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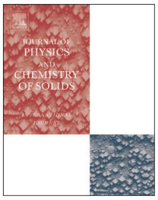

Electron momentum density and Compton profile by a semi-empirical approach

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ABSTRACT

Here we propose a semi-empirical approach to describe with good accuracy the electron momentum densities and Compton profiles for a wide range of pure crystalline metals. In the present approach, we use an experimental Compton profile to fit an analytical expression for the momentum densities of the valence electrons. This expression is similar to a Fermi–Dirac distribution function with two parameters, one of which coincides with the ground state kinetic energy of the free-electron gas and the other resembles the electron–electron interaction energy. In the proposed scheme conduction electrons are neither completely free nor completely bound to the atomic nucleus. This procedure allows us to include correlation effects.

We tested the approach for all metals with $Z=3$–50 and showed the results for three representative elements: Li, Be and Al from high-resolution experiments.

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1. Introduction

Compton profile (CP) spectroscopy is a widely used tool to extract information about the electronic structure of crystalline solids. It provides the electron momentum density (EMD), which, in turn, allows the verification of the quality of the radial electron wave functions, since they are related through Fourier transforms. It is commonly accepted that many properties of the solids can be well represented by dividing the electrons into two groups: inner-core and conduction electrons. The former do not participate in crystalline bonding in solids and can be treated as frozen orbitals. Both bound and conduction electrons contribute to the total CP in different ways according to their spatial localization. Since conduction electrons are less bound, they have largely spread radial orbitals, and are therefore highly localized in momentum space. Thus, they contribute to the CP with a sharp peak located at low momentum transferred [1]. On the other hand, the electrons in the inner shells are strongly bound and have spatial orbits circumscribed to relatively small distances to the atomic nucleus. Their contribution to the CP takes place as a low-intensity broad tail at high momentum transferred.

Historically, CPs obtained in experiments with high-resolution (~ 0.1–0.2 a.u.) X-ray have been successfully compared with those obtained by different theoretical methods, such as Quantum Monte Carlo [2,3], *ab initio* Green's function approximation [4], and DFT calculations with different exchange-correlation functionals [5–8]. The local density approximation (LDA) within the density functional theory (DFT) has been widely used to predict various bulk properties of different solids [9,10]. However, when theoretical CPs obtained by LDA calculations are compared with experimental ones, an overestimation at low momentum transfer and underestimation at high momentum transfer are observed. These discrepancies have been attributed to the incorrect exchange and correlation effects given by the LDA functional. Different methods based on Lam–Platzman correction [11–13] have been proposed to remedy the LDA deficiencies in the CP estimations. However, studies with high-resolution Compton scattering experiments of Li have revealed an anomalous behavior when it is compared with the theory [14–16], given that it has not been possible to describe by means of free-electron or by Fermi-liquid theory. Such deviations from the standard metallic picture can be ascribed to the possible existence of significant pairing correlations in the ground state identified in terms of electron transfers from s-like to p-like character, constituting a possible explanation for the breakdown of the Fermi-liquid picture [13,17].

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For metallic systems one can define the Fermi surface (FS) as the break in the EMD whose presence reveals the existence of quasi-particles and the validity of the Landau–Fermi liquid theory. In this sense, the anti-symmetrized geminal product (AGP) method has been successfully used for a wide range of materials. This provides an orbital-dependent approach in which the electron momentum density is constructed using the natural orbitals, and the corresponding occupation numbers are obtained through a variational procedure [13,18].

In a recent work [19], high accuracy momentum densities and Compton profiles of Be, Cu, Ni, Fe_3Pt, and $YBa_2Cu_4O_8$ were obtained using *ab initio* calculations of the linear tetrahedron method.

In this work, we propose a systematic approach to calculate the CPs of several crystalline metals by using a simple analytical expression for the valence EMD able to reproduce the CP with very high accuracy. The method allows including electron correlation effects based on the joint use of Fermi liquid and Hartree–Fock formalism. The formula proposed resembles the Fermi–Dirac distribution, but the thermodynamic constants are replaced by fitting parameters. A thorough and systematic investigation, led us to recognize that these fitting parameters are related to the Hartree–Fock energy of the free-electron ground state. These energies can be expressed either in terms of the Fermi momentum or, in terms of the Wigner–Seitz radius.

The present approach allows to calculate the CPs of all the metals with $Z=3$–50. Comparison with the experimental results showed good agreement in most of the cases. As an example, we show three selected metals with different valence values.

The rest of the paper is arranged as follows. Sections 2 and 3 describe the theoretical methods, especially the connections between kinetic and exchange energy of electrons in solids with thermodynamic distribution. Section 4 describes the comparison between our semi-empirical calculations and the experimental results for some representative elements. Finally, a brief summary is given in Section 5.

2. Theory

In a nonrelativistic and high-energy transfer regime, theoretical calculations for isotropic CPs are commonly performed under the impulse approximation (IA). It is assumed that energy and momentum are conserved. Limitations to the IA validity in Compton scattering have been widely discussed by [20]. This approach is expected to be valid when the energy transferred in the scattering process is much greater than the binding energy of the electron orbital.

The isotropic valence CP is defined under the IA as

$$J_{val}(q) = \tfrac{1}{2}\int_q^\infty n_{val}(p)p\,dp \qquad (1)$$

being $\int J_{val}(q)\,dq = N$, where N is the number of valence electrons in the atom. Consequently, the valence EMD $n_{val}(p)$, can be obtained from the Compton profile by

$$n_{val}(p) = -\frac{2}{p}\frac{dJ_{val}}{dq}\bigg|_{q=p} \qquad p \neq 0, \qquad (2)$$

and

$$n_{val}(0) = -2\frac{d^2J_{val}}{dq^2}. \qquad (3)$$

The free electron gas (FEG) CP is defined as

$$J^{FEG}(q) = \frac{1}{2}\int_q^\infty \frac{I_r(p)}{p}\,dp \qquad (4)$$

where $I_r(p)dp$ is the probability of an electron at position $\mathbf{r}$ to have a momentum of magnitude between p and $p + dp$. The Thomas–Fermi theory states that, at zero temperature

$$I_r(p)dp = n_0p^2\,dp = \frac{4\pi}{(4/3)\pi k_F^3}p^2\,dp, \qquad (5)$$

where the Fermi momentum k_F is defined as

$$k_F = \frac{(9\pi/4)^{1/3}}{r_{WS}} \qquad (6)$$

and r_{WS} is the Wigner–Seitz radius of a sphere containing a single electron [21]. Inserting Nn_0 in place of n_{val} in Eq. (1), the FEG CP is

$$J^{FEG}(q) = \frac{3N}{4k_F^3}\left(k_F^2 - q^2\right). \qquad (7)$$

The CP given by Eq. (7) has the form of an inverted parabola for $q \leq k_F$ and is zero for $q > k_F$. The same profile is produced by assuming a plane wave function $e^{-i\mathbf{k}\cdot\mathbf{r}}/\sqrt{V}$ for the free electrons.

It should be noted that the valence EMD obtained from the non-interacting FEG CP (using Eq. (2)) coincides with the Fermi–Dirac distribution function:

$$f(p) = \left(1 + \exp\left[\frac{p^2/2 - \mu}{K_B T}\right]\right)^{-1} \qquad (8)$$

where $p^2/2$ is the energy of the single-particle state, μ is the chemical potential ($\sim k_F^2/2$), and $K_B T$ is the thermal energy of the FEG [4]. Unfortunately, FEG model does not produce good results due to the effects of interactions with the periodic lattice potential and mutual electrons Coulomb interactions are neglected in these simple approaches.

3. Semiempirical approach

To generate parametric valence EMDs that lead to the correct CP values, we propose to use a modified Fermi–Dirac distribution function. As pointed out in [22], we can modify the Fermi–Dirac distribution with some broadening energy parameters. In our approach, we introduce μ_e and T_e, called the *electronic chemical potential* and the *electronic Fermi temperature*, respectively, in analogy with the thermodynamic counterparts:

$$n_{val}(p) \equiv n_0\left(1 + \exp\left[\frac{p^2/2 - \mu_e}{K_B T_e}\right]\right)^{-1}. \qquad (9)$$

For a systematic study, we took the data from several CPs of pure crystalline metals ($Z=3$–50) with the purpose to extract the valence EMD, as stated in Eq. (2). The elements and references used were: Li [14], Be [23], B [24], C (graphite) [25], Na [26,3], Mg [27], Al [28], Si [29], K [30], Ca [31], Sc [32], Ti [33], V [34], Cr [35], Mn [36], Fe [34], Co [37], Ni [34], Cu [38], Zn [39], Ga [40], Ge [29], Se [41], Rb [30], Sr [30], Y [42], Zr [43], Nb [30], Mo [44], Ru [45], Rh [46], Pd [47], Ag [48], Cd [39], In [30], and Sn [49].

To follow this approach, we rely on the fact that the derivative of the valence EMD $\partial n_{val}(p)/\partial p$ provides information about the two required energies. This derivative function exhibits a peak at a momentum value corresponding to the electronic chemical potential μ_e, and the spread of this function corresponds to the electronic Fermi energy $k_B T_e$. We must point out that these

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