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Study the electrical resistivity and knight shift of liquid metals

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ABSTRACT

Harrison's First Principle (HFP) has been used to study the liquid electrical resistivity and Knight shift of polyvalent liquid metals with special reference to the energetic of the core electronic states. The role of self consistently computed core energy eigenvalues has been studied in respect of the non-local screened form factor and the computed properties. Reasonable agreement has been obtained.

KEYWORDS

Liquid metal;
Electrical resistivity;
Knight shift;
Pseudopotential.

INTRODUCTION

Harrison's First Principle (HFP) method has some inherent approximations involved in the theoretical framework, these are as under:

Small core approximation

Through this approximation, we assume that the cores are small and clearly distinguishable. The adjacent cores do not overlap and hence there is no direct interaction between ions except Coulomb repulsion. The variation of potential over the core region due to the conduction electrons and the adjacent ions is neglected.

Self–consistent field (SCF) approximation

In this approximation, the interaction between the electrons is replaced by an average potential depending upon the states occupied by the electrons and the states depend upon the potential and they are independent. Hence, their computation is carried out till one reproduces the other.

Perturbation theory approximation

It is assumed that the pseudopotential is so weak that it can be treated through the perturbation theory.

The theoretical study of the physical properties of liquid metals enjoys the attention of several workers since past decades. With the inception of the pseudopotential technique based on the concept of the orthogonalized plane wave (OPW) insurmountable difficulties in such calculations have been surmounted.

The beauty of this technique lies in the fact that the crystal potential <k+q|V|k> can be factorized into potential dependent form factor <k+q|w|k> and the position dependent structure factor a(q). The computations of many physical properties require these two ingredients. The form factor being not measurable, has to be computed by theoretical techniques while a(q) is measurable either through X-ray diffraction (XRD) or neutron diffraction (ND) techniques.

The non-uniqueness of the pseudopotential led to form factors computed through different models proposed by various authors (Aschroft[1], Shaw[2], Srivastava and Singh[3]). Harrison[4] proposed an igenious technique called the Harrison First Principle (HFP) technique. In this the various interacting potentials are arrived at through fundamental considerations employing quantum mechanical and statistical mechanical approaches along with Poisson's equation. Although the technique was much rigorous than the model potential technique and also free arbitrariness in choosing a model or its parameter, it lagged behind due to cumbersome calculations involved. However, this was employed by King and Culter[5] and Hafner[6] along with their co-workers and we have also applied if for the study of physical properties of liquid metals.

Inspite of various good points in favour of HFP technique the workers found that there are several considerations to be kept in mind while choosing the input parameters, the most significant among them was the energetic problem. In computation of the form factor the important input parameters are the eigenfunction and eigenvalues of the core electrons represented by Pnl and $\in_{nl}$ (r), n and l being the quantum numbers of the core states.

Usually the workers in this field obtained these input parameters from Herman-Skillman[7] or generated them with some improvement in his program while some authors preferred to use the experimental eigenvalues. Clementi[8] also published his atomic structure calculations in which he provides the eigenfunction and eigenvalues of elements of one third of the periodic TABLE. When the eigenvalues of a particular metal obtained through self-consistent calculations by different authors were compiled by us it was found that they differ substantially for some states amongst themselves (vide TABLE-1).

In the present paper we study the impact of eigenvalues $\in_{nl}$ on the computation of form factor and consequently on two important properties viz, the liquid electrical resistivity (R) and the Knight shift (K%) for Mg, Al, Zn and Ga.

The cause of discrepancy in eigenvalues is quite understandable because achieving self-consistency is by itself a tedious calculation and then matching with a particular set of eigenvalues is quite difficult. Hence the question arises how much impact these discrepancies of eigenvalues have on the computed form factor and consequently on the computed properties. This has been investigated by us in quite detail[9-11]. It has been observed that the energetics of these computations is more prominent than other input parameters such as Xα-exchange, orthogonalisation hole parameter β or the form of exchange-correlation to be used.

Formalism

(a) Electrical resistivity: The electrical resistivity is computed through the well-known Ziman formula[12] given by

$$R = \frac{3\pi Z\Omega_0}{\hbar e^2 v_F^2}\int_0^1 |w(k,q)|^2\, a(q) 4(q/2k_F)^3\, d(q/2k_F) \quad (1)$$

where Ω_o, Z, v_F, k_F, w(k,q) and a(q) are the atomic volume, valence, Fermi velocity, Fermi wave vector, form factor and structure factor of the metal respectively.

(b) Knight shift (K%) : The Knight shift (K%) = K_1+K_2 is computed through Pake formula (1955)[13]

$$\frac{K_1}{K_0} = -\frac{3Z}{4E_F k_F^2}\int_0^\infty a(q)w(k,q)q\ln\left|\frac{q+2k_F}{q-k_F}\right|dq \quad (2)$$

where E_F is the Fermi energy of the metal and K_0 is the single opw value of the Knight shift of the lines of our previous papers[9-11] through

$$w(k,q) = v^*_{a,b} + v^*_c + v^*_d + v^*_f + W^R \quad (3)$$

where the terms on RHS represent the effective screened values of the valence charge and core electron potential, conduction band-core exchange potential, conduction electron potential, screening potential and the repulsive part of pseudopotential respectively.

The computation of liquid electrical resistivity (R) and Knight shift (K%) has been done through equations (1) and (2) respectively using two forms of exchange-correlation functions G(q) e.g., Vashishta-Singwi (V-S) and Hubbard-Sham (H-S), alongwith the suitable Xα-exchange parameter $\alpha = \alpha_s$ [Swartz[14]] or $\alpha = 2/3$ [Kohn-Sham[15]]. The orthogonalisation hole potential is retained as that of Harrison[4]. Two sets of wave functions namely those of Herman-Skillman (H)[7] and Clementi (C)[8] have been utilized. The experimental liquid structure factor of Woerner et al.[17], Coglioti et al.[18], Gamertsfelder[19] and Page et al.[2] have been used for Mg, Zn, Al and Ga respectively.

Observations : To bring out the energetic problem we present the comparative TABLE 1 of eigenvalues obtained through the self consistent computations of Herman-Skillman[7] and Clementi[8] for the metals under investigation viz., Mg, Zn, Al and Ga (in Rydberg = 2.4258×10^{-18}J).

A perusal of the TABLE brings out the fact that the Clementi eigen values (C) are in general higher than those of Herman-Skillman (H) except for 3d of Zn, 2p of Al and 2s and 2p of Mg, where they are lower than H-values. The maximum departure is found in 1s of Ga (8.436 Ryd.) followed by 1s of Zn (8.208 Ryd.). The departures range from this value to a minimum of 0.3466. However, through the investigation of energy dependent components of the form-factor namely the screening potential v_f^* and W^R, we have come to the conclusion that the impact of eigenvalues on the form factor w(k,q) is most pronounced due to variation in the highest field up s and p states. The contribution of d state is comparatively smaller. The contribution of s state is constant throughout the entire range of $\eta = q/k_F$, k_F being the Fermi wave factor. Hence, it decides the magnitude of W^R and v_f^* and consequently controls the magnitude of form factor w(k,q). The contribution of p state is variable due to the inclusion of polynomial within its formalism. Hence, it controls the gradient of W^R and v_f^* and consequently that of the computed form factor w(k,q) (vide Figure 1).

The impact on the computed properties viz. the electrical resistivity (R) and Knight shift (K%) has been represented in TABLE 2, using the Xα- exchange parameter $\alpha = \alpha_s$ as proposed by Schwartxz[14] except for Zn for which $\alpha = 2/3$ proposed by Kohn and Sham[15] provides a better result.

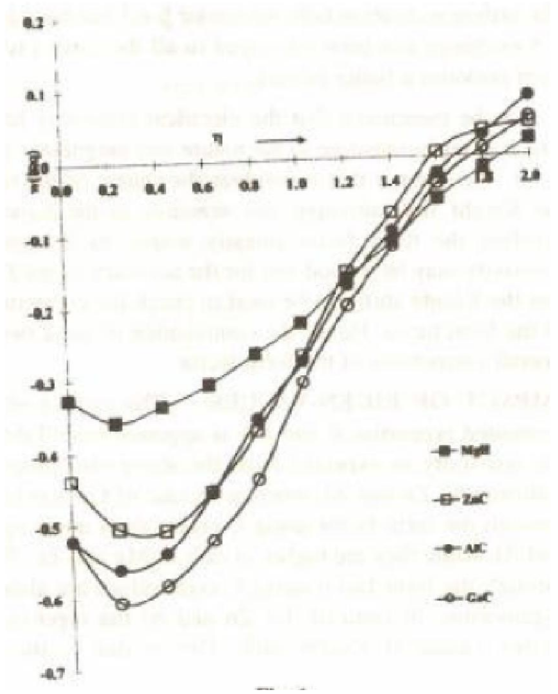

Figure 1

TABLE 1 : Eigenvalues of metals (in Joule)

Metal		Eigenvalues (Ryd = 2.425×10^{-12}J)					
		$\lvert\epsilon_{10}\rvert$	$\lvert\epsilon_{20}\rvert$	$\lvert\epsilon_{21}\rvert$	$\lvert\epsilon_{30}\rvert$	$\lvert\epsilon_{31}\rvert$	$\lvert\epsilon_{32}\rvert$
	C	96.06	5.58	3.02	-	-	-
Mg	H	94.95	6.55	4.14	-	-	-
	E	1.11	-0.97	-1.12	-	-	-
	C	706.60	88.72	77.85	11.28	7.66	0.59
Zn	H	698.40	85.20	75.55	9.79	6.66	1.26
	E	8.21	3.52	2.30	1.48	0.10	-0.40
	C	117.00	9.82	4.20	-	-	-
Al	H	113.66	8.72	5.95	-	-	-
	E	3.34	1.11	-1.74	-	-	-
	C	757.63	96.34	84.99	12.79	8.96	2.39
Ga	H	749.20	92.64	82.63	11.24	6.66	2.04
	E	8.44	3.70	2.36	1.55	2.30	0.35

C-Clementi, H-Herman-Skillman, ΔE- Discrepancy

The orthogonalisation hole parameter β = 1 has been retained as per Harrison[4]. The popular V-S exchange has been employed in all the cases except for Al, where Hubbard-Sham (H-S) form provides better picture.

It is to be mentioned that the electrical resistivity has been acknowledged to be a property which is fairly sensitive to the nature and magnitude of the form factor specially in the region η>1. We observe that it involves the square of the form factor within its integrand, whereas the Knight shift although less sensitive to the form factor and having smaller magnitude, involves the form factor linearly within its integrand. Thus, we infer that the electrical resistivity may be a good test for the accuracy of the form factor in respect of magnitude only. But the Knight shift can be used to check the correctness of the magnitude as well as the sign of the form factor. Hence the combination of these two properties may be used as a test for an overall corresctness of the form factor.

Impact of eigen-values

The impact of eigenvalues on the above mentioned computed properties R and K% is apparent from TABLE 2. The impact is more pronounced on the resistivity as expected from the above observations. For Mg the departure is very high, followed by Zn and Al, whereas in case of Ga it is lower. The electrical resistiv-

TABLE 2 : Computed electrical resistivity ($\mu\Omega$cm) and knight shift (K%)

Metals	Eigenvalues $(\in_{nl})$	Xα-exchange parameter	Exchange	Orthogonalisation hole parameter (β)	R($\mu\Omega$cm)		K%	
					Theo.	Expt.	Theo.	Expt.
	C				213.2		0.209	
Mg		$\alpha = \alpha_s$	V-S	$\beta = 1$		27.4		0.112
	H				26.74		0.159	
	C				32.35		0.363	
Zn	H	$\alpha = 2/3$	V-S	$\beta = 1$		37.4		0.337
					78.8		0.093	
	C				29.08		0.175	
Al		$\alpha = \alpha_s$	V-S	$\beta = 1$		24.7		0.164
	H				71.95		0.144	
	C				25.01		0.460	
Ga		$\alpha = \alpha_s$	V-S	$\beta = 1$		25.8		0.449
	H				14.5		0.043	

H : Herman-Skillman, C:Clementi, V-S : Vashista-Singwi, H-S : Hubbard-Sham

ity computed through the form factor using C eigenvalues are lower than those with H eigenvalues for Zn and Al, while they are higher in case of Mg, and Zn. The Knight shift of Mg and Ga computed through the form factor using C eigenvalues are also higher than those computed through H eigenvalues. In contrast, for Zn and Al the eigenvalues which give lower resistivity, yield higher values of Knight shift. This is due to the peculiar nature of Ziman and Knight integrands. The former is always positive, reaches a maximum, goes to a zero value at a particular value of η (= q/k_F) and finally increases. But the Knight integrand is generally always negative, goes down to a zero and then increases almost linearly.

It is observed from TABLE 2 that for Mg the form factor computed with H eigenvalues using $\alpha = \alpha_s$, $\beta = 1$ and V-S exchange correlation provide a better agreement of electrical resistivity R = 26.74 $\mu\Omega$cm against R (expt.) = 27.4 $\mu\Omega$cm and K% = 0.159 against K% (expt.) = 0.112. For Zn the combination of C-eigenvalues, $\alpha = 2/3$, $\beta = 1$ and V-S exchange correlation and for Al and Ga the eigenvalues of C with $\alpha = \alpha_s$, $\beta = 1$ and H-S and V-S forms of exchange correlation respectively reproduce these properties reasonably well.

Hence, we conclude that the C eigenvalues present better picture than those of H except in case of Mg. Further, the impact of eigenvalues is quite substantial. Hence, precaution must be taken as regards the choice of eigenvalues in the study of physical properties of metals through HFP technique, which is found to be suitable for the study of these properties.

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