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Energetic Harrison's first principle approach to the transport properties of metals : Mg and Ga

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Abstract : Harrison's First Principle (HFP) method owes its existence to the concept of orthogonalised plane wave (OPW). In this technique, the beauty lies in the factorization of the matrix element of the crystal potential into form factor $w(k,q)$ and the structure factor $a(q)$. The latter is available from experimental measurements either though X-ray or neutron diffraction but the former is to be calculated theoretically by suitable theoretical framework.

In Harrison's First Principle method, there is no arbitrary adjustable parametrization and no arbitary model of potential is chosen, rather all the contributing potentials are derived from basic considerations However, there is a controversy regarding the choice of eigenvalues of the core states. This is due to the fact that different self-consistent computations lead to eigenvalues which differ markedly, amongst themselves.

Thus in the present work, the impact of various eigenvalues have been studied both on the form factor $w(k,q)$ and electrical resistivity (R) derived from Ziman's formalism and also Knight shift (K) of Mg and Ga. The study reveals interesting features.

Keywords : Pseudo-potential, liquid metal, electrical resistivity, Knight shift.

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1. Introduction

The pseudo-potential technique has emerged as an effective tool for the study of physical properties of metals and alloys (solids and liquids) be In the past two decades, it has been effectively used for the purpose covering a wide range of condensed material and variety of properties. Among the pseudo-potential methods, the Harrison's First Principle (HPF) technique based on the concept of orthogonalized plane wave (OPW), has several advantages over its counter parts such as free of arbitrary parameterization, minimal input requirement and first principle evaluation of crystal potentials. However, it has lagged behind due to the involvement of heavy computation.

Inspite of the above mentioned fact, some authors have adopted the HFP technique of Harrison [1] in the past decades and have obtained reasonable results with departures at some places in the study of physical properties of condensed materials.

The basic input parameters required for the computation of the form factor $w(k,q)$ and consequently the physical properties are valence Z, atomic volume Ω_0, Fermi wave vector k_F and the core energy eigenvalues $\varepsilon_{n,l}$. The latter have been obtained through self consistent methods such as Fermi-Dirac, Thomas-Fermi models, or other suitable methods by various authors such as Herman-Skillman [2] and Clementi [3]

A study of these computed eigenvalues of metals reveals that they are not consistent rather they differ reasonably at some places. As an example, the eigenvalues of Mg and Ga are presented in Table 1 for comparison.

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Table 1. Eigen values of Mg and Ga.

Metal	Workers	ε_{10}	ε_{20}	ε_{21}	ε_{30}	ε_{31}	ε_{32}
Mg	C	96.06	5.58	3.02	...	...	...
	H	94.95	6.522	4.144	...	...	...
Ga	C	757.636	96.3366	84.988	12.789	8.9648	2.3866
	H	749.2	92.64	82.63	11.238	6.661	2.040

C – Clementi [3] , H – Herman-Skillman [2] ; ε_{nl} . Eigenvalues n,l - Quantum numbers.

Maximum % variation in ε_{nl} is ~37%.

With the above mentioned inconsistencies in eigenvalues ε_{nl}, one gets interested in exploring their impact on the computed form factors and consequently on the computed properties. In this paper, the properties under consideration are the transport properties *viz.*, electrical resistivity and Knight shift.

2. Form factor

In the computation of form factor the exchange-correlation of Vashista-Singwi (V-S) has been used which is the most popular form and satisfies compressibility sum rule. However, the role of some other forms of exchanges have been studied (not reported here). The conduction band-core exchange potential has been evaluated through α_s, the exchange parameter of Schwartz [4] satisfying virial theorem. However, the role of other choices (α = 1) and (α = 2/3) proposed by Slater [5] and Kohn-Sham [6] respectively have also been studied (not reported here).

The form factor $w(k,q)$ is presented by

$$w(k,q) = V^*_{a\,b} + V^*_c + V^*_d + V^*_f + W^R$$

where

$V^*_{a\,b} = V^{a,b}q/\varepsilon^*(q)$,

$V^*_c = V^c q/\ \varepsilon^*(q)$,

$V^*_d = V^d q/\ \varepsilon^*(q)$,

$V^*_f = V^f q(1-G(q))/\ \varepsilon^*(q)$,

$W^R = \langle \underline{k} + \underline{q}/W^R/k \rangle$,

$V_q^{a,b}$ = Valence charge and core electron potential,

V_q^c = Conduction band-core electron exchange potential,

V_q^d = Conduction electron potential,

V_q^f = Screening potential.

As an illustration the form factor of Mg computed with eigenvalues of Herman-Skillman [2] and Clementi have been presented in Figure 1 with ($\alpha = \alpha_s$ and using V-S exchange), $\alpha = x\alpha$-exchange parameter.

A perusal of Figure 1 reveals that in the lower q-region, the form factor $w(k,q)_H$ obtained with H-S eigenvalues is lower than $w(k,q)_C$ obtained with Clementi eigenvalues

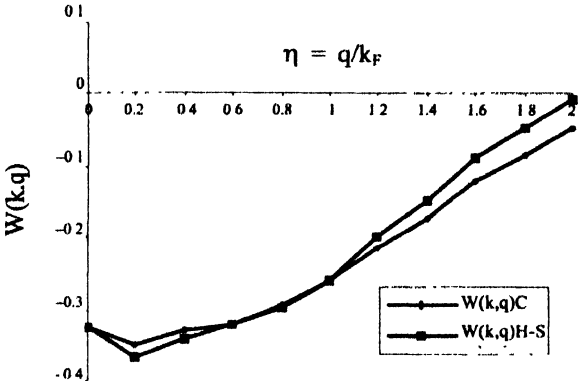

Figure 1. Form factors of Mg with different eigen values using (V-S) exchange-correlation and $\alpha = \alpha_s$.

upto η = 0.5 while the order is reversed in the higher q-region. However, the contribution of lower q-region to the physical properties like transport properties is insignificant due to the very small value of the structure factor $a(q)$ in this region.

In the higher q-region, the most contributing region is beyond η = 1.0 to 2.0. In this region there is marked departure in the two form factors and none of them crosses over the η-axis to become positive as generally found in case of different metals.

3. Electrical resistivity and Knight shift

The computed electrical resitivity with $w(k,q)_H$ is 42.6 μΩ cm and with $w(k,q)_c$ is 213.2 μΩ cm. against the experimental value 27.4 μΩ cm. The computed Knight shifts are 0.060 and 0.165 respectively against the experimental value k = 0.112. Here, the zero-order orthogonalised plane wave method yields k = 0.13.

The various choices of $X\alpha$ exchange parameter α = 1 and α = 2/3 and the exchange-correlation functions have also been attempted which are unable to bring desired improvement in the computed properties.

However, in case of Ga the Clementi eigenvalues with (V-S) exchange and $\alpha = \alpha_s$ present a good picture of electrical resistivity R = 24.9 μΩ cm. against R_{expt} = 25.4 μΩ cm and Knight shift K = 0.580 against K_{expt} = 0.449.

4. Conclusion

This suggests that the departures in eigenvalues computed by different authors are yet to be improved either by using some improved model or technique so as to reproduce good results of the computed properties. We expect to pursue these investigations with recently computed

eigenvalues and wave functions using improved versions of Hartree-Fock, or Thomas-Fermi models as available in the literature [7].

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