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MOMENTUM DISTRIBUTIONS AND COMPTON PROFILES OF COPPER AND ALUMINIUM.

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Abstract

The many body ground state properties of momentum distribution and Compton profiles have been calculated under the Kohn-Sham density functional formalism for solid copper and aluminium. A linear combination of Slater type orbitals (LCSTO) was used in the single particle Kohn-Sham equations to calculate the particle density, $\rho(x)$, and the effective potential, $V_{eff}(x)$. The crystal structure was employed by expansion of functions to first order in nearest neighbours. The particle momentum distributions and associated Compton profiles were then calculated.

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1.0 Introduction

The many body problems when the number of particles $N > 3$ is unwieldy. Therefore, for electrons in a solid with N of the order of Avogadro's number the problem is exactly insoluble, due to the presence of the exponential wall [1]. There have been several approaches to solve the problem Hartree [2] in which the many body problems are reduced to a single particle approximate central field problem. The results have not been in good agreement with experiment, where the problem with the Hartree approach was that the resulting wave function was symmetrical, which did not represent fermions.

An improvement is the density functional theory (DFT) [3,4]. In DFT, the basic variable is the particle density on which the ground state properties depend. In the most widely used form of the DFT, that is, the local density approximation (LDA), the problem of an inhomogeneous electron gas is approximated by that of a homogeneous electron gas.

In this work, the DFT is used to calculate the ground state properties of momentum distributions and Compton profiles of copper and aluminium. The particle density at a point was calculated and then expanded to take into effect non-local contributions from other points. This spherically averaged density was then used as the basic variable for calculations.

2.0 The DFT formalism

In density functional theory, the energy is a functional of the electron density. For a system of N interacting electrons in an external potential $V(x)$, the energy functional is given by

$$E[\rho(x)] = T_s[\rho(x)] + \frac{1}{2}\iint \frac{\rho(x)\rho(x')dx\,dx'}{|x-x'|} + \int V(x)\rho(x)dx + E_{xc}[\rho(x)] \qquad (2.1)$$

where $T_S[\rho(x)]$ is the kinetic energy of non-interacting electron gas with density $\rho(x)$, the second term is the classical Coulombic electrostatic energy, the third term is the potential energy of non-interacting electrons having density $\rho(x)$ in the external field $V(x)$, and $E_{XC}[\rho(x)]$ is the exchange correlation energy.

The kinetic energy is given according to the Kohn-Sham theory from a set of orbitals Φ_n, derived from a one-particle Schrodinger equation. Thus,

$$T_s[\rho(x)] = \sum_n a_n \int \phi_n(x) \left(\frac{-\eta^2 \nabla^2}{2m} \right) \phi_n(x) dx \qquad (2.2)$$

The particle density is given as $$\rho(x) = \sum_n a_n \left| \phi_n(x) \right|^2 \qquad \textbf{(2.3)}$$

The dependence of the kinetic energy of the particles on the particle density is via equations (2.2) and (2.3). Since the first three terms on the right hand side of equation (2.1) are known, the Hohenberg-Kohn-Sham formalism reduces the problem to that of obtaining a suitable form for the exchange correlation energy functional $E_{xc}[\rho(x)]$. Their approximation, known as the local density approximation (LDA), takes the form.

$$E_{xc}[\rho(x)] = \int \rho(x)\, \varepsilon_{xc}^{h}[\rho(x)] dx \qquad (2.4)$$

where $\varepsilon_{xc}^{h}[\rho(x)]$ is the exchange correlation energy per particle of a homogenous electron gas having density $\rho(x)$. The LDA is valid in the limit that the electron density is slowly varying. The ground state electron density is that which minimises $E[\rho(x)]$, that is,

$$\frac{\delta E[\rho(x)]}{\delta \rho(x)} = 0 \qquad (2.5)$$

subject to the constraint $$\int \rho(x) dx = N \qquad (2.6)$$

The resultant is the set of Kohn-Sham single particle Schrodinger equations:

$$\left(\frac{-\eta^2 \nabla^2}{2m} + V_{eff}(x) - \varepsilon_n \right) \phi_n(x) = 0 \qquad (2.7)$$

where $$V_{eff}(x) = V(x) + \int \frac{\rho(x') dx'}{|x - x'|} + V_{xc}[\rho(x)] \qquad (2.8)$$

and the exchange correlation potential

$$V_{xc}[\rho(x)] = \frac{\delta E_{xc}[\rho(x)]}{\delta \rho(x)} \qquad (2.9)$$

With $V_{eff}(x)$ known, equation (2.7) is solved self-consistently to obtain the set of single particle orbital $\Phi_n(x)$. The many body problems reduce to finding a form for the exchange correlation potential, and the form used here is

$$V_{XC}[\rho(x)] = \beta(x) V_{KS}(x) \qquad (2.10)$$

where $$V_{KS}[\rho(x)] = -2 \left[\frac{3\rho(x)}{\pi} \right]^{\frac{1}{3}} \qquad (2.11)$$

$$\beta(x) = 1 + Br \ln\left(1 + r^{-1}\right) \qquad (2.12)$$

$$B = 0 \cdot 7734 \qquad (2.13)$$

and $$r = \frac{1}{21}\left(\frac{3}{4}\pi\rho(x)\right)^{\frac{1}{3}} \qquad (2.14)$$

3.0 Momentum distribution and compton profile

In single atoms, the electrons can be pictured as circulating round the nuclei in stable orbits of fixed energies, angular momenta and velocities. Quantum mechanically, the positions of the electrons are specified by wave functions, and when normalised, these determine the average values of observable. For example, the observed momentum

$$\pi\ p\ \phi = \pi\ \psi\left|\hat{p}\right|\psi\ \phi = \int \psi * \hat{p}\,\psi\, dx \qquad (3.1)$$

where $\hat{p}$ is the momentum operator. The probability that an electron has momentum between p and $p + dp$ is given by $I(p)dp = \phi*(p)\phi(p)dp$ (3.2)

$\phi(p)$ is the wavefunction of the particle in momentum space, and is the Fourier transform of the momentum in real space. That is $$\phi(p) = \frac{1}{\sqrt{2\pi\eta}}\int \psi(x) e^{\frac{-ipx}{\eta}} dx \qquad (3.3)$$

The momentum distribution is given by

$$I(p) = \frac{32\pi^2 p^2}{\eta^3 Z}\int_0^R x^2 dx = \frac{32\pi^2 p^2 R^3}{3\eta^3 Z} \qquad (3.4)$$

where Z is the 'effective' charge, and R is the Wigner-Seitz sphere radius. The relationship between the electron density and momentum is $\rho(x) = \left(\frac{8\pi}{3\eta^3}\right) p^3(x)$ (3.5)

When radiation (X-ray, γ-ray, etc) is incident on a system of particles, e.g. electron gas, the radiation is scattered, and there is energy and momentum transfer. The projection of the electron momentum density unto the scattering vector is known as the Compton profile, and its measurement has proved to be of value in [5]. The Compton profile, $J(q)$, is given by

$$J(q) = \frac{1}{2}\int_q^\infty \frac{I(p)}{p} dp \qquad (3.6)$$

where q is the momentum transfer.

4.0 Calculation methods

The basis wavefunction used was obtained from Slater type orbitals [6]. These were used to calculate V_{eff}, and equation (2.7) solved self consistently. The calculations were done in a sphere with the radius of the Wigner-Seitz cell, and expanding the density function about a point to include contributions from neighbours included crystal structure effects. The result [7]) is

$$\rho(a|x_2) = \frac{1}{2} a x_2 \int_{|a-x_2|}^{a+x_2} x_1 \rho(x_1) dx_1 \qquad (4.1)$$

where, a, is the nearest neighbour distance. This expansion was carried out to the first nearest neighbour with a co-ordination number of 12 (f.c.c. lattice).

The resulting density $\rho(x)$ was used to calculate $p(x)$, then $I(p)$ and $J(q)$ calculated consequently. Numerical integrations were done with the programme IMSL DCADRE, and the single particle Kohn-Sham equations were solved using finite difference algorithm Runge-Kutta. The input parameters for the calculations are listed in Table 1, and calculations were done in atomic units $\frac{e^2}{2} = \frac{\eta}{2m} = 1$ [8].

5.0 Results and discussions

The momentum distribution and Compton profiles calculated are listed in Tables 2 and 3 for copper and aluminium respectively, while the Compton profile plots for copper and aluminium are shown superimposed in Figure 1. The profiles are smooth varying, showing no shell structure. This is a result of the expansion and spherical averaging about a point, which smoothens out the electron density fluctuation. Since the Lowdin alpha coefficients in the expansion of Equation (4.1) was limited to the case $l = m = 0$, this gives spherical averaging, and no direction dependence is obtainable. Experimental Compton profiles are amenable to direction, thereby giving the Compton Profile Anisotropy (COPRAS). [9] have used the linear combination of Gaussian orbitals (LCGO) to compute Compton profiles for copper. They also gave a theoretical basis for COPRAS, and showed that it is experimentally measurable. COPRAS has also been calculated for f.c.c aluminium by [10]. They used the augmented plane wave method, and found improvements in the Compton profile when correlation effects are introduced, compared with the independent particle approach. In this work, the inner core electrons were neglected in the calculations to make comparison with experimental results possible. This is because the experimental long-tail contributions of the inner core electrons are fuzzy, due to Doppler broadening introduced by their high momenta.

6.0 Conclusion

Compton profiles have been calculated for copper and aluminium by solving the single particle Kohn-Sham equations with initial wavefunctions obtained by a linear combination of Slater type orbitals. To show the real effect of the crystal structure, it is hoped that calculation will be carried beyond the first nearest neighbours, and angular dependence highlighted by including the spherical harmonics in the wavefunctions.

Table 1: Input parameters for the calculations

	Copper	**Aluminium**
Nuclear charge, Z	29	13
Effective charge, Z	$11(3d^{10}4s^1)$	$3(3s^23p^1)$
Lattice constant, A (atomic units)	6.83	7.66
Nearest neighbour distance, a (atomic units)	4.83	5.42
Wigner-Seitz sphere radius, R (atomic units)	2.42	2.71

Table 2: Momentum, Momentum Density, and Compton Profile for Copper

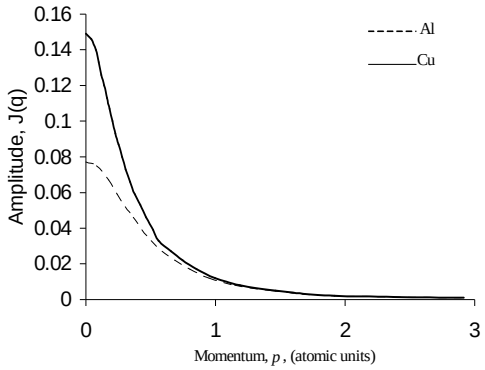
Momentum	**Momentum Density**	**Compton Profile**
p	$I(p)$	$J(q)$
0.000	0.000	0.149
0.042	0.013	0.146
0.079	0.037	0.140
0.100	0.058	0.133
0.121	0.076	0.126
0.142	0.091	0.120
0.163	0.104	0.113

0.183	0.114	0.107
0.205	0.122	0.100
0.228	0.129	0.093
0.253	0.133	0.087
0.280	0.136	0.080
0.309	0.137	0.073
0.341	0.136	0.066
0.378	0.133	0.059
0.419	0.129	0.053
0.465	0.122	0.046
0.519	0.114	0.039
0.561	0.105	0.033
0.659	0.093	0.027
0.745	0.081	0.022
0.856	0.067	0.017
0.998	0.053	0.012
1.189	0.038	0.008
1.466	0.025	0.005
1.920	0.013	0.002
2.918	0.004	0.001

Table 3: Momentum, Momentum Density, and Compton Profile for Aluminium

Momentum	**Momentum Density**	**Compton Profile**
p	$I(p)$	$J(q)$
0.000	0.000	0.077
0.083	0.001	0.075
0.176	0.036	0.067
0.243	0.055	0.059
0.305	0.068	0.052
0.367	0.076	0.046
0.433	0.080	0.039
0.506	0.079	0.033
0.589	0.075	0.027
0.686	0.068	0.022
0.804	0.059	0.017
0.952	0.048	0.012
1.149	0.036	0.008
1.432	0.023	0.005
1.893	0.012	0.002
2.898	0.004	0.001

Figure 1: Compton Profiles



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