential, which serves as a reference energy inside the solid with respect to the vacuum level [30]. Due to the finite imaginary part \( iV_0(E_2) \), the flux of elastically scattered electrons is permanently reduced, and thus the amplitude of the high-energy wave field \( |f\rangle \) can be neglected beyond a finite distance from the surface. It is thus sufficient to restrict oneself to a slab geometry in a practical computation.

\( \Delta \) in Eq. (1) is the dipole operator in the electric dipole approximation which is well justified in the visible and ultraviolet spectral range. It mediates the coupling of the high-energy final state with the low-energy initial states. For the relativistic, possibly ferromagnetic case and for general space-filling potentials, a convenient form of the dipole operator is given in Sec. 4.

The “low-energy” propagator \( G_1^+ \) in Eq. (1), i.e. the one-electron retarded Green function for the initial state in the operator representation, yields the “raw spectrum”. It is directly related to the “bare” photocurrent and thereby represents the central physical quantity within the one-step model. \( G_1^+ \equiv G_1^+(E_1) \) is to be evaluated at the initial-state energy \( E_1 \equiv \epsilon_f - \omega - \mu_0 \), where \( \omega \) is the photon energy (\( \mu_0 \) stands for the chemical potential).

In the framework of the conventional one-step model of Pendry and co-workers [10, 11, 12] the initial-state Green function \( G_1^+ \) is determined for \( \uparrow, \downarrow \) electrons moving in an (effective) one-particle potential \( V_{\text{LDA}}^+(r) \) provided by DFT-LDA. As usual, \( V_{\text{LDA}}^+(r) \)
consists of the external core potential, the Hartree contribution as well as the exchange-correlation potential. In the relativistic generalization of DFT \cite{31, 32} one has to consider the (one-particle) Dirac Hamiltonian ($\hbar = m = e = 1, c = 137.036$):

$$h_{LDA}(r) = -ic\alpha \nabla + \beta c^2 - c^2 + V_{LDA}(r) + \beta \sigma B_{LDA}(r),$$

(2)

where $V_{LDA}(r)$ denotes the (effective) spin-independent potential, and $B_{LDA}(r)$ is the (effective) magnetic field. They are given as \cite{33}:

$$V_{LDA}(r) = \frac{1}{2}(V_{LDA}^+(r) + V_{LDA}^-(r))$$

(3)

and

$$B_{LDA}(r) = \frac{1}{2}(V_{LDA}^+(r) - V_{LDA}^-(r)) b.$$  

(4)

The constant unit vector $b$ determines the spatial direction of the (uniform) magnetization as well as the spin quantization axis. $\beta$ denotes the usual 4 $\times$ 4 Dirac matrix with the nonzero diagonal elements $\beta_{11} = \beta_{22} = 1$ and $\beta_{33} = \beta_{44} = -1$, and the vector $\alpha$ is given by its components $\alpha_k = \sigma_x \otimes \sigma_k$ ($k = x, y, z$) in terms of the 2 $\times$ 2 Pauli-matrices $\sigma_k$.

Within the DFT ground-state formalism, $V_{LDA}(r)$ as well as $B_{LDA}(r)$ are local functions. On the other hand, it is well known that for an in principle exact description of the one-particle excitations one has to consider the Dyson equation for the Green function \cite{4, 9}. This includes the nonlocal, complex and energy-dependent (retarded) self-energy $\Sigma_{\uparrow \downarrow}(r,r', E)$. As the LDA potential, the self-energy must be assumed to be a given quantity for the photoemission theory. Therewith, we can construct a generalized potential,

$$U(r, r', E) = \delta(r - r') (V_{LDA}(r) + \beta \sigma B_{LDA}(r)) + V(r, r', E) + \beta \sigma B(r, r', E),$$

(5)

where the nonlocal contributions $V$ and $B$ are defined as:

$$V(r, r', E) = \frac{1}{2}(\Sigma^+(r, r', E) + \Sigma^-(r, r', E))$$

(6)

and

$$B(r, r', E) = \frac{1}{2}(\Sigma^+(r, r', E) - \Sigma^-(r, r', E)) b.$$  

(7)

The initial state is described by a 4 $\times$ 4 Green matrix $G^+_1(r, r', E_1)$. It can be obtained as the solution of the Dyson equation which can be written as:

$$[E_1 + \mu_0 - h_{LDA}(r)] G^+_1(r, r', E_1) = \int (V(r, r'', E_1) + \beta \sigma B(r, r'', E_1)) \ast G^+_1(r'', r', E_1) dr'' = \delta(r - r') \mathbb{I}.$$ 

(8)

A direct solution of the Dyson equation in real-space representation turns out to be inconvenient. Analogously to Ref. \cite{13}, we therefore turn to a matrix representation and
choose the eigenspinors of the LDA Hamiltonian \( \mathcal{H} \) as basis states. Assuming perfect lateral translational symmetry, the parallel component of the wave vector is a good quantum number, and the LDA eigenvalue problem reads:

\[
h_{\text{LDA}}|n, \mathbf{q}_\parallel\rangle = \epsilon_n(\mathbf{q}_\parallel)|n, \mathbf{q}_\parallel\rangle.
\] (9)

Here \( \mathbf{q}_\parallel \) is a vector of the first two-dimensional Brillouin zone, and \( \epsilon_n(\mathbf{q}_\parallel) \) is the two-dimensional band structure. Using the eigenspinor basis, the Dyson equation for the initial-state Green function can be written:

\[
\sum_{n'} \left( (E_1 + \mu_0 - \epsilon_n(\mathbf{q}_\parallel)) \delta_{nn'} - V_{nn'}(E_1, \mathbf{q}_\parallel) - B_{nn'}(E_1, \mathbf{q}_\parallel) \right) G_{nn'}^{(+)}(E_1, \mathbf{q}_\parallel) = \delta_{nn'}.
\] (10)

Here we have introduced the matrix representation of the nonlocal terms \( V \) and \( B \):

\[
V_{nn'}(E_1, \mathbf{q}_\parallel) = \langle n, \mathbf{q}_\parallel|V(E_1)|n', \mathbf{q}_\parallel\rangle,
\]

\[
B_{nn'}(E_1, \mathbf{q}_\parallel) = \langle n, \mathbf{q}_\parallel|\beta \sigma \mathbf{B}(E_1)|n', \mathbf{q}_\parallel\rangle.
\] (11)

Lateral translational symmetry requires \( V \) and \( B \) to be diagonal with respect to \( \mathbf{q}_\parallel \).

In the eigenspinor basis Pendry’s formula reads:

\[
I \propto \text{Im} \sum_{nn'} M_n(\epsilon_f, \mathbf{k}_\parallel) G_{nn'}^{(+)}(E_1, \mathbf{q}_\parallel) M_{n'}^*(\epsilon_f, \mathbf{k}_\parallel),
\] (12)

where

\[
M_n(\epsilon_f, \mathbf{k}_\parallel) = \langle \epsilon_f, \mathbf{k}_\parallel|G_{2}^+ \Delta|n, \mathbf{q}_\parallel\rangle
\] (13)

is the matrix element of the dipole operator between the final state \( |f\rangle = G_2^+ |\epsilon_f, \mathbf{k}_\parallel\rangle \) and the LDA eigenspinor \( |n, \mathbf{q}_\parallel\rangle \). In Eq. (12) \( \mathbf{q}_\parallel \) is fixed by translational symmetry: A nonzero matrix element \( \mathbf{q}_\parallel \) requires \( \mathbf{q}_\parallel = \mathbf{k}_\parallel + \mathbf{g}_\parallel \), where \( \mathbf{g}_\parallel \) is a reciprocal lattice vector. Furthermore, \( \mathbf{k}_\parallel \) is given by the photoelectron energy at the detector and by the emission angles. This implies that \( \mathbf{g}_\parallel \) and thus \( \mathbf{q}_\parallel = \mathbf{q}_\parallel(\mathbf{k}_\parallel) \) are uniquely determined by demanding \( \mathbf{q}_\parallel \) to lie within the first two-dimensional Brillouin zone.

To work out the differences with respect to the original formulation, let us briefly discuss the case \( \Sigma \equiv 0 \). Energy and momentum conservation then implies that the final state \( |f\rangle \) can couple via \( \Delta \) to a single “initial” spinor \( |n, \mathbf{q}_\parallel\rangle \) only: Its eigenenergy is given by \( \epsilon_n(\mathbf{q}_\parallel) = \epsilon_f - \omega \), and \( \mathbf{q}_\parallel = \mathbf{k}_\parallel + \mathbf{g}_\parallel \). This implies that we can set

\[
G_1^+ = |n, \mathbf{q}_\parallel\rangle \frac{1}{E_1 - (\epsilon_n(\mathbf{q}_\parallel) - \mu_0) + i0^+} |n, \mathbf{q}_\parallel\rangle
\] (14)

in Eq. (1). I. e. the conventional one-step model is characterized by a one-pole structure of the low-energy (hole) propagator. It is because of this (implicit) one-pole structure that the original formulation does not allow to include a general nonlocal self-energy term. (Essentially the same argument applies if the infinitesimal \( i0^+ \) is replaced by a small finite imaginary constant as is oftenly done.)
On the contrary, for the general case $\Sigma = V + B \neq 0$ we have:

$$G_1^+ = \sum_{nn'} |n, q_\parallel\rangle \left[ \frac{1}{E_1 - (\epsilon(q_\parallel) - \mu_0) - \Sigma(E_1, q_\parallel)} \right]_{nn'} \langle n', q_\parallel|.$$  \hspace{1cm} (15)

The imaginary part of the self-energy causes an energy, wave-vector and band dependent broadening of the initial state. The hole acquires a finite lifetime (except for $E_1 = 0$, i.e. for $\epsilon_f - \omega = \mu_0$ where the self-energy is Hermitian). The energy dependence of $\Sigma$ may introduce a band-narrowing effect, an enhancement of the effective electron mass at the Fermi edge and, for a strongly correlated system, may give rise to satellite features in the spectrum. All this implies that for a given photon energy $\omega$ the final state $|f\rangle$ necessarily couples to different initial states $|n, q_\parallel\rangle$. Furthermore, since $\Sigma$ is generally nondiagonal in the band index $n$, interference terms $n \neq n'$ have to be considered.

The number $N_n$ of possible values for the band index $n$ in Eqs. (10) and (12) is given by $N_n = N_\perp N_A N_K$ where $N_\perp$ is the number of layers in the slab and $N_A$ is the number of atoms in the two-dimensional unit cell. $N_K$ is determined by the maximum order in the spin-angular momentum expansion (see next section) that is necessary for convergence. $N_\perp$ can be assumed to be finite since the damping of the final-state wave field implies that contributions to the photocurrent are negligibly small beyond a finite distance from the surface. In fact, a finite $N_\perp$ is decisive for a numerical solution of the Dyson equation (10) by matrix inversion. One inversion is necessary to get one $|\epsilon_f, k_\parallel\rangle$ point in the PES spectrum.

Formulas (10), (12) and (13) generalize our approach of Ref. [15]. The latter is obtained in the nonrelativistic approximation. On the other hand, in the limit $\Sigma^{\uparrow\downarrow}(r, r', E) \equiv 0$ the initial state is treated as in the original (relativistic) formulation of the one-step model [7, 13].

The actual and remaining task, however, consists in the according recalculation of the transition-matrix elements (13). This is done in the following. We thus consider the initial states $|n, q_\parallel\rangle$ (Sec. 3), the final state $G_2^-|\epsilon_f, k_\parallel\rangle$ (Sec. 4), and the dipole operator $\Delta$ (Sec. 5) to derive the final expression for the matrix elements in Sec. 6.

3 The initial states

For the evaluation of the matrix elements, we need a one-center expansion of the LDA eigenstates $|n, q_\parallel\rangle$. This will finally allow for a separation of the matrix elements into radial and angular parts. Such a one-center expansion is available within the relativistic version of the KKR approach for arbitrary space-filling potentials [17].

We consider the slab to be built up from layers $i_\perp = 1, ..., N_\perp$ parallel to the surface. The two-dimensional unit cells within a layer $i_\perp$ are labeled by an index $i_\parallel$ and the atoms within the unit cells by an index $i_A$. The position vector of a particular atom in the semi-infinite lattice $i = (i_\parallel, i_\perp, i_A)$ is then given by: $R_i = R_{i_\parallel} + R_{i_\perp} + R_{i_A}$, where $R_{i_\parallel}$ is a vector of the two-dimensional lattice, $R_{i_\perp}$ denotes the local origin of layer $i_\perp$, and $R_{i_A}$ the position vector of the $i_A$-th atom with respect to the local origin of the unit cell. The
material space is decomposed into (three-dimensional) polyhedra (atomic cells) \( \Omega_i \) with one atom \( i \) at the center of each such that the LDA potential \( V_{\text{LDA}}(r) \) (and analogously the effective magnetic field \( B_{\text{LDA}}(r) \)) can be written as a sum over cell potentials \( V_i(r - R_i) \) that vanish outside \( \Omega_i \):

\[
V_{\text{LDA}}(r) = \sum_i V_i(r - R_i) .
\]

A cell \( \Omega_i \) is circumscribed by a bounding sphere \( S_i \) of radius \( R_i \). Due to translational symmetry the potential within the cell \( \Omega_i \) or within the sphere \( S_i \) only depends on \( i_\perp \) and \( i_A \). We have: \( V_i(r) = V_{i_\perp i_A}(r) \). The same notation also applies for the effective magnetic field etc.

For the practical calculation, slabs consisting of \( N_\perp \) layers each are arranged in a super-cell geometry with a sufficiently large distance in between. This formally restores full three-dimensional periodicity and thus allows the application of the conventional KKR method. It can be shown [21] that the wave function \( \Psi^{(n)}(r) \equiv \langle r|n, q|| \) of the initial spinor \( |n, q|| \) can be expanded in locally exact basis spinors \( \Phi_{i\kappa\mu}(E, r) = \Phi_{i_\perp i_A\kappa\mu}(E, r) \):

\[
\Psi^{(n)}(r) = \sum_{\kappa\mu} A_{i\kappa\mu}(\epsilon_n(q||), q||) \Phi_{i\kappa\mu}(\epsilon_n(q||), r - R_i) .
\]

The expansion converges within each cell \( \Omega_i \) and for each \( \epsilon_n(q||) \) [21]. The basis spinors satisfy

\[
\left( E + ic\alpha \nabla - \beta c^2 + c^2 - V_i(r) - \beta q\sigma B_i(r) \right) \Phi_{i\kappa\mu}(E, r) = 0 \tag{18}
\]

for all \( r \). They differ in their behavior close to the center of \( \Omega_i \). For \( |r| \to 0 \):

\[
\Phi_{i\kappa\mu}(E, r) = J_{\kappa}^\mu(k, r) ,
\]

where

\[
J_{\kappa}^\mu(k, r) = \left( \begin{array}{c} \chi_\kappa^\mu(\hat{r}) j_l(kr) \\ i\chi_{-\kappa}^\mu(\hat{r}) \left( \frac{k S_{\kappa} c}{E + 2c^2} \right) j_l(kr) \end{array} \right) ,
\]

with the spherical Bessel function \( j_l(kr) \) and \( k, S_\kappa, \) and \( \tilde{l} \) defined by \( k = \sqrt{2E + E^2/c^2} \), \( S_\kappa = \kappa/|\kappa| \), and \( \tilde{l} = l - S_\kappa \). \( \kappa \) and \( \mu \) are the relativistic spin-angular momentum indices according to Rose [34]. The spin-angular functions \( \chi_\kappa^\mu(\hat{r}) = \sum_s C_{\kappa\mu s} Y_\tilde{l}^s(\hat{r}) \chi_s \) are given in the usual way [34] in terms of Clebsch-Gordan coefficients \( C_{\kappa\mu s} \), spherical harmonics \( Y_\tilde{l}^m \) and Pauli spinors \( \chi_{1/2} = (1,0)^{\dagger}, \chi_{-1/2} = (0,1)^{\dagger} \).

Eq. (18) is a well-defined (effectively atomic) problem which together with (19) uniquely determines the \( \Phi_{i\kappa\mu}(E, r) \). It can be solved using the (nonspherical) phase-functional ansatz of Calogero generalized to the relativistic case [18, 19]. We separate radial and angular parts and write:

\[
\Phi_{i\kappa\mu}(E, r) = \sum_{\kappa'\mu'} \left( \begin{array}{c} \chi_{\kappa'}^\mu(\hat{r}) \phi_{\kappa'\mu'\kappa\mu}(E, r) \\ i\chi_{-\kappa'}^\mu(\hat{r}) \phi_{\kappa'\mu'\kappa\mu}(E, r) \end{array} \right) 
\equiv \sum_{\kappa'\mu'} \left( J_{\kappa'}^\mu(k, r) C_{\kappa'\mu'\kappa\mu}(E, r) - N_{\kappa'}^\mu(k, r) S_{\kappa'\mu'\kappa\mu}(E, r) \right) ,
\]

\(8\)
where $N^\nu_k(k, \mathbf{r})$ is defined analogous to Eq. (20) replacing $j_\nu(kr)$ by the spherical Neumann functions $n_\nu(kr)$. The superscripts $u$ and $l$ refer to the upper and lower components of the four-component spinor, respectively. Inserting into (18) eventually yields the coupled channel equations [21] for the coefficient matrices $C_i$ and $S_i$. The coupled channel equations may be solved by outward integration from the origin to the radius of the bounding sphere $R_i$ for any effective potential that is less singular than $r^{-2}$ ($p \equiv k(E + 2c^2)/c$):

$$
C_{nk\mu\nu}(E, r) = \delta_{nk} \delta_{mu} - p \int_0^r r'^2 \, dr \int_{(4\pi)} \, d\mathbf{r} \, N^\mu_k(k, \mathbf{r}) (V_i(\mathbf{r}) + \beta \sigma \mathbf{B}_i(\mathbf{r})) \Phi_{ik'\nu}(E, \mathbf{r}),
$$

$$
S_{nk\mu\nu}(E, r) = -p \int_0^r r'^2 \, dr \int_{(4\pi)} \, d\mathbf{r} \, J^\mu_k(k, \mathbf{r}) (V_i(\mathbf{r}) + \beta \sigma \mathbf{B}_i(\mathbf{r})) \Phi_{ik'\nu}(E, \mathbf{r}).
$$

Expanding $V_i(\mathbf{r})$ and $\mathbf{B}_i(\mathbf{r})$ in spherical harmonics, the angular integrations can be done analytically. Outside the bounding sphere where $V_i(\mathbf{r}) = \mathbf{B}_i(\mathbf{r}) = 0$, the coefficient matrices $C_{nk\mu\nu}(E, r)$ and $S_{nk\mu\nu}(E, r)$ are constant.

Using the result (22) in Eq. (21) and inserting into Eq. (17) yields the desired one-center expansion of the initial states. The coefficients $A_{ik\nu}(\epsilon_n(\mathbf{q}_\parallel), \mathbf{q}_\parallel)$ in (17) can be obtained from the KKR secular equation [21] which for a slab geometry reads:

$$
\sum_{i'_{\perp} i'_{\parallel}} \sum_{\kappa' \mu'} \left( \delta_{i_{\perp} i'_{\perp}} \delta_{i_{\parallel} i'_{\parallel}} C_{i_{\perp} i'_{\perp} \kappa \mu \kappa' \mu'}(E, R_{i'}) - \sum_{\kappa'' \mu''} B_{i_{\perp} i_{\parallel} \kappa \mu, i'_{\perp} i'_{\parallel} \kappa'' \mu''}(E, \mathbf{q}_\parallel) S_{i_{\perp} i'_{\perp} \kappa'' \mu'', \kappa' \mu'}(E, R_{i'}) \right) A_{i'_{\parallel} i'_{\parallel} \kappa' \mu'}(E, \mathbf{q}_\parallel) = 0.
$$

$B$ are the usual (three-dimensional) KKR structure constants (cf. Ref. [21]) for the supercell geometry (each super-cell consists of $N_{\perp} \times N_{\parallel}$ atoms).

4 The final state

The final state $\Psi^{(f)}_{\mathbf{k}_\parallel}(\mathbf{r}) \equiv \langle \mathbf{r} | G_2 | \epsilon_f, \mathbf{k}_\parallel \rangle$ is an eigenspinor of $h_{\text{LDA}}$ with eigenenergy $E_2 = \epsilon_f$ and could thus be constructed in the same way as the initial states. However, for an appropriate description of the photoemission process we must ensure the correct asymptotic behavior of $\Psi^{(f)}_{\mathbf{k}_\parallel}(\mathbf{r})$ beyond the crystal surface, i.e. a single outgoing plane wave characterized by $\epsilon_f$ and $\mathbf{k}_\parallel$. Furthermore, the damping of the final state due to the imaginary part of the inner potential $iV_\parallel(E_2)$ must be taken into account. We thus construct the final state within SPEEED theory considering a single plane wave $|\epsilon_f, \mathbf{k}_\parallel\rangle$ advancing onto the crystal surface. Using the standard layer-KKR method [13] generalized for the relativistic, full-potential case (cf. e.g. Ref. [7]), we first obtain the SPEEED state $U\Psi^{(f)}_{\mathbf{k}_\parallel}(\mathbf{r})$. The final state is then given as the time-reversed SPEEED state ($U = -i\sigma_y K$ is the relativistic time inversion).

The scattering properties of an atomic cell $\Omega_i$ can be determined from the solution of the coupled channel equations (22) for the final-state energy $\epsilon_f$. From $C_{ik\nu\mu'}(E = \epsilon_f, r = r_{\Omega_i})$.

9
The matrix $\Gamma$ where the new coefficient matrices $U_i$ and $V_i$ are given by:

$$
U_{i\kappa \mu \nu'} = C_{i\kappa \mu \nu'}(\epsilon_f, R_i) + i S_{i\kappa \mu \nu'}(\epsilon_f, R_i),
$$

(25)

$$
V_{i\kappa \mu \nu'} = C_{i\kappa \mu \nu'}(\epsilon_f, R_i) - i S_{i\kappa \mu \nu'}(\epsilon_f, R_i).
$$

(26)

The matrix $\Gamma_i \equiv \Gamma_{i_\perp i_A}$ together with the crystal geometry determine the scattering matrix $M_{i_\perp}$ for a single layer $i_\perp$ [7]:

$$
M_{i_\perp gg'} = \delta_{gg'} + \frac{8\pi^2}{k^2} \sum_{\kappa \mu} \sum_{\kappa' \nu'} \sum_{i_A} i^{i_A} C_{\kappa \mu \nu'} Y_{\mu'-s}(k_{g}) e^{-ik_{g} R_{i_A}}
$$

$$
* \Gamma_{i_\perp i_A \kappa \mu \nu'}(1 - X)_{i_\perp i_A \kappa' \nu'} i^{i_A} C_{\kappa' \nu'} V_{\mu'-s'}(k_{g'}) e^{-ik_{g'} R_{i_A'}}.
$$

(27)

$k^\pm$ denotes the wave vector and $\tau = \pm$ defines the direction of a plane wave (incoming or outgoing) with respect to the layer $i_\perp$. The parallel component of $k^\pm$ differs from $k_\parallel$ by a two-dimensional reciprocal lattice vector $g$ while the perpendicular component is fixed by the plane wave energy $\epsilon_f$. Multiple scattering processes within the layer $i_\perp$ are taken into account via the $X$ matrix of layer-KKR theory [11, 16]:

$$
X_{i_\perp, i_A \kappa \mu, i_A' \kappa' \mu'}(\epsilon_f, k_\parallel) = \sum_{\kappa' \mu' s} \sum_{i_{\parallel}} e^{ik_{\parallel}(R_{i_A'} - R_{i_A} - R_{i_{\parallel}})} C_{\kappa \mu \nu'},
$$

$$
* \Gamma_{i_{\parallel} i_A \kappa \mu \nu'}(R_{i_A'} - R_{i_A} - R_{i_{\parallel}}) C_{\kappa' \nu'} Y_{\mu'-s'}(k_{g'}) e^{-ik_{g'} R_{i_A'}}.
$$

(28)

The prime on the summation over $i_{\parallel}$ indicates that the term where $R_{i_{\parallel}} = 0$ and at the same time $i_A = i_A'$ is omitted. An explicit expression for the lattice sum $\Gamma_{i_{\parallel} i_A \kappa \mu \nu'}(R_{i_A'} - R_{i_A} - R_{i_{\parallel}})$ can be found in Ref. [11].

Therewith, the scattering properties of all layers are known. We consider a plane wave $|\epsilon_f, k_\parallel\rangle$ advancing onto the crystal from the vacuum side. From the scattering matrices (27) the coefficients $u_{i_{\parallel} g s}$ of an expansion into plane waves $|g, \tau, s\rangle$ in front of all layers $i_\perp$ can easily be found using standard recursive layer-by-layer schemes [11, 27]. Time reversal then yields the final-state wave function $\Psi_{k_\parallel}^{(f)}(r)$.

Within each atomic cell $\Omega_i$ the final state may be expanded,

$$
\Psi_{k_\parallel}^{(f)}(r) = \sum_{\kappa \mu} A_{\kappa \mu}(\epsilon_f, k_{\parallel}) \Phi_{\kappa \mu}(\epsilon_f, r - R_i),
$$

(29)

in the locally exact basis of time-reversed ("T") phase functions:

$$
\Phi_{i_{\perp} \kappa \mu}(E, r) = \sum_{\kappa' \mu'} \chi_{\kappa' \mu'}(\bar{r}) \phi_{i_{\perp} \kappa' \mu'}(E, r),
$$

(30)
Here $\chi^{(T)}_{\kappa}(\hat{r})$ is a time-reversed spin-angular function:
\[
\chi^{(T)}_{\kappa}(\hat{r}) \equiv U \chi^{(T)}_{\kappa}(\hat{r}) = \sum_{s}(-2s)C_{\kappa\mu s}Y_{l}^{\mu+s}(\hat{r})^*\chi_{s}.
\] (31)

The expansion coefficients in (29) are derived within SPLEED theory as usual. Starting from the bare coefficients,
\[
A_{i \perp \nu A, \kappa \mu}^{(0)} = \sum_{\kappa', \mu'} \sum_{i, \kappa' \mu' \kappa'' \mu''} \sum_{s} (-2s)(-)^{\mu'-s} C_{\kappa' \mu' s} V_{i \perp \nu A, \kappa'' \mu''}^{-1}
\left[ u_{i \perp A s}^{+} Y_{l}^{\mu'-\mu}(k_{g}^{\perp}) e^{i k_{g}^{\perp} \cdot R_{\kappa''}} + u_{i \perp A s}^{-} Y_{l}^{\mu-\mu'}(k_{g}) e^{i k_{g} \cdot R_{\kappa'}} \right],
\] (32)
and correcting for intra-layer multiple scattering, we obtain:
\[
A_{i \perp i A, \kappa' \mu'} = \sum_{\kappa'' \mu''} \sum_{i, \kappa'' \mu''} \sum_{s} (-1)^{s} V_{i \perp i A, \kappa'' \mu''}^{-1} (1 - X)^{-1} V_{i \perp i A, \kappa'' \mu''} A_{i \perp i A, \kappa'' \mu''}^{(0)}. \] (33)

The one-center expansion (29) is formally very similar to the one-center expansion (17) of the initial states. The main difference, however, is the calculation of the expansion coefficients. For the final state they are obtained from (full-potential) SPLEED theory instead of solving the KKR secular equation. Thereby, we account for the final-state damping effects and the correct asymptotics corresponding to the experimental situation.

5 The dipole operator

In the relativistic theory the dipole interaction of an electron with the electromagnetic field is given by the dipole operator $\Delta = -\alpha A_{0}$ where $A_{0}$ is the spatially constant vector potential inside the crystal. In a matrix element $\langle \Psi_{f} | \Delta | \Psi_{i} \rangle$ between eigenspinors $| \Psi_{f} \rangle$ and $| \Psi_{i} \rangle$ of the Dirac Hamiltonian (3) with energies $E_{f}$ and $E_{i}$, respectively, $\Delta$ can be written as:
\[
\Delta(r) = E_{fi} (A_{0} \nabla + \frac{i \omega}{c} \alpha A_{0}) V_{\text{LDA}}(r) + E_{fi} (A_{0} \nabla) \beta \sigma B_{\text{LDA}}(r) + E_{fi} \frac{\omega}{c} \beta A_{0} \times \sigma B_{\text{LDA}}(r),
\] (34)
with $E_{fi} = -2ic/[(E_{f} + c^{2})^{2} - (E_{i} + c^{2})^{2}]$. The expression is derived by making use of commutator and anticommutator rules analogously to the nonrelativistic case in Ref. (17).

Using the decomposition of the LDA potential and the effective magnetic field (16), we immediately get:
\[
\Delta(r) = \sum_{i} \Delta_{i}(r),
\] (35)
where $\Delta_{i}(r)$ vanishes outside $\Omega_{i}$. In the following we calculate the dipole operator for a given atomic cell. Distinguishing between contributions due to $V_{i}(r)$ and due to $B_{i}(r)$, the $4 \times 4$ matrix in (34) can be written more explicitly as:
\[
\Delta_{i}(r) = E_{fi} \left( \begin{array}{cc}
\Delta^{(uu)}_{V,i}(r) & \Delta^{(ul)}_{V,i}(r) \\
\Delta^{(lu)}_{V,i}(r) & \Delta^{(ll)}_{V,i}(r)
\end{array} \right) + \left( \begin{array}{cc}
\Delta^{(uu)}_{B,i}(r) & \Delta^{(ul)}_{B,i}(r) \\
\Delta^{(lu)}_{B,i}(r) & \Delta^{(ll)}_{B,i}(r)
\end{array} \right),
\] (36)
A straightforward calculation yields
\[ \Delta_{y,i}^{(u)}(\mathbf{r}) = A_0 \nabla V_i(\mathbf{r})I_{(2 \times 2)} \]  \[ \Delta_{y,i}^{(l)}(\mathbf{r}) = \Delta_{y,i}^{(u)}(\mathbf{r}) \]
\[ \Delta_{y,i}^{(u)}(\mathbf{r}) = (A_0 \nabla)(\sigma B_i(\mathbf{r})) - \frac{\hbar}{\epsilon} \sigma A_0 \times B_i(\mathbf{r}) \]  \[ \Delta_{v,i}^{(u)}(\mathbf{r}) = \frac{\hbar}{\epsilon} \sigma A_0 V_i(\mathbf{r}) \]  \[ \Delta_{v,i}^{(u)}(\mathbf{r}) = \Delta_{v,i}^{(l)}(\mathbf{r}) \]
\[ \Delta_{v,i}^{(l)}(\mathbf{r}) = \Delta_{v,i}^{(u)}(\mathbf{r}) \]
\[ \Delta_{v,i}^{(u)}(\mathbf{r}) = \Delta_{v,i}^{(l)}(\mathbf{r}) = 0 \]  \[ \Delta_{v,i}^{(l)}(\mathbf{r}) = -\Delta_{v,i}^{(u)}(\mathbf{r}). \]  \[ \text{(37)} \]

As for the initial states and the final state we need a separation into radial and angular parts. For this purpose the cell potential \( V_i(\mathbf{r}) \) inside the bounding sphere is expanded into spherical harmonics, \( V_i(\mathbf{r}) = \sum_{l,m} V_{ilm}(r)Y_{lm}^m(\hat{\mathbf{r}}) \) (and \( B_i(\mathbf{r}) = \mathbf{b} \sum_{l,m} B_{ilm}(r)Y_{lm}^m(\hat{\mathbf{r}}) \)). The expansion has to be done in a way that guarantees \( V_{LDA}(\mathbf{r}) = B_{LDA}(\mathbf{r}) = 0 \) in the segments between the bounding sphere and the atomic cell \( (S_i - \Omega_i) \). For the two terms in \( (37) \) involving the gradient the expansion needs to be considered in detail:

\[ A_0 \nabla V_i(\mathbf{r}) = \sum_{a=1}^2 \sum_{lm} V_{ilm}(r)W_{ilm}^{(a)}(\hat{\mathbf{r}}) \]  \[ \text{(38)} \]

\[ (A_0 \nabla)(\sigma B_i(\mathbf{r})) = \sum_{a=1}^2 \sum_{lm} B_{ilm}(r)(\sigma \cdot \mathbf{b})W_{ilm}^{(a)}(\hat{\mathbf{r}}) \]  \[ \text{(39)} \]

A straightforward calculation yields

\[ V_{ilm}^{(1)}(r) = \left( \frac{\partial}{\partial r} + \frac{l+1}{r} \right) V_{ilm}(r), \quad V_{ilm}^{(2)}(r) = \left( \frac{\partial}{\partial r} - \frac{l}{r} \right) V_{ilm}(r), \]  \[ \text{(40)} \]

\[ B_{ilm}^{(1)}(r) = \left( \frac{\partial}{\partial r} + \frac{l+1}{r} \right) B_{ilm}(r), \quad B_{ilm}^{(2)}(r) = \left( \frac{\partial}{\partial r} - \frac{l}{r} \right) B_{ilm}(r). \]  \[ \text{(41)} \]

for the radial parts \( V_{ilm}^{(a)} \) and \( B_{ilm}^{(a)} \) due to \( V_i(\mathbf{r}) \) and \( B_i(\mathbf{r}) \), respectively, and

\[ W_{ilm}^{(1)}(\hat{\mathbf{r}}) = \sum_{m'=1}^{m'} Y_{m'}^{m'}(\hat{e}_{A_0}) \chi_{ilm}^{(1)} Y_{l-1}^{m+m'}(\hat{\mathbf{r}}), \]  \[ \text{(42)} \]

\[ W_{ilm}^{(2)}(\hat{\mathbf{r}}) = \sum_{m'=1}^{m'} Y_{m'}^{m'}(\hat{e}_{A_0}) \chi_{ilm}^{(2)} Y_{l+1}^{m+m'}(\hat{\mathbf{r}}), \]

with

\[ \chi_{ilm}^{(1)} = \sqrt{\frac{3}{4\pi}} (-)^m \left( \frac{l-m}{2l+1} \frac{2l-m'(m+m'(l+1))}{2(l+m'm')} \right), \]  \[ \text{(43)} \]

\[ \chi_{ilm}^{(2)} = \sqrt{\frac{3}{4\pi}} \left( \frac{l+1-m}{2l+3} \frac{2(l+1)+m'(m-m'l)}{2(l+1-m'm')} \right). \]

for the angular parts \( W_{ilm}^{(a)} (a = 1, 2) \). \( \hat{e}_{A_0} \) is the unit vector in the direction of the vector potential \( \mathbf{A}_0 \).
6 The transition-matrix elements

Now we are in the position to calculate the transition-matrix elements

\[ M_n(\epsilon_f, k_\parallel) = \langle \epsilon_f, k_\parallel | G_2^+ \Delta | n, q_\parallel \rangle = \int d^3r \quad \Psi_{k_\parallel}^{(f)}(r) \Delta(r) \Psi_{q_\parallel}^{(n)}(r). \] (44)

Inserting the one-center expansions for the initial and the final states \((17)\) and \((29)\), respectively, and using the decomposition \((35)\) of the dipole operator yields:

\[
M_n(\epsilon_f, k_\parallel) = \sum_{i} \sum_{\kappa \mu \kappa' \mu'} A_{i \kappa \mu}(\epsilon_f, k_\parallel) M_{i \kappa \mu \kappa' \mu'}(\epsilon_f, \epsilon_n(q_\parallel)) A_{i \kappa' \mu'}(\epsilon_n(q_\parallel), q_\parallel)
\]

\[ = N_\parallel \sum_{i \perp \iota} \sum_{\kappa \mu \kappa' \mu'} A_{i_\perp \iota \kappa \mu}(\epsilon_f, k_\parallel) M_{i_\perp \iota \kappa \mu \kappa' \mu'}(\epsilon_f, \epsilon_n(q_\parallel)) A_{i_\perp \iota \kappa' \mu'}(\epsilon_n(q_\parallel), q_\parallel), \]

where \(N_\parallel\) is the number of two-dimensional unit cells per layer and

\[ M_{i \kappa \mu \kappa' \mu'}(E_f, E_i) = \int_{\Omega_i} d^3r \quad \Phi_{i \kappa \mu}^{(T)}(E_f, r) \Delta_i(r) \Phi_{i \kappa' \mu'}^{(T)}(E_i, r), \]

is the atomic matrix element of the dipole operator between the phase functions at the respective eigenenergies. The integration extends over the volume of the polyhedron \(\Omega_i\). Since \(V_i(r) = B_i(r) = 0\) and thus \(\Delta_i(r) = 0\) in the segments between \(\Omega_i\) and the bounding sphere \(S_i\), the integration may be performed over \(S_i\) as well which is more convenient. In the following we suppress the atomic index \(i\). Using \((57)\) we get eight dipole matrix elements,

\[ M_{\kappa \mu \kappa' \mu'}(E_f, E_i) = E_{fi} \sum_{dd'} \int_S d^3r \quad \Phi_{\kappa \mu}^{(dd')}(E_f, r) \left( \Delta_{V}^{(dd')}(r) + \Delta_{B}^{(dd')}(r) \right) \Phi_{\kappa' \mu'}^{(d')}(E_i, r), \]

each of which can be separated into radial and angular parts:

\[ M_{\kappa \mu \kappa' \mu'}(E_f, E_i) = E_{fi} \sum_{\kappa' \mu' \kappa'' \mu''} \sum_{lm} \left\{ \right. \]

\[ \frac{2}{\omega} R_{I}^{(uu)} \left[ V_{lm}^{(a)} \right] A_{\kappa'' \mu'' \kappa''}^{\mu'' \mu''} \left[ W_{lm}^{(a)} \right] - \frac{\omega}{C} R_{I}^{(uu)} \left[ V_{lm} \right] A_{\kappa'' \mu'' \kappa'' \mu''}^{\mu'' \mu''} \left[ \sigma A_0 Y_l^m \right] \]

\[ \left. - \frac{\omega}{C} R_{I}^{(uu)} \left[ V_{lm} \right] A_{\kappa'' \mu'' \kappa'' \mu''}^{\mu'' \mu''} \left[ \sigma A_0 Y_l^m \right] \right\} \]

\[ + \frac{2}{\omega} R_{I}^{(uu)} \left[ B_{lm}^{(a)} \right] A_{\kappa'' \mu'' \kappa'' \mu''}^{\mu'' \mu''} \left[ \sigma b W_{lm}^{(a)} \right] - \frac{\omega}{C} R_{I}^{(uu)} \left[ B_{lm} \right] A_{\kappa'' \mu'' \kappa'' \mu''}^{\mu'' \mu''} \left[ \sigma A_0 \times b Y_l^m \right] \]

\[ + \frac{2}{\omega} R_{I}^{(uu)} \left[ B_{lm} \right] A_{\kappa'' \mu'' \kappa'' \mu''}^{\mu'' \mu''} \left[ \sigma b W_{lm} \right] - \frac{\omega}{C} R_{I}^{(uu)} \left[ B_{lm} \right] A_{\kappa'' \mu'' \kappa'' \mu''}^{\mu'' \mu''} \left[ \sigma A_0 \times b Y_l^m \right] \right\} \right\}.
\] (48)
with $I \equiv (\kappa \mu \nu \kappa' \mu' \gamma' \gamma'' \kappa'' \mu'' \nu'' \mu''')$ and:

$$
\mathcal{R}_I^{(df')}[f] \equiv \int_0^R r^2 dr \phi_{\kappa' \mu' \gamma' \gamma''}(r, E_f) f(r) \phi_{\kappa'' \mu'' \gamma''}(r, E_i),
$$

(49)

$$
\mathcal{A}_{\kappa \kappa'}^{\mu \mu'}[f] \equiv \int_{(4\pi)} d\hat{r} \chi_{\kappa}(\hat{r}) \chi_{\kappa'}^{\mu}(\hat{r}) 
\int_{(4\pi)} d\hat{r} \chi_{\kappa}(\hat{r}) \chi_{\kappa'}^{\mu}(\hat{r}),
$$

(50)

for $d = u, l$ and $d' = u, l$.

This completes our formalism. From the different contributions (48) we can calculate the atomic matrix element (46) for each layer $i_\perp$ and each atom $i_A$ in the two-dimensional unit cell. Inserting into (45), one obtains the full transition-matrix element (13) which enters the expression (12) for the PES intensity. For a single point $(\epsilon_f, k_\parallel)$ in the spectrum, it is necessary to determine the matrix elements at the energies $E_f = \epsilon_f$ and $E_i = \epsilon_n(q_\parallel)$ for each $n$ ($q_\parallel$ is fixed) where there is a nonnegligible contribution of the imaginary part of the initial-state Green function $G_{nn'}(E_1, q_\parallel)$.

The different types of radial matrix elements (49) result from the different possible combinations of the upper and lower components of the Dirac spinor. In the nonrelativistic case only the $d = d' = u$ term survives. All one-dimensional integrals are well defined since for $r \rightarrow 0$ there is a $r^{-2}$ singularity of $f(r)$ at most. This can be seen from Eq. (41).

Furthermore, the radial parts of the phase functions are regular at $r = 0$ [Eq. (19)].

For the paramagnetic case $b = 0$ there are two types of angular matrix elements (50). The first in Eq. (48), $\sim W_{lm}^{(a)}$, is well known from the nonrelativistic theory [23]. For spherically symmetric potentials $V_i(r) = V_{00}(r)Y_0^0(\hat{r}) \ [l = m = 0$ in (45) only the term for $a = 2$ yields a nonvanishing contribution. In this case the angular matrix element further reduces to the muffin-tin form [15]. The second type of matrix elements, $\sim \sigma A_0 Y_l^m$, represents a relativistic correction [23]. In the ferromagnetic case two new types of matrix elements, $\sim \sigma b W_{lm}^{(a)}$, and $\sim \sigma A_0 \times b Y_l^m$, occur. All angular matrix elements are simply related to usual Gaunt coefficients and can thus be calculated analytically.

7 Summary

In this paper we have described in detail a new formalism to evaluate Pendry’s formula for the one-step model of (inverse) photoemission spectroscopy. The initial-state Green function represents the central physical quantity of the one-step model. Compared with previous work, we propose a different treatment of the initial state and determine the Green function from the Dyson equation rather than within the DFT-LDA ground-state theory. Generally, this is a necessary condition for a correct description of one-particle excitations. Given the electronic self-energy, our formalism allows to include the corresponding many-body effects such as temperature dependencies, quasi-particle damping, band narrowing, satellites, etc. in the one-step description of the photoemission process. Within the framework of the original theory [10, 11, 12] and its subsequent improvements [13], one is unable to deal with an in general nonlocal self-energy correction since this is incompatible with the KKR multiple-scattering formalism on which the original theory
is solely based [15]. Our main idea is thus to disentangle the calculation of the Green function from the calculation of the dipole matrix elements. This is achieved by considering the low-energy LDA eigenstates merely as basis states to set up the Dyson equation. Solving the Dyson equation to get the PES raw spectrum is then independent from the calculation of the actual dipole matrix element. Note that it is necessary to work within an eigenstate basis of the LDA Hamiltonian since this leads via Eq. (34) to the important spatial decomposition (35) of the dipole operator which eventually allows for a convenient calculation of the transition-matrix elements.

The present paper has shown that the alternative evaluation of the one-step model can formally be performed consistently for very general cases, namely for complex geometries with more than one atom per unit cell, for general space-filling nonspherical LDA potentials, for situations which require a fully relativistic treatment, and for the ferromagnetic case, in particular when exchange and spin-orbit splitting must be treated on equal footing.

It goes without saying that the presented formalism can also be applied without taking into account the self-energy correction. Even in the case Σ ≡ 0 it should be advantageous since it is more transparent and more simple compared with the corresponding (full-potential, relativistic) theory [23] based on the original concept [11]: (i) Simple one-dimensional integrals (49) have to be performed instead of two-dimensional integrations [23] for the calculation of the radial matrix elements. Furthermore, their number is reduced considerably. (ii) Only the regular instead of both, the regular and the irregular solution of the atomic Dirac equation is needed [see Eq. (19)]. (iii) There are no additional intra-layer and inter-layer contributions as in the original theory [23]. The partitioning of the photocurrent into atomic, intra-layer and inter-layer contributions in the original formulation is only due to formal reasons, and a direct physical interpretation is difficult. (iv) Contrary, the separate calculation of the initial-state Green function and the matrix elements allows to distinguish clearly between the raw spectrum and its modifications due to secondary effects.

The ferromagnetic Gd(0001) surface represents a prototype system for the application of the theory. Since Z = 64 for Gd, a fully relativistic evaluation of the one-step model is meaningful even if it is based on a potential and self-energy input from scalar-relativistic LDA calculations [25] and from two-component many-body theory [23], respectively. Recent many-body calculations show that striking temperature-dependent correlation effects should be observable in the (5d, 6s) conduction band as a consequence of intra-atomic exchange coupling to the subsystem of localized and ferromagnetically ordered 4f moments [25, 35]. The interpretation of several PES/IPE spectra from Gd (cf. e. g. Ref. [35]) is controversial up to now and may be resolved by supplementing the electronic-structure calculations with a reliable treatment of the secondary effects. Calculations based on the presented formulation of the one-step model are intended for the future.
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