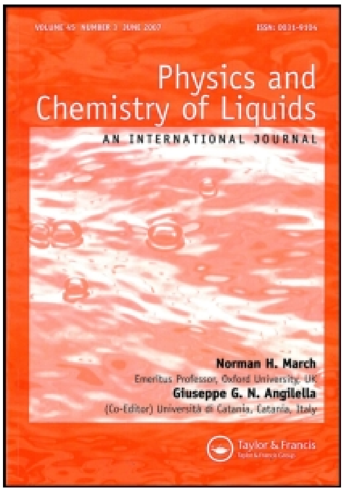

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Study of electron dispersion curves in liquid alkalis

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Study of electron dispersion curves in liquid alkalis

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Ashcroft's empty core local model of pseudopotentials in the second-order perturbation theory is used to study the electron dispersion relation, the Fermi energy and deviation in the Fermi energy from free-electron values for the liquid alkali metals. The influence of the six different forms of the local-field correction functions proposed by Hartree, Vashishta–Singwi, Taylor, Ichimaru–Utsumi, Farid *et al.* and Sarkar *et al.* on the aforesaid electronic properties is examined explicitly, which reflects the varying effects of screening. The depth of the negative hump in the electron dispersion of liquid alkalis decreases in the order Li→K; except for Rb and Cs, where it increases.

Keywords: pseudopotential; fermi energy; electron dispersion curves; local-field correction functions; alkali metals

1. Introduction

During the last few years there has been an increasing interest in the properties of non-crystalline conductors such as liquid metals and liquid metallic alloys. Such a liquid exhibits metallic as well as fluid-like behaviour, and hence can help to make a link between the theory of the liquid states and the theory of the electronic states in metals. Thus the study of the electronic properties of liquid metals and their alloys remains one of the favourite research areas, either experimentally or theoretically [1–5]. The pseudopotential-based investigation of the Fermi surface and its distortion from free-electron value for the metals in the solid phase are quite often well recognised. Very recently, we have also reported successfully the Fermi surface distortion (FSD) and Fermi energy (FE) of solid solutions [6,7]. However, the attempts of studying the FE and its deviation from the free-electron value for liquid metals are very rare [8–10].

Therefore, in the present article, an interesting task is taken up: to investigate electron dispersion relation, FE and deviation in the FE from the free-electron value for liquid alkali metals, based on the well-known empty core model (EMC) potential of Ashcroft [11]. In the present work, the theoretical structure factors are computed from the well-known Percus–Yevick (PY) hard sphere model with proper packing density [12]. The influence of the six different forms of the local-field correction functions proposed by Hartree (H) [13], Vashishta–Singwi (VS) [14], Taylor (T) [15], Ichimaru–Utsumi (IU) [16],

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Farid *et al.* (F) [17] and Sarkar *et al.* (S) [18] on the aforesaid electronic properties is examined explicitly, which reflects the varying effects of screening.

2. Computational methodology

The electronic structure of liquid metals using the pseudopotential theory and second-order perturbation theory is given as [8–10]:

$$E(k) = E_0(k) + E_1(k) + E_2(k), \tag{1}$$

where

$$E_0(k) = \frac{\hbar^2 k^2}{2m}, \tag{2}$$

$$E_1(k) = N\langle k|w(q)|k\rangle, \tag{3}$$

and

$$E_2(k) = \frac{2m}{\hbar^2}\sum_q \frac{S(q)S^*(q)\left|W(q)\right|^2}{\mathbf{k}^2 - \left|\mathbf{k}+\mathbf{q}\right|^2}. \tag{4}$$

Using the liquid structure factor $a(q) = N|S(q)|^2$, we write Equation (1) as:

$$E(k) = \frac{\hbar^2 k^2}{2m} + \frac{2m}{\hbar^2}\left[\sum_q \frac{a(q)\left|W(q)\right|^2}{\mathbf{k}^2 - \left|\mathbf{k}+\mathbf{q}\right|^2} - \frac{a(q)\left|W(q)\right|^2}{q^2}\right]. \tag{5}$$

For liquid metals, this equation is restructured as [8–10]:

$$E(k) = \frac{\hbar^2 k^2}{2m} + \Delta(k) - \Delta(0), \tag{6}$$

$$\Delta(k) = \frac{3Z}{8k_F E_F k}\int_0^\infty a(q)W(q)^2 q \ln\left|\frac{2k+q}{2k-q}\right| \mathrm{d}q, \tag{7}$$

and

$$\Delta(0) = \frac{3Z}{2k_F E_F}\int_0^\infty a(q)W(q)^2 \mathrm{d}q. \tag{8}$$

Hence the electron dispersion relation is derived as:

$$\Delta E(k) = \Delta(k) - \Delta(0). \tag{9}$$

At the Fermi level, i.e. at $k = k_F$, Equations (6)–(9) are written as [8–10]:

$$E_F(k)|_{k=k_F} = \frac{\hbar^2 k^2}{2m} + \Delta(k_F)|_{k=k_F} - \Delta(0)|_{k=k_F}, \tag{10}$$

with

$$\Delta(k_F)|_{k=k_F} = \frac{3Z}{8k_F^2 E_F}\int_0^{2k_F} a(q)W(q)^2 \ln\left|\frac{2k+q}{2k-q}\right| \mathrm{d}q, \tag{11}$$

and

$$\Delta(0)|_{k=k_F} = \frac{3Z}{2k_F E_F}\int_0^{2k_F} a(q)W(q)^2 \mathrm{d}q. \tag{12}$$

Hence the deviation in the FE ΔE_F from free-electron value at the Fermi level is given by

$$\Delta E_F = \Delta(k_F)|_{k=k_F} - \Delta(0)|_{k=k_F}, \tag{13}$$

where E_F, k_F, Z and $W(q)$ are the Fermi energy, Fermi wave vector, valence and model pseudopotential, respectively.

In the present computation of the electronic structure of liquid alkali metals, we have used Ashcroft's well-known EMC model potential [11], including six different types of the local-field correlation functions [13–18]. The form factor explored in the present investigation is of the form [11]:

$$W(q) = \frac{-4\pi Z e^2}{\Omega_O q^2 \varepsilon(q)}\cos(q r_C), \tag{14}$$

where Ω_O is the atomic volume, r_C is the parameter of the potential and $\varepsilon(q)$ is the modified Hartree dielectric function [13]. The parameter of the potential r_C is determined using the first zero of the form factor [6,7,10]. The modified Hartree dielectric function $\varepsilon(q)$ is given by [13]:

$$\varepsilon(q) = 1 + (\varepsilon_H(X) - 1)(1 - f(X)). \tag{15}$$

Here, $\varepsilon_H(X)$ is the static Hartree dielectric function [13] and the expression of it is given by:

$$\varepsilon_H(X) = 1 + \frac{me^2}{2\pi k_F \hbar^2 \eta^2}\left(\frac{1-\eta^2}{2\eta}\ln\left|\frac{1+\eta}{1-\eta}\right| + 1\right); \quad \eta = \frac{q}{2k_F}, \tag{16}$$

where $f(X)$ is the local-field correction function. In the present investigation, the local-field correction functions due to Hartree (H) [13], Vashishta–Singwi (VS) [14], Taylor (T) [15], Ichimaru–Utsumi (IU) [16], Farid *et al.* (F) [17] and Sarkar *et al.* (S) [18] are incorporated to see the impact of exchange and correlation effects. The details of all the local-field corrections are below.

The H-screening function [13] is purely static, and it does not include the exchange and correlation effects. The expression of it is:

$$f(X) = 0. \tag{17}$$

Vashishta–Singwi (VS) [14] have introduced an analytical expression for the local-field correction function, which is written as:

$$f(X) = A_{VS}\left\{1 - \exp\left(\frac{-B_{VS} q^2}{k_F^2}\right)\right\}. \tag{18}$$

Table 1. Input parameters and other constants.

Metals	Z	Ω_O (au)^3	σ (au)	η	r_C (au)
Li	1	146.46	5.0484	0.46	1.9898
Na	1	266.08	6.1601	0.46	1.8558
K	1	480.84	7.5033	0.46	2.1159
Rb	1	627.15	8.0158	0.43	2.1245
Cs	1	775.73	8.6045	0.43	2.1507

Table 2. Fermi energy $-E_F$ (10^{-12} erg) for liquid alkali metals.

	Present results						
Metals	H	VS	T	IU	F	S	Others [8,10]
Li	7.1468	7.0443	6.9480	7.1023	6.9855	7.0679	6.8584, 6.9623, 7.0021, 7.0633, 7.0805, 7.0861, 7.0961, 7.0662, 7.1149, 7.2530, 7.2965, 7.3989, 7.4199
Na	4.9856	4.9709	4.9406	4.9755	4.9596	4.9724	4.6934, 4.7008, 4.7057, 4.7199, 4.7388, 4.9170, 4.9283, 4.9544, 4.9578, 5.0477, 5.0566, 5.0879, 5.0986
K	3.3725	3.3688	3.3448	3.3664	3.3610	3.3663	3.1559, 3.1701, 3.2081, 3.2184, 3.2811, 3.2922, 3.3030, 3.3105, 3.3270, 3.3306, 3.3328, 3.3404, 3.3493
Rb	2.7025	2.6250	2.5617	2.6752	2.6042	2.6503	2.7448, 2.7620, 2.7697, 2.7703, 2.7755, 2.7668, 2.7699, 2.7802, 2.7919, 2.8390, 2.8662, 2.8755, 2.9007
Cs	2.3292	2.2436	2.1800	2.3012	2.2262	2.2744	2.1582, 2.1592, 2.1783, 2.1977, 2.2119, 2.3293, 2.3354, 2.3488, 2.3559, 2.4294, 2.4396, 2.4617, 2.4724

Taylor (T) [15] has introduced an analytical expression for the local-field correction function, which satisfies the compressibility sum rule exactly. This is the most commonly used local-field correction function and covers the overall features of the various local-field correction functions proposed before 1972. According to him:

$$f(X) = \frac{q^2}{4k_F^2}\left[1 + \frac{0.1534}{\pi k_F^2}\right]. \tag{19}$$

The Ichimaru–Utsumi (IU) local-field correction function [16] is a fitting formula for the dielectric screening function of the degenerate electron liquids at metallic and lower densities, which accurately reproduces the Monte-Carlo results, and also satisfies the

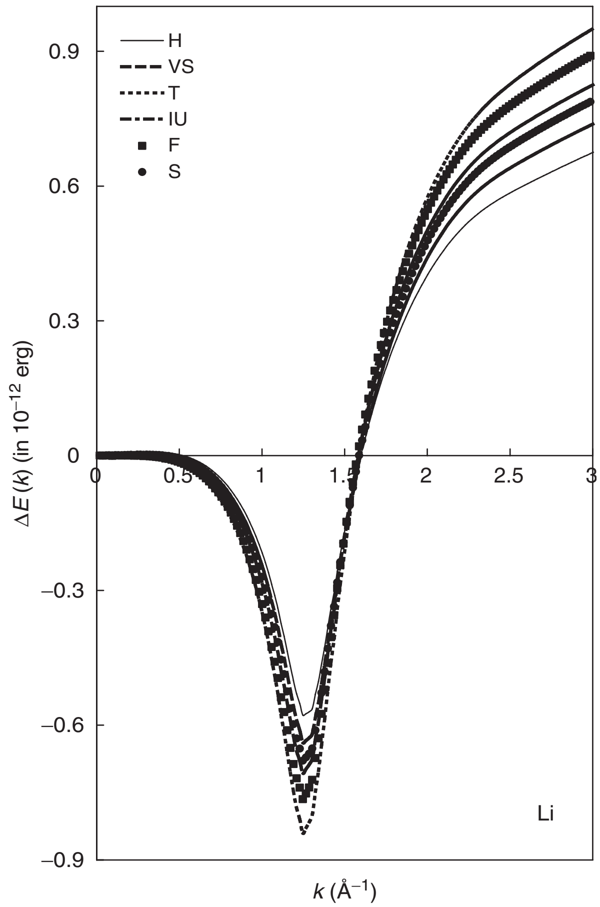

Figure 1. Electron dispersion curves for liquid Li.

self-consistency condition in the compressibility sum rule and short range correlations. The fitting formula is:

$$f(X) = A_{\mathrm{IU}}Q^4 + B_{\mathrm{IU}}Q^2 + C_{\mathrm{IU}} + \left[A_{\mathrm{IU}}Q^4 + \left(B_{\mathrm{IU}} + \frac{8A_{\mathrm{IU}}}{3}\right)Q^2 - C_{\mathrm{IU}}\right]\left\{\frac{4-Q^2}{4Q}\ln\left|\frac{2+Q}{2-Q}\right|\right\}. \tag{20}$$

On the basis of Ichimaru–Utsumi (IU) [16] local-field correction function, Farid *et al.* (F) [17] have given a local-field correction function of the form:

$$f(X) = A_{\mathrm{F}}Q^4 + B_{\mathrm{F}}Q^2 + C_{\mathrm{F}} + \left[A_{\mathrm{F}}Q^4 + D_{\mathrm{F}}Q^2 - C_{\mathrm{F}}\right]\left\{\frac{4-Q^2}{4Q}\ln\left|\frac{2+Q}{2-Q}\right|\right\}. \tag{21}$$

Based on Equations (20) and (21), Sarkar *et al.* (S) [18] have proposed a simple form of local-field correction function, which is of the form

$$f(X) = A_{\mathrm{S}}\left\{1 - \left(1 + B_{\mathrm{S}}Q^4\right)\exp\left(-C_{\mathrm{S}}Q^2\right)\right\}, \tag{22}$$

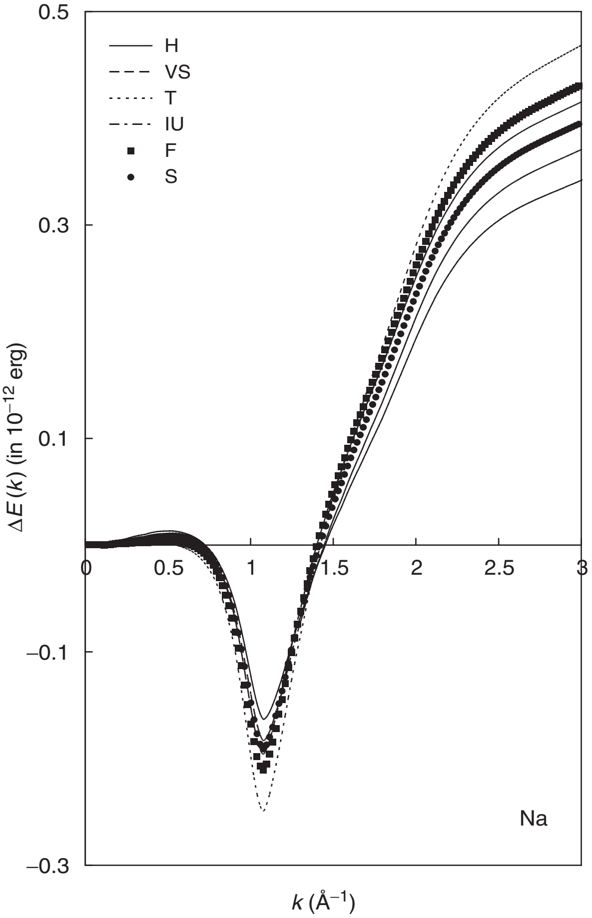

Figure 2. Electron dispersion curves for liquid Na.

where $Q = 2X$ with $X = q/2k_F$. The parameters A_{VS}, B_{VS}, A_{IU}, B_{IU}, C_{IU}, A_{F}, B_{F}, C_{F}, D_{F}, A_{S}, B_{S} and C_{S} are the atomic volume dependent parameters of VS, IU, F and S local-field correction functions. The mathematical expressions of these parameters are narrated in the respective papers of the local-field correction functions [13,16–18].

The set of Equations (6)–(13) are used for computing the electron dispersion relation, FE, and deviation in the FE from free-electron values at the Fermi level of liquid alkali metals. Simpson's 1/3 method is used to evaluate numerically the integration appearing in the Equations (7), (8), (11) and (12). The step size of the integration in each case is of the order of $10^{-3}k_F$.

3. Results and discussion

The input parameters and other constants used in the present computations are narrated in Table 1. The input parameters are taken from [5]. The FE at the Fermi level of liquid alkali metals is narrated in Table 2.

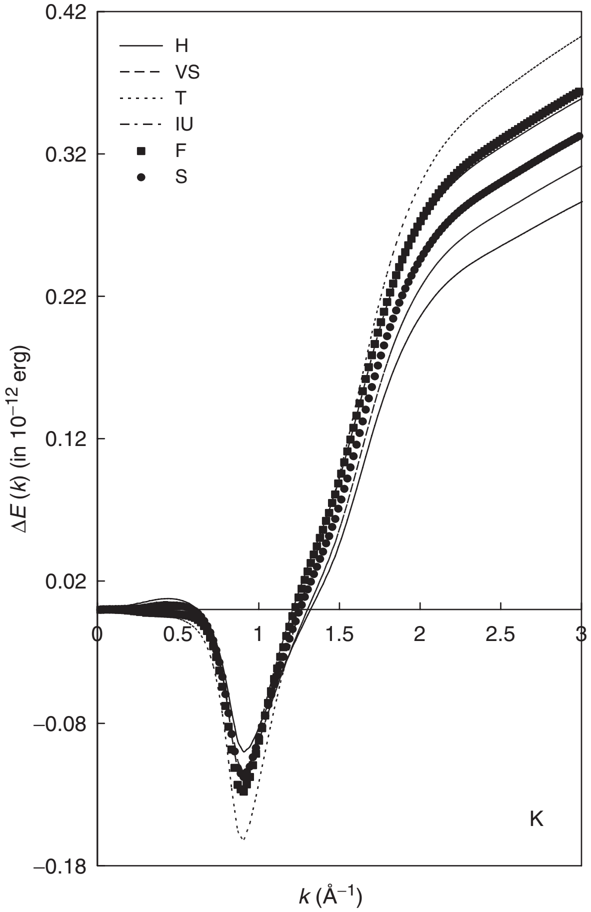

Figure 3. Electron dispersion curves for liquid K.

From Table 2 it is noticed that the present results of the FE at the Fermi level of the liquid metals are found in qualitative agreement with the theoretical [8,10] findings. Also, it is noted that, among the six employed local-field correction functions, the local-field correction function due to T gives the minimum numerical value of the FE at the Fermi level, while the local-field correction function due to H (without exchange and correlation) gives the maximum value. It was also concluded that among all the alkali metals, minimum deviation in the FE at Fermi level is obtained for liquid Cs, and the maximum for liquid Li. In comparison with the static H-function, the percentile influences of various local-field correction functions, namely, VS, T, IU, F and S on the FE at Fermi level are found for Li, Na, K, Rb and Cs of the order of 0.62–2.78%, 0.20–0.90%, 0.11–0.82%, 1.01–3.64% and 1.20–4.42%, respectively.

The computed results of electron dispersion relations for liquid alkali metals are shown in Figures 1–5. From Figures 1–5, it is observed that, for all five alkali metals, the negative hump is observed around $k = 1.3$, 1.1, 0.94, 0.77 and 0.81 Å^{-1} for Li, Na, K, Rb and Cs, respectively. Also, the higher negative hump is observed for the T-function, while that obtained for the H-function is lower. As we move from Li → Cs, the magnitude of the first

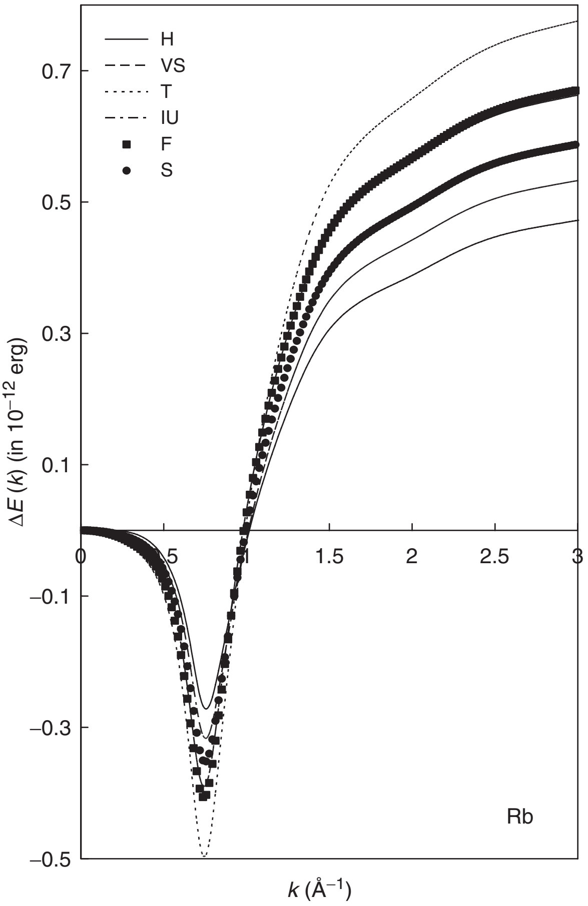

Figure 4. Electron dispersion curves for liquid Rb.

peak decreases, except those for Rb and Cs, where it increases, and the positions of this peak also move towards the lower wave vector. The largest negative hump is observed for the Rb element, while for K the lowest hump is observed.

Also, one can note from Figures 1–5 that, for the system of higher atomic mass and atomic volume, the influence of the exchange and correction function is greater. The effect of various local-field correction functions is clearly visible for higher values of wave vectors. It is also observed that the incorporation of exchange and correlation effects via various local-field correction functions suppresses the FE in comparison with the static H-screening effect. The maximum influence of local-field correction is observed due to T-screening function and minimum influence is observed for H-function. Most of the local-field correction functions due to VS, IU, F and S are found between those of H- and T-screening functions, as a direct comparison of the experimental properties for the liquid alkali metals is not available in the literature. But the present results are found in a predictive nature. The oscillatory behaviour in Figures 1–5 indicates that electron dispersion may have an important effect on the electronic properties of liquid metals.

A good description of Cs or Rb is rather more complicated than that of the other alkali elements. This problem stems from the fact that at pure Cs or Rb density, the

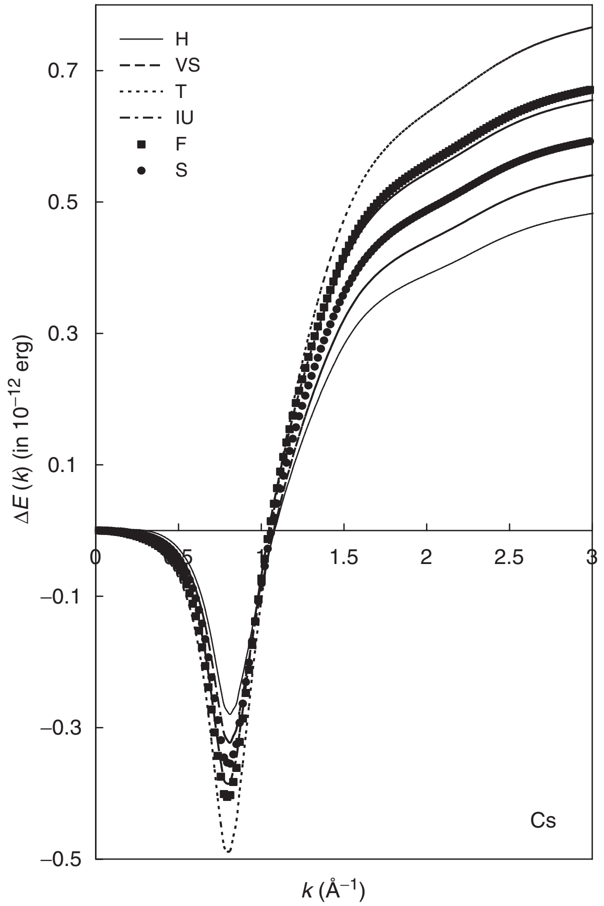

Figure 5. Electron dispersion curves for liquid Cs.

compressibility of the electron gas is close to zero, and is conceivably negative. Hence, the normal pseudopotential perturbation approach based on the electron gas as the zero order approximation is rather dubious. This is because one is starting with a thermodynamically unstable system to provide a description of one which is thermodynamically stable. The way out of this dilemma is to scale the electron gas density parameter, i.e. the Wigner–Seitz radius r_S, by the band structure effective mass m^*, which then means that one is dealing with an effective density for which the electron gas compressibility was large and positive. The physical meaning of this approach is not clear, but it bears a close resemblance to the fact that the effect of large core polarisation of Cs or Rb could be taken into account by a suitable scaling of r_S, also in the direction of large, positive compressibility [19]. But, in the present results of the electron dispersion curves of the liquid alkali metals like Rb or Cs, we have made straightforward computations without any assumptions or relativistic corrections.

Here, the *k*-vector is good quantum value for electronic states in liquid. Since a liquid metal is a disordered system, the corresponding eigenstates are not a combination of plane waves. So strong an imaginary part of energy depending on the *k*-vector should be taken into account. The reason behind this is the damping of electron states with any fixed *k*-vector according to the spherical form of the Fermi surface. Also, the peak of the structure factor *a*(*q*) is also affected by the damping of the electronic states of the liquid alkali metals. Therefore, we have seen the humping nature of the electron dispersion curves of the liquid alkali metals.

4. Conclusions

From the present study we conclude that, among all the liquid alloy metals, it was observed that liquid Rb has the largest negative hump in the electron dispersion among all of the alkalis. The depth of the negative hump in the electron dispersion of liquid alkalis decreases in the order Li→K, except for Rb and Cs, where it increases. It was also concluded that among all the liquid alkali metals, a minimum deviation in the FE at Fermi level is obtained for liquid K and a maximum for liquid Li. The EMC model potential with more advanced IU, F and S local-field correction functions generate consistent results regarding the electronic properties of liquid alkalis. Hence, the EMC model potential is found to be suitable. Also, the present investigation predicts that the present study of electronic properties is sensitive to the selection of the proper local-field correction function.

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