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Harrison's First Principle pseudopotential approach to study the effect of various types of exchange correlation functions on dielectric screening function of alkali metals Li, Na, K and its binary alloys Li-Na, Li-K and Na-K.

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ABSTRACT

In this research paper an investigation was made to determine the influence of the electronic exchange and correlation function G(q) on correlated dielectric screening function $\epsilon^*(q)$ using Harrison's first-principles (HFP) nonlocal pseudopotential theory. Different modified forms of the local statistical exchange and correlation approximation are used to compute the correlated dielectric screening function $\epsilon^*(q)$.

We have summarized the effect of various types of exchange correlation functions on dielectric screening function of alkali metals. Using various form exchange correlation we obtain dielectric screening function for selected alkali metals Li, Na, K and its binary alloys Li-Na, Li-K and Na-K. Using Vashishta – Sangwi (V-S) exchange correlation, which we find most suitable in our studies, form factor of these selected alkali metals were also computed for different sets of eigen values.

I. INTRODUCTION

Pseudopotential techniques is one of the most popular techniques among the solid state physicist to study various properties of metals, semiconductors, alloys, compounds and non-crystalline substances like metallic glasses and liquids. The ion in a metal together with its screening charge are called pseudo-atom, (J. M. Ziman, 1963).

The smallness of these pseudopotentials allows us for many purposes to treat it as a perturbation and to calculate many more properties of a simple metal than is possible for any other state of condensed matter. In fact, the pseudopotential can be optimised so that, in practice, it is even weaker than the frozen core potential, Walter A. Harrison (1970).

The Orthogonalised Plane Wave (OPW) method proposed by Harrison (1966) has been termed as Harrison's First Principle (HFP) pseudopotential technique. The First principle method expanded the states in Orthogonalised Plane Waves, plane waves with terms added to make them orthogonal to the core state, as the true band state must be. The matrix elements of the pseudopotential $\langle k+q|W|k\rangle$ were defined to be the matrix elements of the Hamiltonion between the OPW's.

The present form of OPW is mainly due to the work of Philips and Kleinmann (1959), Antoncick (1959), Harrison (1963a, b, c, 1964, 1966, 1969) and by Cohen and his co-workers (1961, 1965, 1970).

Hafner (1977) has used the HFP pseudopotential technique to study the structure, bonding and stability of topologically closed packed inter metallic compounds and also the structure and thermodynamics of liquid metals alloys Li-Na, Na-K, K-Rb, K-Cs, Rb-Cs, and Al-Mg.

In our present work we have used HFP pseudopotential approach. Dielectric screening function for selected alkali metals Li, Na, K and its binary alloys Li-Na, Li-K and Na-K were obtained using various forms of exchange correlation. Also, Faber-Ziman (1966) form-factor was computed using exchange and correlation of Vaishishta-Singwi (1972) for different set of eigen values in case of selected alkali metals Li, Na, K and its binary alloys.

In an earlier paper Sunil et al. (2016), using Shaw Optimized Model Potential study the electrical resistivity of Na, K and their alloy was carried out. V-S form of exchange correlation was successfully applied to the computation of electrical resistivity of Na, K and their alloy for different composition. This prompts us to consider a further study of different forms of exchange correlation function.

II. THEORY AND FORMALISM

2.1 Exchange and correlation:

The fact that exchange and correlation both tend to keep electrons apart gave way to the description of the exchange and correlation contribution in terms of a hole surrounding each electron and keeping other electrons from approaching it. The correlation energy is defined as the difference between the total exact energy and the sum of kinetic and exchange energies. Correlations are a result of the collective behaviour of electrons to screen and decrease the Columbic interaction.

The Hartree dielectric function

$$\epsilon(q) = 1 + \frac{2}{\pi k_F \eta^2}\left[1 + \frac{4-\eta^2}{4\eta}\ln\left|\frac{2+\eta}{2-\eta}\right|\right]$$

where $\eta = q/k_F$

as $q \to o, \epsilon(q) \to \frac{4k_F}{\pi q^2}$ i.e., as q becomes very small, $\epsilon(q)$ goes to ∞.

as $q \to \infty, \epsilon(q) \to 1 + \frac{16k_F^3}{3\pi q^4}$ i.e., as q becomes very large, $\epsilon(q)$ becomes 1.

This simply means that long-wavelength (small q) components of the potential are well screened; short-wavelength (large q) components are very weakly screened. This might be due to the fact that the static dielectric function obtained in the Hartree approximation does not incorporate the effect of the correlated motion of the electron. In this approximation the electron sees a potential only due to the time average charge density and is known as ‘correlation hole’ its effect on the electron potential may be approximately included by adding a position dependent potential corresponding to the average potential. The effective-average potential Harrison (1966) may be written as –

$$v_l(q) = 1 - G(q)\frac{4\pi n(q)}{q^2}$$

where $G(q)$ is some function of wave number and consider the exchange and correlation effect. Here $n(q)$ is the Fourier transform of the charge density $n(r)$ and is defined by

$$n(q) = \Omega^{-1}\int exp(-i\boldsymbol{q}.\boldsymbol{r})n(r)d^3r$$

Hubbard (1958) incorporated smoothly between long and short wavelength limits. Since the classic work of Hubbard, the matter has been subject of interest for many years for many researchers and, thus, many different forms of $G(q)$ have been proposed. The subject has been reviewed by many authors like Nozier and Pines (1958), Pines (1964), Heine and Abarenkov (1964), Sham (1965), Ziman (1965), Tosi (1969) and others. Saw (1970) proclaimed that this approach can be justified from the general many body theory. It leads to the correlated dielectric screening function $\epsilon^*(q)$ represented by –

$$\epsilon^*(q) = [\{1 - G(q)\}\{\varepsilon(q) - 1\} + 1]$$

2.1.1 Hubbard-Sham (HS) form of screening-

The Hubbard and Sham dielectric function is due to the inclusion of exchange between electrons of parallel spin. It also reveals that the effect of exchange on the screening in the high q-limit should be to cancel half the direct Coulomb contribution to the screening. The modified form of $G(q)$ obtained by sham (1965) using Coulomb interaction matrix element different from Hubbard (1957) is represented by-

$$G(q) = \frac{1}{2}\left(\frac{\eta^2}{\eta^2 + \beta + 1}\right)$$

where

$\eta = \frac{q}{k_F}$, $\beta = \frac{k_o^2}{k_F^2}$

On the ground that exchange keeps all parallel spin electrons away, Hubberd justified the short wavelength limit,

i.e. at $q \to \infty; G(q) \to 1/2$

However, the compressibility sum rule is not obeyed.

Through the interpolation scheme of Noizeres and Pines (1958) such that $\epsilon(q)$ satisfy the compressibility sum rule; Hafner and Schmuck (1974) reproduced $G(q)$ as –

$$G(q) = \frac{1}{2}\left(\frac{\eta^2}{\eta^2 + \gamma}\right)$$

Here, $\gamma = 2/[1 + 0.53/(\pi k_F)]$

Thus, we get -

at $q \rightarrow 0; G(q) \rightarrow \frac{1}{2\gamma}$ and

at $q \rightarrow \infty; G(q) \rightarrow \frac{1}{2}$

2.1.2 Shaw (S) form of screening –

Shaw (1967) systematically reformulated the screening of a generalized Heine-Abarenkov model potential and calculated the electron density in a metal in terms of model-potential parameters. An important feature of Shaw reformulated theory is that it is no longer necessary to renormalize the dielectric function to obtain the correct long-wavelength limit for the model-potential form factor.

Shaw and Harrision (1968) found that the depletion-hole contribution cancels a term arising from the energy dependence of the potential at long wavelengths. The Shaw form of exchange parameter was obtained by utilising the self-consistent technique relating the exchange parameter with the pair correlation function g(r). In calculating the self-consistent screening of the model potential, they take account of both the nonlocality and the energy dependence of the model potential.

Here $G(q)$ is represented as –

$$G(q) = 1 - \exp(-0.535\, \eta^2)$$

This form has the same magnitude for all metals which does not seem reasonable.

2.1.3 Kleinmann-Langreth (K-L) form of screening-

Kleinmann(1967) derive the dynamic dielectric constants appropriate to electrons and to test charges which differ with the inclusion of screened Hartree-Fock exchange. According to Kleinmann(1967) (1968) the exchange parameter $G(q)$ does not tend to ½ for short wavelength and hence through a self-consistent method obtained the expression –

$$G(q) = \frac{1}{4}\left[\frac{\eta^2}{\eta^2 + \beta + 1} + \frac{\eta^2}{\beta + 1}\right]$$

Where $\beta = \frac{k_o^2}{k_F^2}$

This form was supported by Langreth (1968) on the basis of variation consideration. In this case compressibility sum rule is only slightly violated. It is to be noted that at $q \rightarrow \infty; G(q) \rightarrow \infty$ which is physically unsound.

2.1.4 Vashishta – Singwi (V-S) form of screening-

K. S. Singwi, et al. (1968) proposed an expression for the theory of the dielectric function of the electron liquid in the metallic density range, which took into account the short-range correlations arising from both Coulomb and exchange effects through a local-field correction depending on the pair correlation function.

Allowing for the adjustment of the pair correlation function to the external field K. S. Singwi, et al. (1970) proposed an extension to the above theory and results in a screening of the Coulomb potential entering the local field. In contrast to the earlier theories, the present theory satisfies closely the compressibility sum rule and also gives reasonable values for the pair correlation function.

P. Vashishta and K. S. Singwi. (1972) present a modification on theory of Singwi *et al.* (1969) (1970) allowing for the change of the pair correlation function g(r) in an external weak field via the density derivative of the equilibrium pair correlation function. Vashishta - Singwi suggested a form of G(q) satisfying equation-

$G(q) = 1 - \eta \int_0^{\infty} j_l(\eta r) \mathrm{g}(r) dr$

The exchange function for $\eta \leq 2$ has been analytically approximated by-

$$G(q) = A\left(1 - exp(-B\eta^2)\right)$$

Here, the V-S constants A and B are parameters that depend on Thomas –Fermi radius $r_{s.}$

2.2 Form Factor:

The form factor w(**k, q**) = <**k**+**q**|w|**k**> is the Fourier transform of crystal potential in the reciprocal lattice. In present work the form factor w(**k, q**) of the constituent metals has been derived through the well-known HFP pseudopotential technique.

The HFP technique has been claimed to be superior to the model potential techniques as no arbitrarily adjustable parameter is introduced and no arbitrary model is proposed. Although the HFP technique is much rigorous than the model potential technique and also free from arbitrariness in choosing a model and its parameter, it lagged behind due to some cumbersome calculations involved. However, this was employed by King and Cutler (1971) and Hafner (1975) along with their co-workers and is still a choice of few researchers.

The non-local screened form factor may be expressed as-

$$w(\boldsymbol{k}, \boldsymbol{q}) = \left\{\frac{v_q^{a,b} + v_q^c + v_q^d}{\varepsilon^*(\boldsymbol{q})}\right\} + \left\{\frac{1 - G(\boldsymbol{q})}{\varepsilon^*(\boldsymbol{q})}\right\} v_q^f + W^R$$

where symbols are those of Harrison (1966) viz

$v_q^{a,b} = \text{Valance charge and core electron potential}$

$v_q^c = \text{Conduction band} - \text{core exchange potential}$

$v_q^d = \text{Conduction electron potential}$

$v_q^f = \text{Screening potential}$

$W^R = \text{Repulsive potential}$

$\varepsilon^*(q) = \text{Dielectric screening function}$

$$\varepsilon^*(q) = [\{1 - G(q)\}\{\varepsilon(q) - 1\} + 1]$$

here

$\varepsilon(q)$ is Hartree dielectric function given by

$$\varepsilon(q) = 1 + \frac{2}{\pi k_F \eta^2}\left[1 + \frac{4-\eta^2}{4\eta}\ln\left|\frac{2+\eta}{2-\eta}\right|\right]$$

where $\eta = q/k_F$; and G(q) is the exchange correlation function.

In our present work we have used V-S exchange correlation function given as

$$G(q) = A\,[1 - \exp(-B\eta^2)]$$

V-S exchange correlation function satisfies compressibility sum rule and provides a better inter-ionic potential.

The non-local screened form factor of the alloy is given by Faber-Ziman Formalism (1965)

$$|w(k,q)|^2 = c_1|w(k,q)_1|^2 + c_2|w(k,q)_2|^2 + 2\,(c_1c_2)^{1/2}|w(k,q)_1||w(k,q)_2|$$

where c_1 and c_2 are concentration of constituent metals.

III. COMPUTATION AND RESULTS

3.1 Dielectric screening function

The computed value of $\epsilon^*(q)$ has been plotted below. The impact of local field correction function on correlated dielectric screening function $\epsilon^*(q)$ can be comprehended from this.

Hubbard-Sham produced a modified form of local field correction function, for which Hubberd (1957) also justified the short wavelength limit, on the ground that exchange keeps all parallel spin electrons away. However, the compressibility sum rule is not obeyed.

Shaw (1967) (1968) form of exchange parameter does not satisfy the compressibility sum rule and has the same magnitude for all metals which does not seem reasonable

Kleinman -Langreth approximation is quite good in the static large-k limit, but otherwise incorrect. Compressibility sum rule is only slightly violated, but in this case at $q \to \infty; G(q) \to \infty$ which is physically unsound.

P. Vashishta and K. S. Singwi. (1972) presented a new expression for the local-field correction satisfying almost exactly the compressibility sum rule.

we conclude that Vashishta - Singwi theory has superiority over the other forms of exchanges with the merit of satisfying almost exactly the compressibility sum rule and of giving a satisfactory pair correlation function.

Computed values of dielectric screening function ϵ^*(q) of selected alkali metals Li, Na, K and its binary alloys Li-Na, Li-K and Na-K were obtained with local field exchange and correction function of Hubbard-Sham (HS)(1965), Shaw (S)(1968), Kleinmann-Langreth (K-L) (1969) and Vashishta – Singwi (V-S) (1972) forms of exchange correlation.

For comparative study of variation of $\epsilon^*(q)$ with $\eta\ \left(=\frac{q}{k_F}\right)$ computed results are plotted in fig, 1, 2, 3, 4, 5, & 6 below –

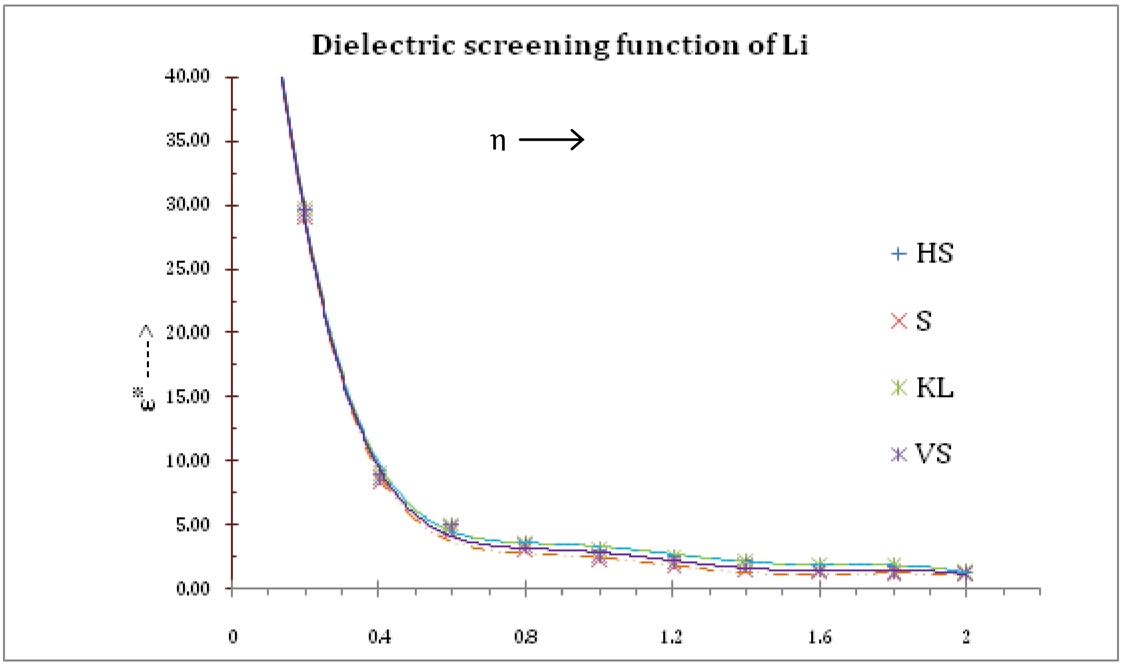

Fig 1: Dielectric screening function Li using Hubbard-Sham (HS), Shaw (S), Kleinmann-Langreth (K-L) and Vashishta – Singwi (V-S) forms of exchange correlation.

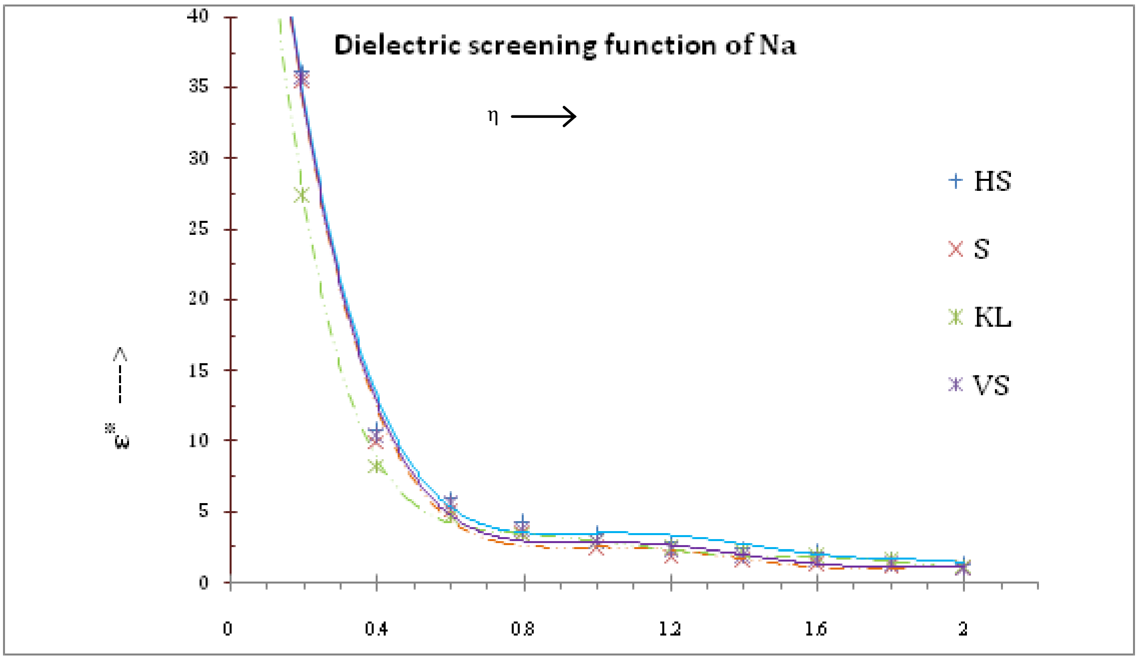

Fig 2: Dielectric screening function Na using Hubbard-Sham (HS), Shaw (S), Kleinmann-Langreth (K-L) and Vashishta – Singwi (V-S) forms of exchange correlation.

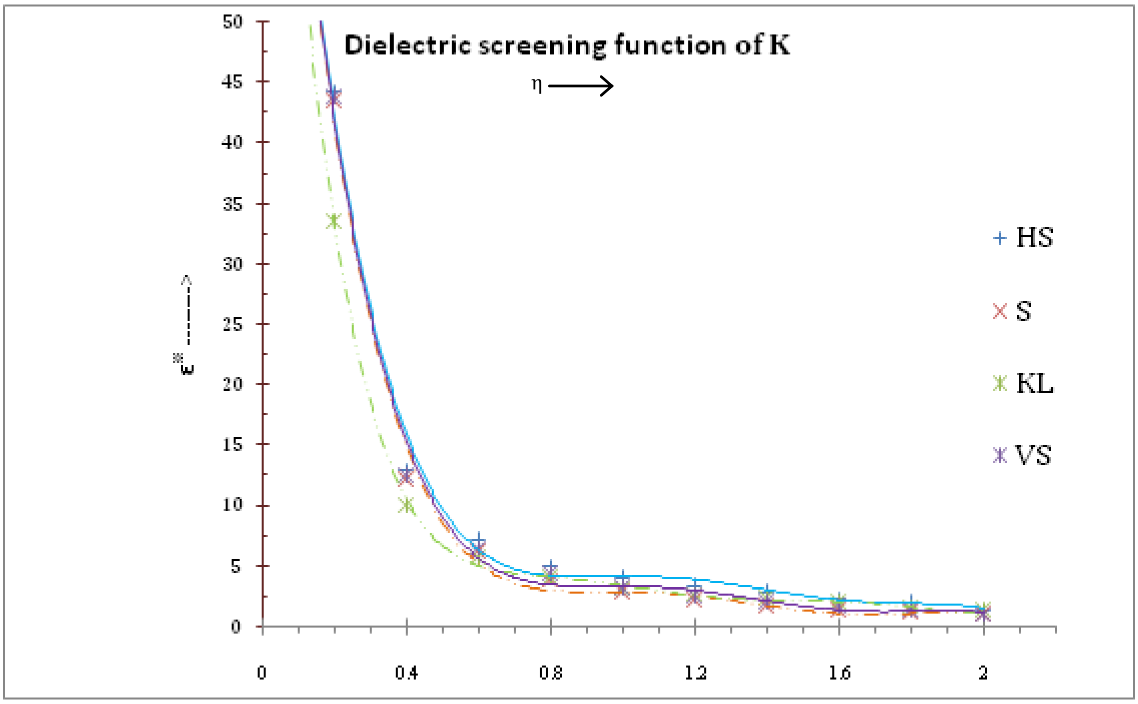

Fig 3: Dielectric screening function Li using Hubbard-Sham (HS), Shaw (S), Kleinmann-Langreth (K-L) and Vashishta – Singwi (V-S) forms of exchange correlation.

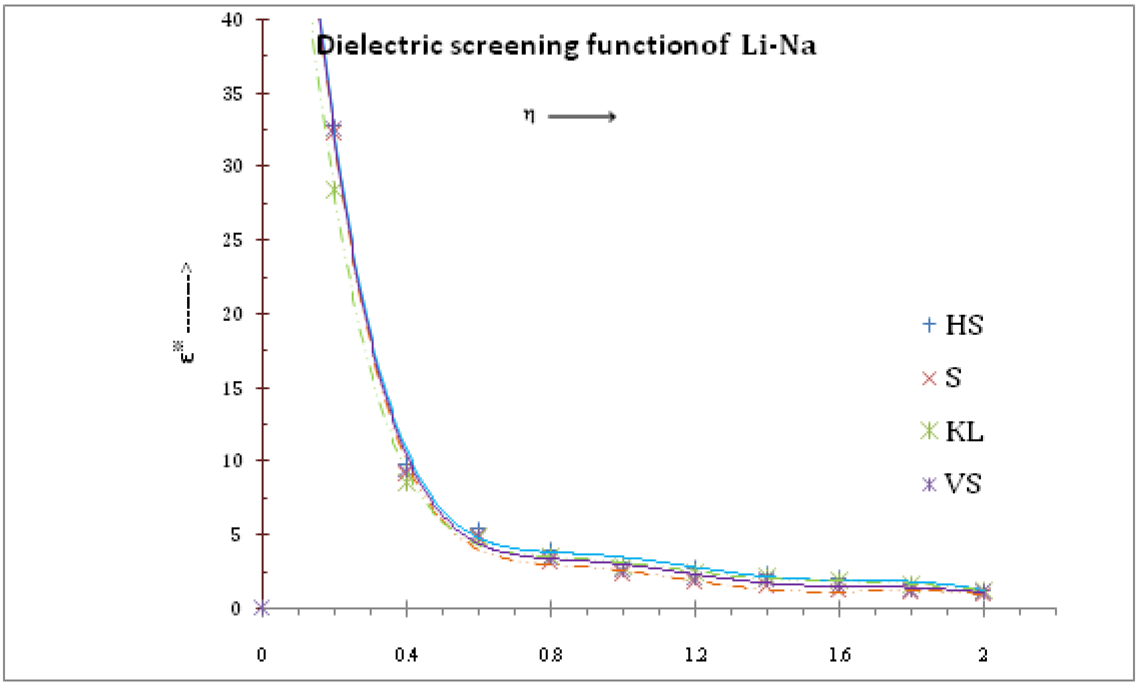

Fig 4: Dielectric screening function Li-Na using Hubbard-Sham (HS), Shaw (S), Kleinmann-Langreth (K-L) and Vashishta – Singwi (V-S) forms of exchange correlation.

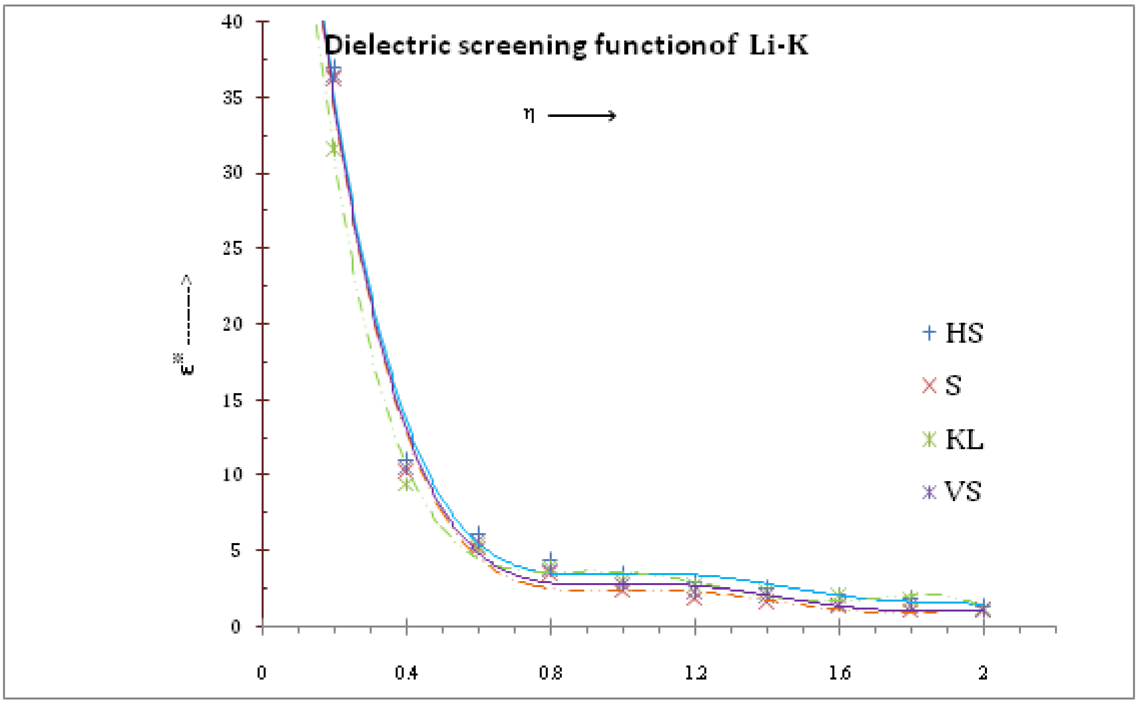

Fig 5: Dielectric screening function Li-K using Hubbard-Sham (HS), Shaw (S), Kleinmann-Langreth (K-L) and Vashishta – Singwi (V-S) forms of exchange correlation.

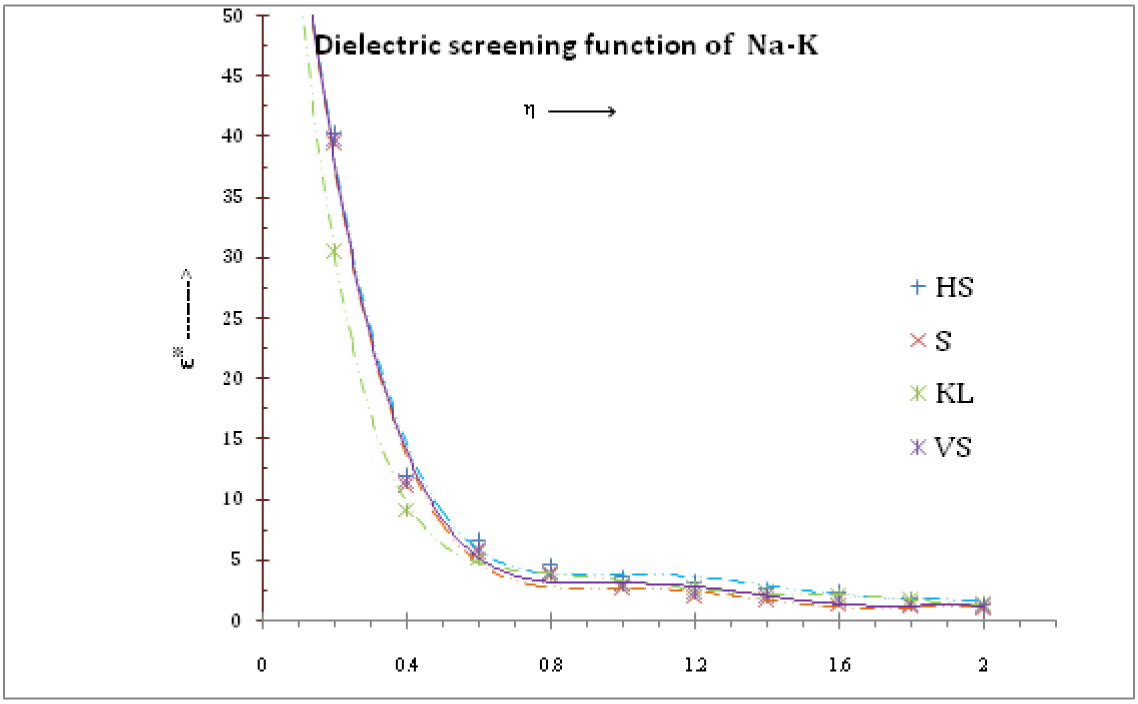

Fig 6: Dielectric screening function Na-K using Hubbard-Sham (HS), Shaw (S), Kleinmann-Langreth (K-L) and Vashishta – Singwi (V-S) forms of exchange correlation.

3.2 Form Factors:

We have computed the form factor of alkali metals Li, Na, K and its binary alloys Li-Na, Li-K and Na-K using eigen values of Herman-Skillman (1963), Hafner (1975) and Clementi (1965) near melting points. In this computation exchange and correlation of Vaishishta-Singwi form has been employed.

It seems to us that both experimentally and theoretically, the information about the form factors for the binary alloys of simple metals is not enough in the study of various electronic properties of these alloys.

To determine the non-local screened form factor for each of the following liquid binary alloys Li-Na, Li-K and Na-K we use a well tested Faber-Ziman Formalism (1965)

$$|w(k,q)|^2 = c_1|w(k,q)_1|^2 + c_2|w(k,q)_2|^2 + 2\,(c_1c_2)^{1/2}|w(k,q)_1||w(k,q)_2|$$

where c_1 and c_2 are concentration of constituent metals.

The plot of form factor is furnished in Figure 7, 8 and 9 for Li, Na and K respectively.

The form factor of binary alloys Li-Na, Li-K and Na-K was computed from Faber-Ziman Formalism and plotted as Figure 10, 11 and 12 respectively.

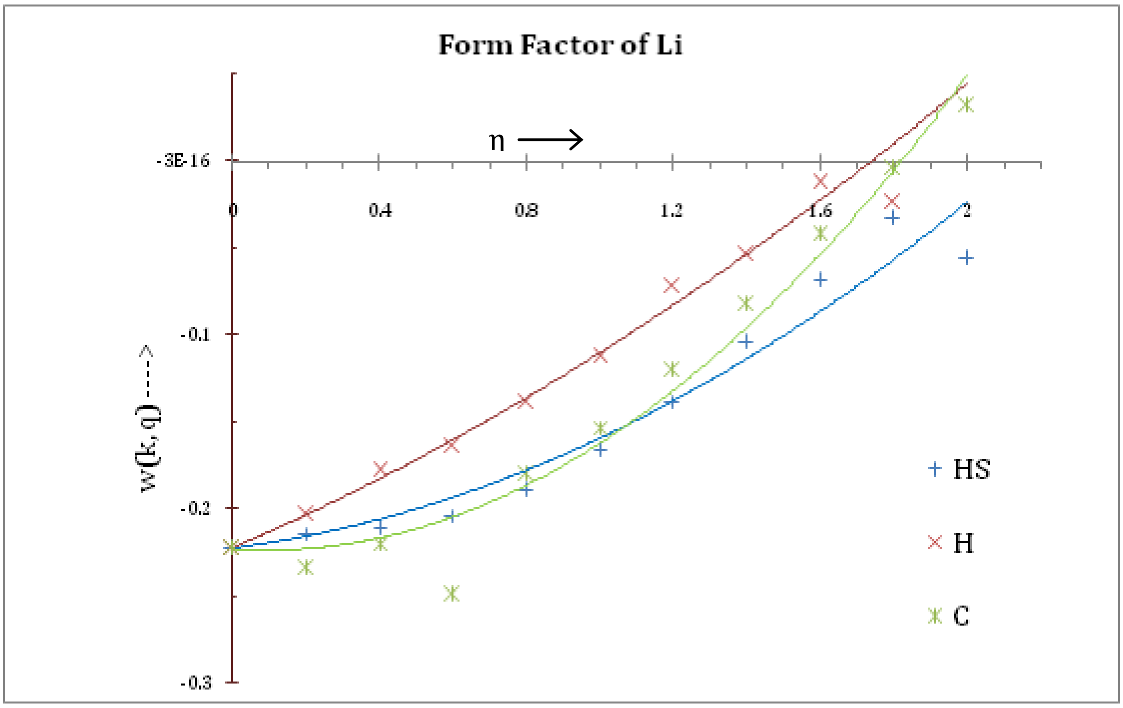

Fig 7: **Form Factor of Li with V-S exchange using eigen values of Herman-Skillman (HS), Hafner (H) and Clementi (C) near melting point.**

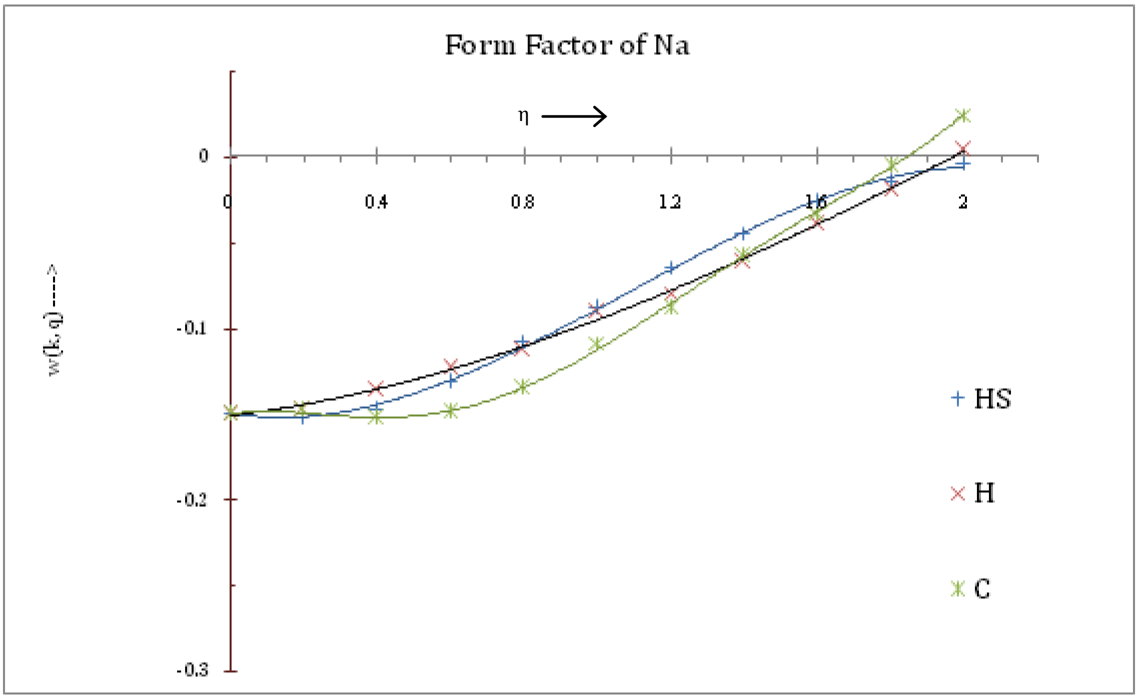

Fig 8: Form Factor of Na with V-S exchange using eigen values of Herman-Skillman (HS), Hafner (H) and Clementi (C) near melting point.

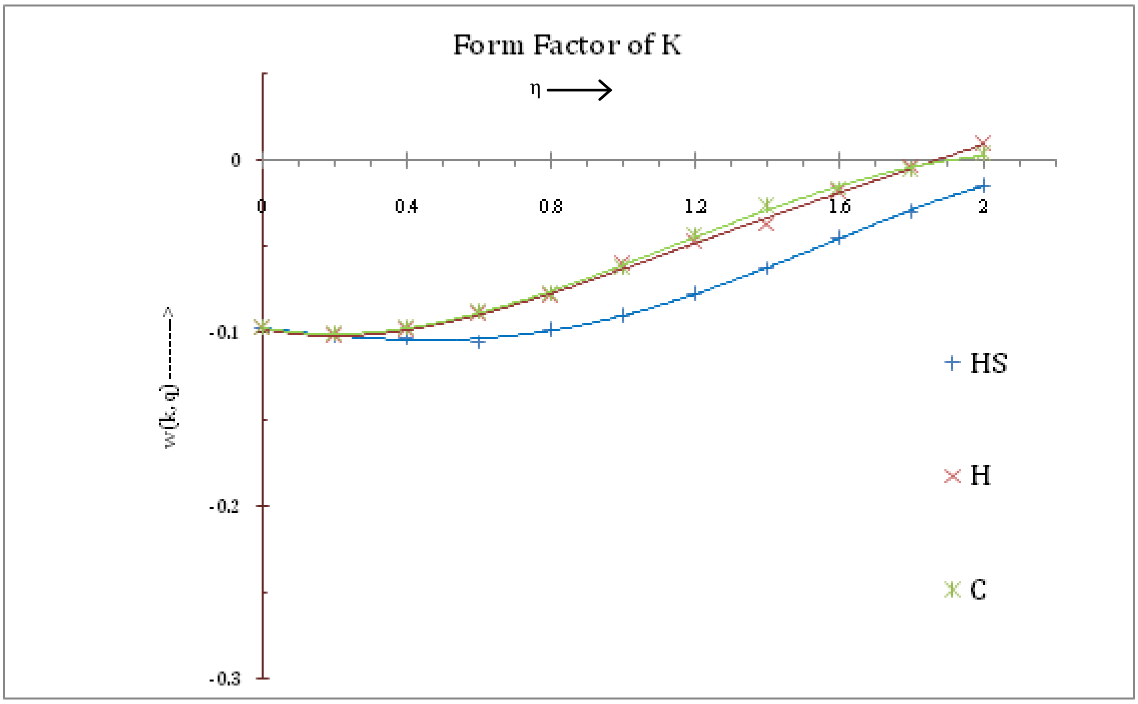

Fig 9: Form Factor of K with V-S exchange using eigen values of Herman-Skillman (HS), Hafner (H) and Clementi (C) near melting point.

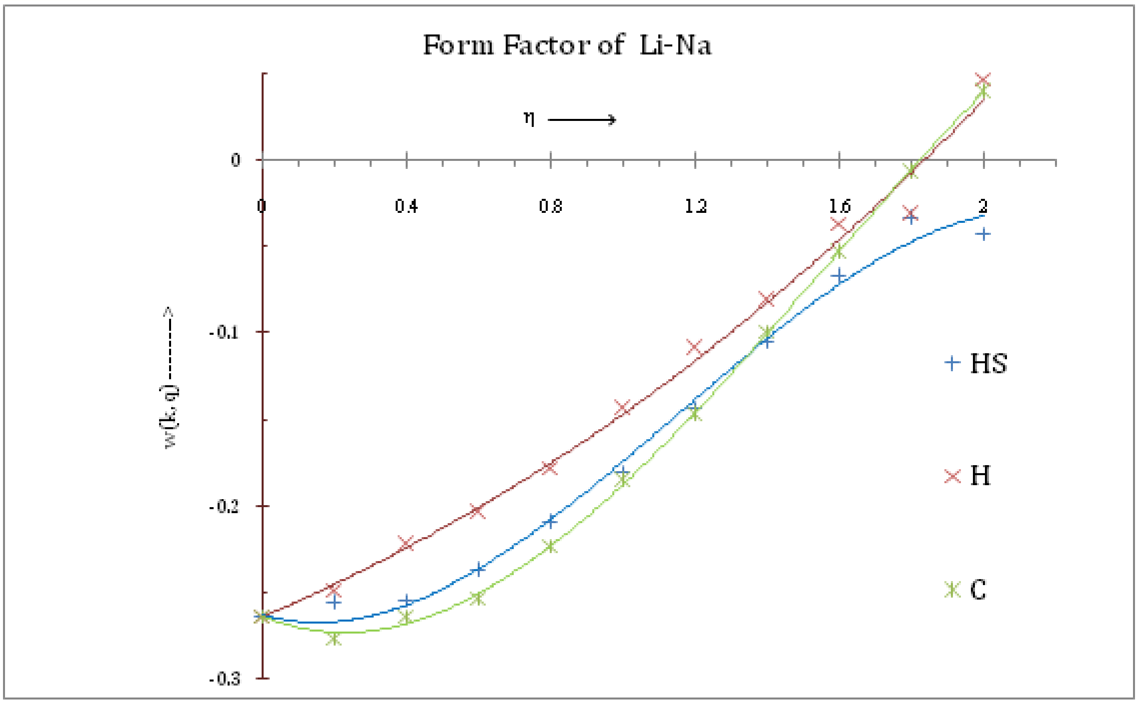

Fig 10: Form Factor of Li-Na with V-S exchange using eigen values of Herman-Skillman (HS), Hafner (H) and Clementi (C) near melting point.

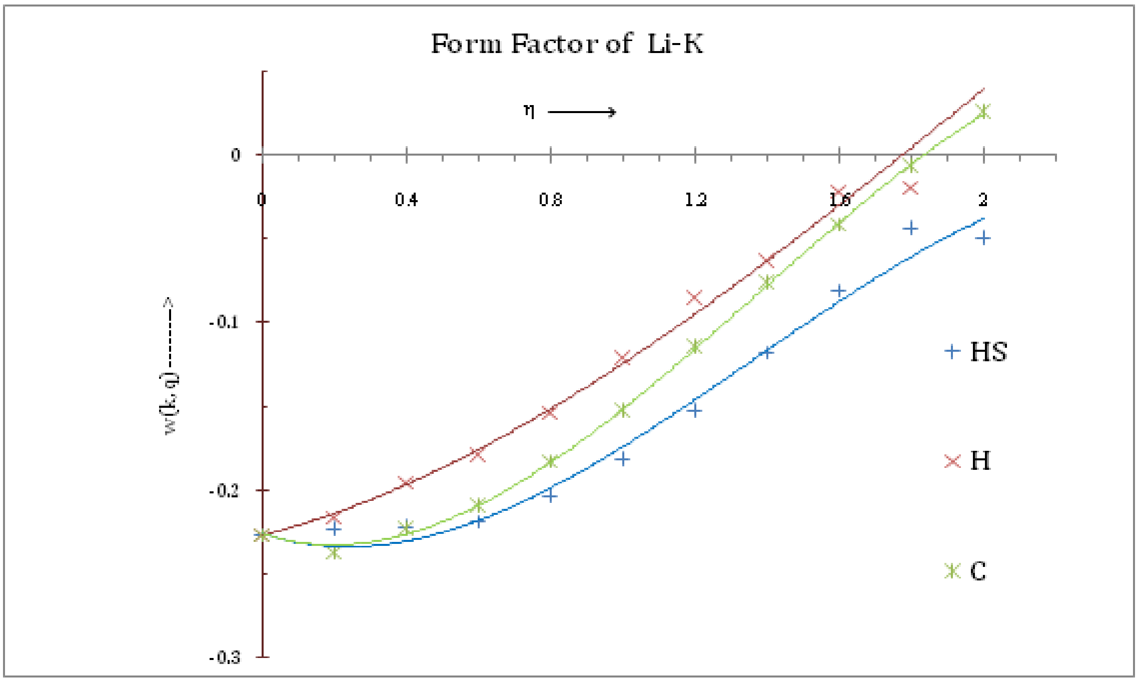

Fig 11: Form Factor of Li-K with V-S exchange using eigen values of Herman-Skillman (HS), Hafner (H) and Clementi (C) near melting point.

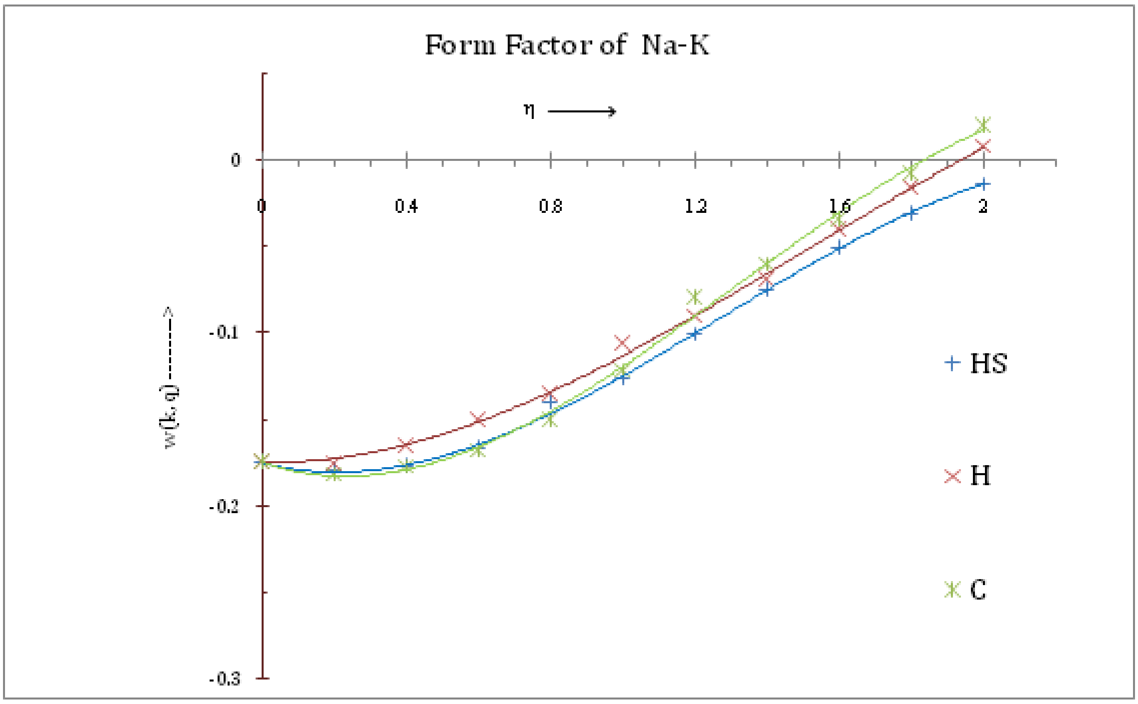

Fig 12: **Form Factor of Na-K with V-S exchange using eigen values of Herman-Skillman (HS), Hafner (H) and Clementi (C) near melting point.**

IV.CONCLUSIONS

HFP pseudopotential technique and well known Faber-Ziman Formalism has been used to compute the dielectric screening function of alkali metals Li, Na, K and its binary alloys Li-Na, Li-K and Na-K. Different forms of exchange correlation were used. Our computation reveals that V-S form of exchange correlation is appropriate to be used. Similar conclusion has been arrived by other researcher S. M. Rafique (1983), J. Yadav et al. (2008), J. Yadav et al. (2009), S. K. Chakrabarti (2016) and S. K. Chakrabarti et al. (2016) with different superconducting systems.

The form factor of alkali metals Li, Na, K and its binary alloys Li-Na, Li-K and Na-K using eigen values of Herman-Skillman (1963), Hafner (1975) and Clementi (1965) near melting points using V-S exchange. As HPF technique is based on various approximation reproduction of exact value is not desired. However, with proper choice of eigen values our results are quite acceptable as compared to the values obtained by previous researchers.

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