Photoemission theory for nonlocal potentials: application to Ni(100)

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Abstract

A one-step theory of photoemission for nonlocal potentials which overcomes different limitations of the original theory has been applied to Ni(100). The theory is formulated for 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. In the framework of this theory the final state is calculated using multiple scattering techniques. The initial state, which is described by the energy- and temperature dependent spectral function, results from a combination of a one-particle slab calculation with many-body techniques. Here we present temperature-dependent photoemission intensities calculated for different excitation energies from the (100)-surface of ferromagnetic Ni. © 2000 Elsevier Science B.V. All rights reserved.

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1. Introduction

For investigating the electronic properties of crystalline materials, ultraviolet photoemission spectroscopy (PES) [1–5] and inverse photoemission spectroscopy (IPE) [6–10] have been developed into powerful tools. Using these techniques, it is possible to measure the dispersion of occupied states as well as unoccupied states around the Fermi edge. The theoretical interpretation of experimental intensity distributions is commonly given within a one-step theory of photoemission [11,12]. For the description of the underlying electronic structure, it is widely acceptable to use the results of band-structure calculations that are based on density functional theory (DFT) and the local density approximation (LDA) [13–16]. Nevertheless, for a 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. Provided that the self-energy is known, one can deduce a PES/IPE spectrum by solving first the Dyson equation [16,17], which gives the corresponding Green’s function, and, consequently, the spectral function. Combining these quantities with the transition-matrix elements, one can obtain a reliable interpretation of photoemission experiments. The main disadvantage of a conventional formulation of a one-step model lies in the fact that it is intrinsically based on a local potential. In our theory [18], we have included a non-local self-energy term in reformulating the original one-step model introduced first by Pendry [11]. The LDA potential and the self-energy are assumed to...
be given quantities that must be obtained from a preceding electronic-structure calculation [19]. In Section 2, a short introduction to the non-local photoemission theory will be given. Section 3 deals with the calculation of the spectral function for Ni(100), and finally, we present a series of temperature-dependent photoemission spectra that we obtained for different excitation energies.

2. Photoemission theory for nonlocal potentials

We start our considerations with Pendry’s formula for the photocurrent, which defines the one-step model of PES [11]:

\[ I \propto \text{Im}(\varepsilon_f, \mathbf{k}_f) G^0(\varepsilon_f) G^r(\varepsilon_f, \mathbf{k}_f, \mathbf{k}_i). \]  \hspace{1cm} (1)

This expression can be derived from Fermi’s golden rule for the transition probability per unit time [20]. The photoelectron state at the detector is written as \( |\psi_f, \mathbf{k}_d, s\rangle \), where \( \mathbf{k}_d \) is the component of the wave vector parallel to the surface, \( \varepsilon_f \) is the kinetic energy of the photoelectron and \( s \) is the spin index. The advanced Green’s function, \( G^r \), in Eq. (1) characterizes the scattering properties of the material at the final-state energy \( E_2 \). Via \( |\psi_f, \mathbf{k}_d, s\rangle = G^0|\psi_i, \mathbf{k}_i, s\rangle \), all multiple-scattering corrections are formally included. Using standard Korringa-Kohn-Rostocker (KKR) multiple scattering techniques [21–24], we can calculate the final state, \( |\psi_f, \mathbf{k}_d, s\rangle \), as a time-reversed LEED state. As far as the final state is concerned, many-body effects are included only phenomenologically by using a parameterized, weakly energy-dependent and complex inner potential, \( V_0(E_2) = V_0(E_1) + V_0(E_2) \), as usual [25]. The dipole operator, \( \mathbf{\Delta} \), in Eq. (1) is used in the electric dipole approximation. In order to calculate the initial state Green’s function \( G^0 \), a direct solution of the Dyson equation in real space representation turns out to be inconvenient. We therefore turn to a matrix representation and choose the eigenfunctions of the LDA Hamiltonian as basis states. For the present evaluation of the Green’s function, \( G^0 \), we used a LMTO basis which we obtained from a tight-binding LMTO cluster calculation.

![Central cluster for Ni consisting of six layers embedded into a surrounding cluster. The z-axis is directed perpendicular to the Ni(100) surface.](image)
The spectral function is given by:

\[ \Phi_\text{slm}(r) = -\frac{1}{\pi} \Im G_{\text{slm}}(E_i + \theta^*, k_i). \]  

(5)

In the Bloch-sum basis, Pendry’s formula reads [18]:

\[ I^\text{s} = \sum_{i=0}^{N} M_{\text{si}\text{lm}}^\text{f}(\epsilon_f, k_d) A^\text{slm}(E_i, k_d). \]  

(6)

where \( M \) is the matrix element of the dipole for a central cluster that must be large enough to achieve convergence in the two-dimensional Bloch sum \( |i, lm, k_d \rangle \). In real-space representation, it follows:

\[ M^\text{f}_{\text{si}\text{lm}}(\epsilon_f, k_d) = \int \Psi^\text{f}(r) \delta \Phi^\text{slm}_{\epsilon_f}(r) d^3r. \]  

(7)

Herein, \( \Psi \) denotes the final state, which is calculated as a time-reversed LEED state. For the initial state, an approximate solution has been used in neglecting the layer-dependence:

\[ \Phi^\text{slm}(r) = \Phi_{\text{slm}}(r). \]  

Consequently, Eq. (6) reduces to the form:

\[ I^\text{s} = \sum_{i=0}^{N} M^\text{f}_{\text{si}\text{lm}}(\epsilon_f, k_d) \Phi_{\text{slm}}(E_i, k_d). \]  

(8)

where \( \Phi \) defines the spectral function for which the summation over different layers has been performed before.

3. Calculation of the spectral function

To calculate the spectral function, \( \Phi \), we start with the determination of the elements of the real-space Hamiltonian, \( H \), using a cluster approach for a central cluster that must be large enough to achieve convergence in the two-dimensional Fourier transformation. As shown in Fig. 1, the central cluster is embedded into a surrounding cluster in such a way that surface effects are negligible for the elements of the central cluster. The real-space TB-LMTO method is used, employing self-consistent potential parameters obtained from TB-LMTO bulk calculations for the same geometrical arrangement. Keeping these potential parameters fixed, the real-space Hamiltonian for

Fig. 2. Spin-resolved quasi-particle bandstructure of Ni projected onto the \( \Sigma^\uparrow \) and \( \Sigma^\downarrow \) directions of the surface Brillouin zone together with the real and imaginary parts of the corresponding self-energy.
Fig. 3. Spin-resolved temperature dependent photoelectron spectra calculated in normal emission for different excitation energies from the Ni(100) surface.
the central cluster is calculated up to a given accuracy by increasing the number of atoms in the surrounding cluster. The present calculation has been performed with a central cluster consisting of six layers with 75 atoms in total. An accuracy in the Hamiltonian elements better than $1 \times 10^{-7}$ could be achieved using a surrounding cluster with 520 atoms.

The self-energy has been calculated within a multi-band Hubbard model including s, p, and d states and the complete (on-site) Coulomb matrix [19]. Using atomic symmetries, the Coulomb-matrix elements can be expressed by essentially two parameters, $U=2.47 \text{ eV}$ and $J=0.5 \text{ eV}$, the values of which have been fixed by assuming a ratio $J/U\approx 0.2$ typical for the 3d transition metals and by fitting the measured magnetic moment at $T=0$. The present calculation has been performed by means of a standard second-order perturbation theory in the interaction parameters [17]. The resulting Curie temperature turns out to be $T_C=1655 \text{ K}$, which is about a factor of 2.6 larger than the measured value but considerably smaller than the Hartree–Fock (Stoner) value.

The Hamiltonian, $H$, together with the self-energy allows us to obtain the spectral function, $A$. Fig. 2 shows the spin-resolved quasi-particle band structure of Ni projected onto the $\pi \times \pi$ and $\pi \times \Gamma$ directions of the surface Brillouin zone together with the corresponding self-energy for $e_g$ and $t_{2g}$ symmetry [19] as a density plot of the single electron spectral function, $A$. Values of high spectral density are visible by the dark grey regions. Sharp features correspond to long-living quasiparticles.

4. Results of photoemission calculations for Ni(100)

In this section, the results of our photocurrent investigation on ferromagnetic Ni are presented. According to Eq. (8), we have calculated spin-resolved normal emission spectra from Ni(100) for different temperatures and excitation energies. The three pictures on the top of Fig. 3 show the results for $T=0 \text{ K}$ and $h\omega=16.85, 21.2$ and $30 \text{ eV}$. The calculated intensity distributions clearly depend on the excitation energy as well as on the different spin directions. As expected [26], the main peak structure is located about 1.5 eV below the Fermi level. Also, a variation with temperature is visible for the different photocurrent intensities. Comparing the spectra calculated at $T=1500 \text{ K}$, with those at $T=0 \text{ K}$, a sharp structure near the Fermi level occurs in the spin-up channel. Also, the shape of the particular intensities is different for different temperatures. For $T=1655 \text{ K}$, which means $T=2T_c$, the paramagnetic case is shown at the bottom of Fig. 3. It should be mentioned here that no further parameters have been used for this calculation. Only the imaginary part of the self-energy has been introduced in a phenomenological way for the final state. It has been fixed for all excitation energies to $V_\gamma(E_F)=1.8 \text{ eV}$.

5. Summary

In this paper, we have applied a new formalism to evaluate Pendry’s formula for the one-step model of (inverse) photoemission spectroscopy. We propose a different treatment of the initial state and determine the Green’s function from the Dyson equation rather than within the DFT-LDA ground-state theory. Given the electronic self-energy, our formalism allows the inclusion of corresponding many-body effects such as temperature dependencies, quasi-particle damping, band narrowing, satellites, etc. in the one-step description of the photoemission process. Furthermore, we have presented the first results of photoemission calculations on Ni(100) for different temperatures and excitation energies, which are useful for a quantitative interpretation of temperature-dependent and spin-resolved photoemission measurements.

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References