Application of APW Pseudopotential Form Factor in the Calculation of Liquid Metal Resistivities.

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Abstract

The APW pseudopotential form factor developed by comparative analysis with the Slatters old APW matrix elements and presented in a closed form was applied in the computation of liquid metal resistivities for metals. The computed values were in perfect agreement with the experimental result showing that the developed form factor is quite good.

Keywords: APW, Pseudopotential, Form-factor, Liquid-metal, Resistivity.

Introduction

Slater formulated the Augmented Plane Wave (APW) method in 1937 for rational explanation of condensed matter properties [1]. Six years later, close to one hundred APW calculations on energy bands and Fermi surfaces had been reported in literature. Contrary to the expectations that this accelerated pace would continue and the application diversified, there was general shift of interest to other methods of calculation. This, the critiques argue was not due to any defect in the formulation, but due to (i) the complex nature of the matrix elements (ii) the rigorous and extensive calculations involved, considering the memory size of the computers at that time. Applications were also limited to condensed matter properties having direct bearing to the form of the matrix elements only. The advantage of APW method is that it can be applied in transition, non-transition metal, noble and alloys [2]. Computationally, the APW method is demanding because the basis functions are energy dependent and the eigenvalue problem nonlinear. In 1974, the connection between the APW method and the Abarenkov model pseudopotential method was explored in connection with the electronic structure and properties of transition metals [3]. Further development of the APW method led to linearization of the APW method (LAPW) [4, 5], where the energy dependence is removed by selecting a fixed set of suitable muffin-tin radial functions and their energy derivatives. The Full-Potential Linear Augmented Plane
Wave (FLAPW) method [6, 7] considered to be the most accurate electronic structure calculation scheme has its origin in Slater’s earliest work. In this approach, there is no sharp approximation for either the charge density or the potential, and all electrons are treated in the self consistent process; and the core electrons are treated fully relativistically and the valence electrons are treated semi-relativistically [8].

The interest to revisit the Slater’s original APW is motivated by the current numerical computations of electronic properties of condensed matter which has taken on an increased momentum with the new age of advanced computer algorithms using the giga bytes of even lap top computers. The idea is to apply the APW pseudopotential form factor developed by Amah et al [9] in 2006 to calculate the liquid metal resistivity of metals.

Theory

The APW matrix elements originally proposed by Slater [1] have the familiar form.

\[
M^y = \sum_{r} \delta_{ij} S^2 \mathcal{E}^{k,y}_r \rho^{y}_r
\]

Where

\[
\left[ (\vec{k}, \vec{k} - \vec{E}) \mathcal{E}_L(k_y, S_y) | k_y - \sum_{j=0}^{\infty} (2j + 1) P_L(k, k_j) \mathcal{E}_L(k, S_y) R'_L(S_y) | R_L(S_y) \right]
\]

- PL = Legendre polynomials
- R(L(Sv)) = radial wave function at vth sphere surface
- R’(L(Sv))/R(L(Sv)) = logarithmic derivative evaluated at the surface of the sphere using radial Schrodinger equation.

From the work of Amah, et al [9], the APW matrix elements developed is given by

\[
M^y = \Omega_y (\vec{k}^2 - \vec{E}) \rho^y_x + < x_j | v | x_L >
\]

Where xL ≡ a linear combination of a set |v> = APW function.

Comparatively, equation (2) corresponds to the APW matrix elements in equation (1) developed by Slater. The third term of equation (2) i.e. \( < x_i | v | x_L > = \int (x_j vL) d\Omega = \langle k + q | v | k > \)

corresponds to the surface integral of the APW matrix elements and is therefore the APW form factor. This can be defended because it is implicitly dependent on the muffin-tin potential through the logarithmic derivatives of the radial party of the muffin-tin functions, which are the solutions of Schrodinger equation \( H|r> = E|r> \).

Therefore, the APW form factor becomes
Application of APW Pseudopotential Form Factor

\[ V(q) = \langle k+q|v(r)|k> = -4\pi \sum_v S_v^2 e^{i k r} G_v \] (3)

In this closed form, calculation can now be extended to other condensed matter properties like liquid metal resistivities, optical properties etc which depend directly on form factors. This liquid metal resistivity is given by the expression[10]

\[ \rho = \frac{4\pi^3 \hbar}{e^2} \frac{z}{k_f} \int_0^1 S(q)|<k+q|vb|k>|^2 \left( \frac{q}{2k_f} \right)^3 d\left( \frac{q}{2k_f} \right) \] (4)

Where

\[ S(q) = \text{structure factor} \]

\[ <k+q|vb|k> = \text{form factor} \]

\[ V_b = \text{bare potential} \]

\[ z = \text{valence} \]

\[ K_f = \text{Fermi wave vector} \]

Computation of liquid metal resistivity using the form factor

The first step in this application is to screen the APW pseudo-potential form factor evaluated using the Thomas Fermi dielectric function. The charge densities, the muffin-tin potentials that approximate the actual crystal potential and the form factor for all metals had been calculated [9].

In order to evaluate the integral in equation (4) numerically, the equation is reduced further if we let

\[ \left( \frac{q}{2k_f} \right) = x \text{ and } d\left( \frac{q}{2k_f} \right) = dx. \text{ Then equation } (4) \text{ becomes} \]

\[ \rho = 4\left( \frac{\pi^3 \hbar}{e^2} \right) \left( \frac{z}{k_f} \right) \int_0^1 a(x)|V_{sc}(x)|^2 x^3 dx \]

\[ = 4K \left( \frac{z}{k_f} \right) \int_0^1 a(x)|V_{sc}(x)|^2 x^3 dx \] (5)

\[ \rho = 4K \left( \frac{z}{k_f} \right) \int_0^1 f(x) dx \] (6)

Where

\[ x \equiv \sin^{1/2} \theta; 0 \leq x \leq 1 \]

\[ a(x) = \text{structure factor} \]
e = electronic charge

\[ V_{sc} = \langle k_f + q|v_b(x)|k_f \rangle / \varepsilon(q) \] = screened form factor

\[ \varepsilon(q) = \text{Thomas Fermi dielectric function} \]

\[ f(x) = a(x)|v_{sc}(x)|^2x^3 \]

and

\[ K = \frac{\pi^3 h}{e^2} = 31.00627667 \text{ in the unit of } \hbar = e = 1 \]

By Simpson’s rule [11]

\[ I = \int_a^b f(x)dx = \frac{h}{3} \left( f_a + f_N + 4 \sum_{m \text{ odd}} f_m + 2 \sum_{m \text{ even}} f_m \right) \approx \frac{h}{3} (4f_i + f_{i+1} + f_{i-1}) \] (7)

Where there must be an even number of intervals and odd number of points. To avoid the problem with \( \varepsilon(q) \) at \( x = 0 \), we started the integration at \( x = 0.00001 \) approximately. It is in the form of equation (5) and (7) that the liquid metal resistivities were calculated using a computer programme.

Table 1 shows the computed liquid metal resistivities and their corresponding experimental values.

**Results and Discussions**

**Table 1:** Computed resistivity values and corresponding experimental values

<table>
<thead>
<tr>
<th>S/N</th>
<th>Metal</th>
<th>( \rho \text{(cal. values)} \Omega^{-6}\text{cm} )</th>
<th>( \rho \text{(exp. values)} \Omega^{-6}\text{cm} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Lithium</td>
<td>*24.5</td>
<td>24.7</td>
</tr>
<tr>
<td>2</td>
<td>Potassium</td>
<td>13.7</td>
<td>13.0</td>
</tr>
<tr>
<td>3</td>
<td>Rubidium</td>
<td>22.3</td>
<td>22.5</td>
</tr>
<tr>
<td>4</td>
<td>Silver</td>
<td>*16.4</td>
<td>17.0</td>
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<tr>
<td>5</td>
<td>Cadmium</td>
<td>34.2</td>
<td>34.0</td>
</tr>
<tr>
<td>6</td>
<td>Caesium</td>
<td>35.9</td>
<td>36.0</td>
</tr>
<tr>
<td>7</td>
<td>Gold</td>
<td>*32.4</td>
<td>31.0</td>
</tr>
<tr>
<td>8</td>
<td>Thallium</td>
<td>73.9</td>
<td>73.0</td>
</tr>
<tr>
<td>9</td>
<td>Lead</td>
<td>97.2</td>
<td>95.0</td>
</tr>
</tbody>
</table>

Key: * means absolute values

The APW method was developed in 1937. The application was restricted to the computation of energy bands and Fermi surfaces due to the complex nature of the
matrix elements. However, with the development of APW pseudo-potential form factor in a closed form out of the matrix elements, the application has been diversified to other condensed matter properties having direct bearing to form factor. The application to liquid metal resistivities has proved the form factor to be elegant (i.e. Table 1). The calculated values of all metals investigated agreed with their experimental values except those asterisked which have negative values.

**Conclusion**
The application of APW pseudopotential form factor in the calculation of liquid metal resistivities for nine metals has proved to be quite adequate in predicting the liquid metal resistivities for all metals. This has extended the application of APW method from energy bands and Fermi surfaces to liquid metal resistivities. The form factor can also be used to predict the optical properties of materials.

**References**
