

## INTERATOMIC PAIR POTENTIALS AND LIQUID STRUCTURE OF SOME HCP RARE-EARTH METALS

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Effective pair potentials for some HCP liquid rare-earth metals near their melting points have been derived from the second order perturbation theory with the Heine-Abarenkov pseudopotential and the transferable electron-ion potential of Fiolhais and coworkers which was originally developed for the solid state. We have also constructed the Wills-Harrison (WH) model potentials. The *s* electron contribution to the effective potential has been taken into account with these potentials using different screening functions. In this work, recently proposed Karmakar-Joarder form of modified WH potentials has been applied to some HCP liquid metals, as Tb, Dy, Ho, Er and Lu in order to obtain the *d* state and *f* state contributions. The Singh form of WH potentials has also been calculated for comparison with those obtained by others. The liquid structure has been computed with both random phase approximation and the variational modified hypernetted chain (VMHNC) integral equation theory. It has been shown that the VMHNC results of static structure factors and pair distribution functions are in good agreement with the experimental data.

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### 1. Introduction

The rare-earth metals are more complicated metallic systems than the simple and transition metals. Although many experimental data on various properties of these metals are now available in the literature [1], the theoretical understanding of structural and thermodynamic properties of their solids and liquids has been still progressing in last two decades. One of the route applied to derive the effective pair potentials for rare-earth metals based on the standard pseudopotential theory [2-4]. For this purpose the simple metal (SM) theory has been applied directly to calculate the liquid structure for some rare earth metals using the empty core (EC) pseudopotential in conjunction with one component plasma (OCP) [5]. Very recently, S. Dalgic et al. [6] have also successfully applied the SM theory to the calculations of liquid structure for early rare earth metals with the self consistent integral equation theory of VMHNC [7-9]. An alternative method to the SM theory has been extended for the incomplete 4f-bands [10] in a similar model concept of Wills-Harrison (WH) for transition metals [11]. This is the so called the modified Harrison model (MH) potential [10,11]. Recently Karmakar and Joarder (KJ) [12] have used the MH model for the effective pair potential of 4f liquid metals in conjunction with Gibbs – Bogolyubov variational method with charge hard sphere (CHS) reference in order to obtain liquid structure and thermodynamic properties. Here the use of MH potential led to promising results. However, in our previous work [6] we have noted that when the MH potential is used together with accurate liquid state theories [7-9], it fails to produce results for the structure factor  $S(q)$  of the 4f rare-earth metal with half and less than half filled *f* bands. On the other hand Bhuiyan et al. [13] have carried out the structural calculations for most rare earth metals

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using Embedded Atom Method (EAM) derived effective pair potentials with the VMHNC theory of liquids that are in a good agreement with the experimental data [1].

To our knowledge, there is no theoretical work on the structural properties of late liquid rare earth metals, Tb, Dy, Ho, Er, Lu, which is based on the standard pseudopotential theory and the MH model potential with integral equation theories. Our first aim in this work is to present the effective pair potentials derived from the local pseudopotentials which are capable of predicting the structure of liquid rare-earth metals. For this purpose we have used the local Heine-Abarenkov (LHA) pseudopotential [14] and recently proposed a local transferable potential of Fiolhais' [15,16] which is the first application for rare-earth metals. Our second aim is to extract the pair potentials using the MH model potential method. The validity of these effective potentials have been checked by calculating the structural properties near their melting points using both the random phase approximation (RPA) and VMHNC integral equation theory.

The layout of the paper is as follows; in section 2, we outline the theoretical basis of our work. Then we present the results and discussion in section 3. Finally, in Section 4, we sum up and briefly comment the results of our work.

## 2. Theory

### 2.1 Effective pair potentials

The effective pair potential using the SM pseudopotential theory can be written as,

$$\phi(r) = \frac{Z_{\text{eff}}^2}{r} \left[ 1 - \frac{2}{\pi} \int_0^\infty \frac{F_N(q, \rho)}{q} \sin(qr) dq \right], \quad (1)$$

where

$$F_N(q, \rho) = \left( \frac{q^2 \omega(q)}{4\pi Z_{\text{eff}}} \right)^2 \left( 1 - \frac{1}{\epsilon(q, \rho)} \right) \quad (2)$$

where  $Z_{\text{eff}}$  for the effective number of valence electrons per ion and  $\rho$  the number density of ions. Here  $\omega(q)$  is the local pseudopotential and  $\epsilon(q)$  is the dielectric screening function. In the present work we use the local Heine –Abarenkov (LHA) pseudopotential given as,

$$\omega(q) = -(4\pi Z_{\text{eff}} / q^2) [(1 - A) \cos qR_M + \frac{A}{qR_M} \sin qR_M] \quad (3)$$

where  $A, R_M$  are the pseudopotential parameters and  $R_M$  denotes the core radius. In present work, we use the evanescent core (EC) type local pseudopotential of Fiolhais *et al.* [15],

$$\omega(q) = 4\pi Z_{\text{eff}} R^2 \left[ -\frac{1}{(qR)^2} + \frac{1}{(qR)^2 + \alpha^2} + \frac{2\alpha\beta}{[(qR)^2 + \alpha^2]^2} + \frac{2A}{[(qR)^2 + 1]^2} \right] \quad (4)$$

where  $R$  is the core decay length,  $\beta$  and  $A$  parameters are given in terms of  $\alpha$  given in Ref. [15-17]. The values  $\alpha$  and  $R$  of the universal version of Fiolhais' potential can be obtained using the parameterization procedure given in Ref. [17]. The resulting effective pair potential for liquid rare earth metals contains three parameters,  $R$ ,  $\alpha$  and  $Z_s$  whose choice is discussed in the next section. In this paper we employ the well known screening function of the Ichimaru-Utsumi (IU) [18] and we

have also used the rational dielectric function to get the analytic Pettifor-Ward (PW) pair potential [19] as,

$$\phi(r) = \frac{Z_{\text{eff}}^2}{R} \sum_m A_m \text{Cos}(k_m R + \alpha_m) e^{-\chi_m R} \quad (5)$$

where the parameters  $A_m$ ,  $\alpha_m$  are related to poles  $q_m$ ,  $q_m = k_m + i\chi_m$  depend only the density of the free electron gas representative of the system, and depend also on the pseudopotential used. We refer the interested reader to Refs. [6,19].

We assume that the MH model potential for the effective pair potential of rare-earth metals in the solid state is applicable to liquid state. The rare earth metal pair potential for the electron configuration  $5d^1 6s^2 4f^n$ , with  $n=8,9,10, 11$  and  $14$  for Tb, Dy, Ho, Er and Lu, respectively, can be written as in Ref.[6]

$$\phi(r) = \phi_s(r) + \phi_d(r) + \phi_f(r) + \phi_{\text{ff}}(r) \quad (6)$$

where  $\phi_s(r)$  denotes the s contribution to the pair potential which can be calculated here from Eqs. (1) and (5) replacing the number of s electrons  $Z_s$ , by  $Z_{\text{eff}}$ .  $\phi_d(r)$  is the one d state contribution which can be obtained in the same way [11]. The f-state contribution due to coupling that broadens the f-states into bands taking a simple rectangular model of density of f-states suggested by Friedel [20] can be written as,

$$\phi_f(r) = -Z_f \left( 1 - \frac{Z_f}{14} \right) \left( \frac{1}{N_c} \right)^{1/2} \frac{(5.06 r_f)^5}{r^7} \quad (7)$$

if the ions were interacting with only nearest neighbours. Here  $r_f$  is the f-state radius,  $Z_f$  is the number of the electrons in the f-band. The last term corresponds to the shift in the f-band centre. Thus the nonorthogonal potential due to f-states as in Ref. [10,11]

$$\phi_{\text{ff}}(r) = 2Z_f \frac{(3.11 r_f)^{10}}{r^{12}} \quad (8)$$

Following Singh [21] and others [10,11] the ion-ion interaction for f-band metals which includes the temperature dependence in the pair potential can be written as,

$$\phi(r)_{\text{eff}} = [\phi_s(r) + \phi_d(r) + \phi_f(r) + \phi_{\text{ff}}(r)] \exp(-\pi k_B \text{Tr} / \hbar v_F) \quad (9)$$

where  $\phi_s(r)$ ,  $\phi_d(r)$ ,  $\phi_f(r)$  and  $\phi_{\text{ff}}(r)$  are the same meaning given in Eq.(6). The exponential factor in the above equation obtained by Takanaka and Yamamoto [22] denotes the temperature dependence in the rare earth pair potential.

## 2.2 The liquid state theory

With the effective pair potential known, integral equations are able to provide us the liquid structure for metals. For the structural calculations, one of the the integral equation theory which has shown to be very reliable theory of liquids, VMHNC has been carried out [7-9]. Like most liquid-state theories the VMHNC solves the Ornstein-Zernike(OZ) equation [23], which relates the direct correlation function  $c(r)$  to the pair distribution function  $g(r)$ , within an approximate closure, for which the bridge function. In this work we use the Percus-Yevick (PY) hard sphere bridge function,  $B(r) = B_{\text{PY}}(r, \eta)$  where the packing fraction  $\eta = \eta(\beta, \rho)$  is variationally determined by minimising

the VMHNC configurational Helmholtz free energy  $f^{\text{VMHNC}}(T, \rho; \eta)$  at a temperature  $T$ . The value of  $\eta$  thus obtained is used to solve the OZ equation to calculate  $g(r)$  and the structure factor  $S(q)$  when evaluating the bridge function.

### 3. Results and discussion

#### 3.1 Effective pair potentials

We present below the effective pair potentials for HCP liquid rare–earth metals such as Tb, Dy, Ho, Er and Lu, which is derived from both the second order perturbation theory and the MH model potential in the forms of KJ and Singh. Calculations in the present work are performed at temperatures near melting in the liquid phase. The thermodynamic states studied in this work specified by the temperatures and number densities are taken from Waseda [1] and given in Table 1. In order to calculate the pair potentials, we shall use a couple of sets of  $Z$  and pseudopotential parameter values for LHA and Fiolhais'. We note that the pseudopotential parameters used in this work depend on the value of  $Z$ . The LHA pseudopotential parameters  $A$  and  $R_M$  are obtained using the value of  $Z$  from the values of  $A$  which are fitted the solid state properties given in Ref. [21]. The universal choice of Fiolhais' potential parameters  $R$  and  $\alpha$  can be obtained using the parameterization procedure given in Ref. [17]. Since the optimum set of parameters were chosen to give the best possible results for the liquid structure calculations, there is no reason that these are obtained by fitting to the heights or positions of the first peak of the static structure factor.

Firstly, we present the results of effective pair potentials obtained by the SM theory. We replace  $Z$ , by  $Z_{\text{eff}}$  in our simple metal calculations. For the choice of  $Z_{\text{eff}}$  values in this work, we have changed  $Z_{\text{eff}}$  from 1.5 to 3. Thus the value of  $Z_{\text{eff}}$  obtained is used to evaluate the parameters which, in turn, is used to calculate effective pair potentials and liquid structure factors. The optimized potential parameters used in the determination of the effective pair interaction with the standard pseudopotential theory are reported in Table 1. The calculated LHA pair potentials for liquids Tb, Er and Lu with different screening functions are shown in Fig. 1. The pair potential obtained using the Fiolhais' electron-ion model potential with IU approximation are plotted in Fig. 2.

We have observed the same trends for the presented group of metals using both LHA and Fiolhais' potentials including small change in depth of the minimum seen between Dy and Lu. As we go down column of the periodic table, the attractive part of the potential increases, and becomes softer, the depth and width decreases, and the position of the principal minimum is displaced to smaller value of  $r$ . As for the long range behaviour, it is observed that the Friedel oscillations are rather marked in Tb, slightly dumped for Dy, and very similar for Ho, Er and Lu. We have note that the calculated Fiolhais' pair potentials show one additional positive minima at short distance when  $Z_{\text{eff}}$  changes from 1.7 to 3.

Table 1. Input parameters used in our standard pseudopotential calculations.

Metal	T(°K)	$\rho(\text{atoms}/\text{Å}^3)$	$Z_{\text{eff}}$	A	$R_M(\text{a.u})$	R (a.u)	$\alpha$
Tb	1653	0.0274	1.7	0.416	2.450	0.491	3.320
Dy	1703	0.0301	1.8	0.448	2.410	0.465	3.340
Ho	1753	0.0301	1.9	0.475	2.401	0.467	3.325
Er	1793	0.0302	2	0.503	2.385	0.465	3.305
Lu	1953	0.0316	1.9	0.477	2.310	0.454	3.356

It appears in Fig. 1 that the IU gives rise to a deep potential well while the others yield a shallow potential well. It is observed that this difference becomes more marked when going towards the heaviest metals.

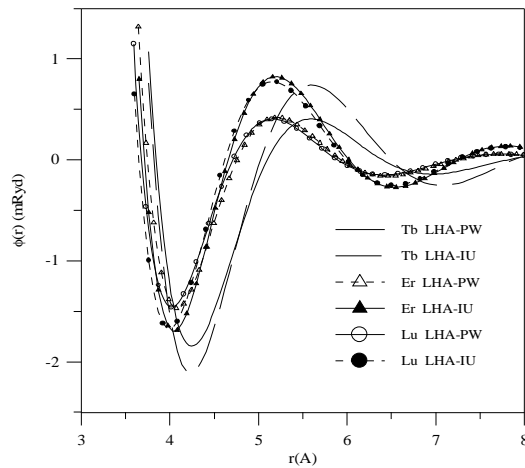


Fig. 1. Effective pair potentials  $\phi(r)$  derived from standard pseudopotential theory for liquids Tb, Er and Lu.

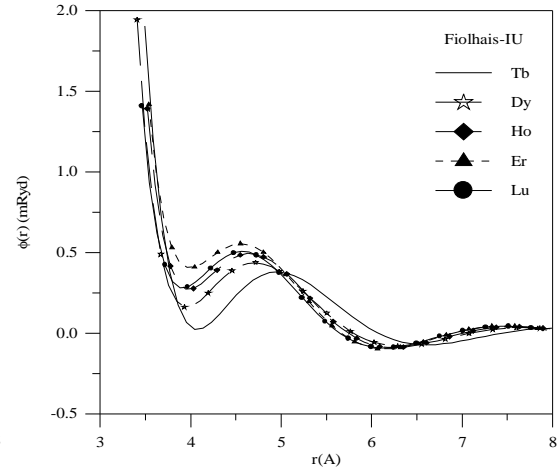


Fig. 2. Fiolhais' pair potentials for liquids Tb, Dy, Ho, Er and Lu.

The second data set for MH potentials are given in Table 2. Following Singh and Karmakar, d- state radius is taken equal to that for lanthanum ( $r_d = 1.286$  a.u) (in solid state) for all interested metals.

Table 2. Input parameters for MH model effective pair potentials of 4f liquid metals.

Metal	A	$R_M$ (a.u)	R (a.u)	$\alpha$	$Z_s$	$Z_d$	$Z_f$	$R_f$ (a.u.)
Tb	0.490	2.450	0.490	3.251	2	1	8	0.8442
Dy	0.498	2.410	0.466	3.303	2	1	9	0.8427
Ho	0.500	2.401	0.466	3.303	2	1	10	0.8442
Er	0.503	2.385	0.465	3.305	2	1	11	0.8453
Lu	0.502	2.310	0.455	3.327	2	1	14	0.8399

The calculated modified Harrison model potentials in the forms of KJ and Singh with using the LHA electron-ion potential for s contribution and the PW dielectric screening function are shown in Figs. 3a and 3b, respectively. The depth of the MH model potential is larger than those obtained by standard pseudopotential theory. The MH potential is sum of three distinct contributions s electron like term and attractive potential proportional to both the d-band and f-band with, and a repulsive potential arising from the shift of the centre of gravity of both the d-band and f-band. The last term are responsible for the fairly hard repulsive behaviour of  $\phi(r)$  and for the rather flat bottom in the first minimum. It has been noted that the s electron contribution affects the attractive part of the MH model effective potential most and Friedel oscillations are observed at large r region as in simple metals.

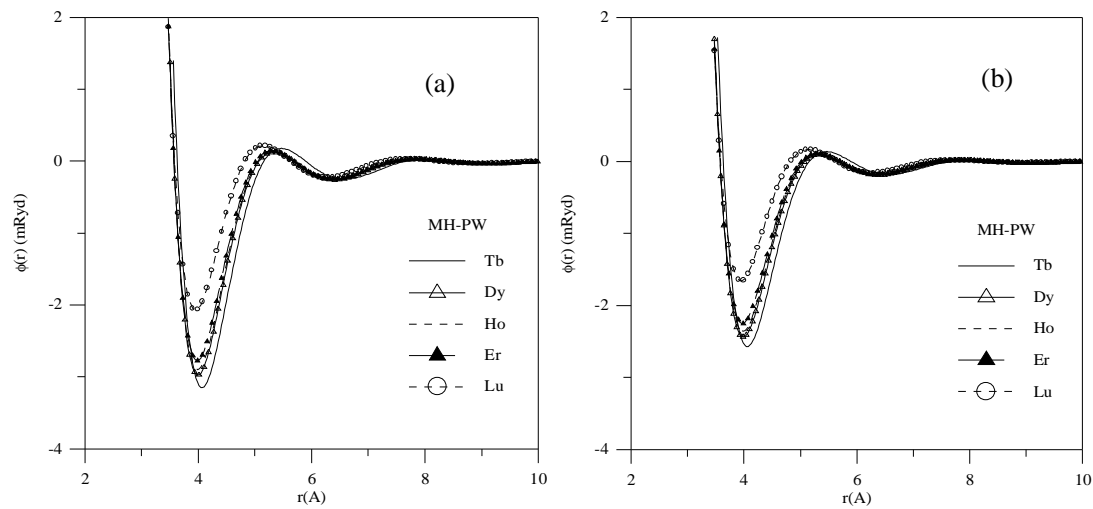


Fig. 3. MH potentials for liquid rare-earth metals using LHA pair potentials with PW screening function for s contribution. a) Karmakar-Joarder form, b) Singh form.

Also, Fig. 3 shows that the repulsive part of the potential and the position and depth of potential minimum are sensitive to variations of  $R_M$  and calculated WH potentials for Lanthanides show correct trends with periodic table. Contrary to the other liquid metals, the f- electron contribution to Lu is found repulsive because of full filled f- band of this liquid metal.

We have also compared the pair potentials of Er which have been calculated using MH pair interaction in forms of KJ and Singh with LHA pair potentials and different screening functions for s-band contribution in Fig. 4. The total MH pair interaction is considerably stronger than a typical simple-metal pair potential that means the depth of the MH potentials is larger than  $k_B T$ . However, the positions of minima of calculated pair potentials for same metals is not change because of s- electron contribution to the potential is responsible for this. The calculated MH+LHA potential with IU screening function is deeper than that of PW screening function as in simple metal calculations. Figs. 3 and 4 show that the potential which is calculated from Singh form of WH potential shallower and softer than that of KJ form because of exponential factor. There is not phase difference between WH potentials in the KJ and Singh forms.

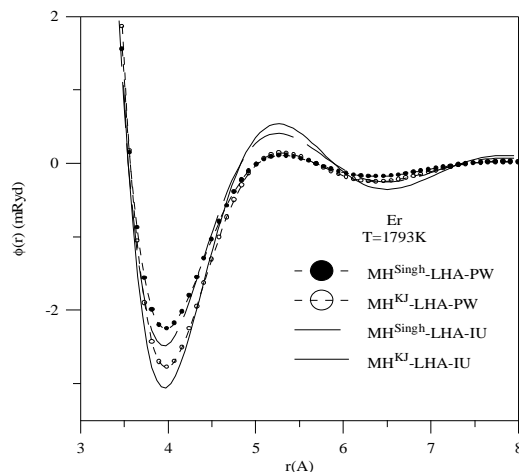


Fig. 4. The MH potentials of liquid Er for s contribution LHA potential with different screening.

### 3.2. Structure factors and pair distribution functions

The VMHNC approximation is employed to calculate the liquid state structure factors  $S(q)$  and pair distribution functions  $g(r)$ . The calculated results using pair potentials in Figs. 1 and 2 for liquids Tb, Er and Lu are shown in Figs. 5a and 5b along with experimental data of x-ray diffraction [1]. In our calculations, for the numerical solution of the Ornstein-Zernike equation [23] and the closure relation we have used Zerah's algorithm [24]; in all cases we use 2048 points with a step size  $\Delta r = 0.0523 \text{ \AA}$ .

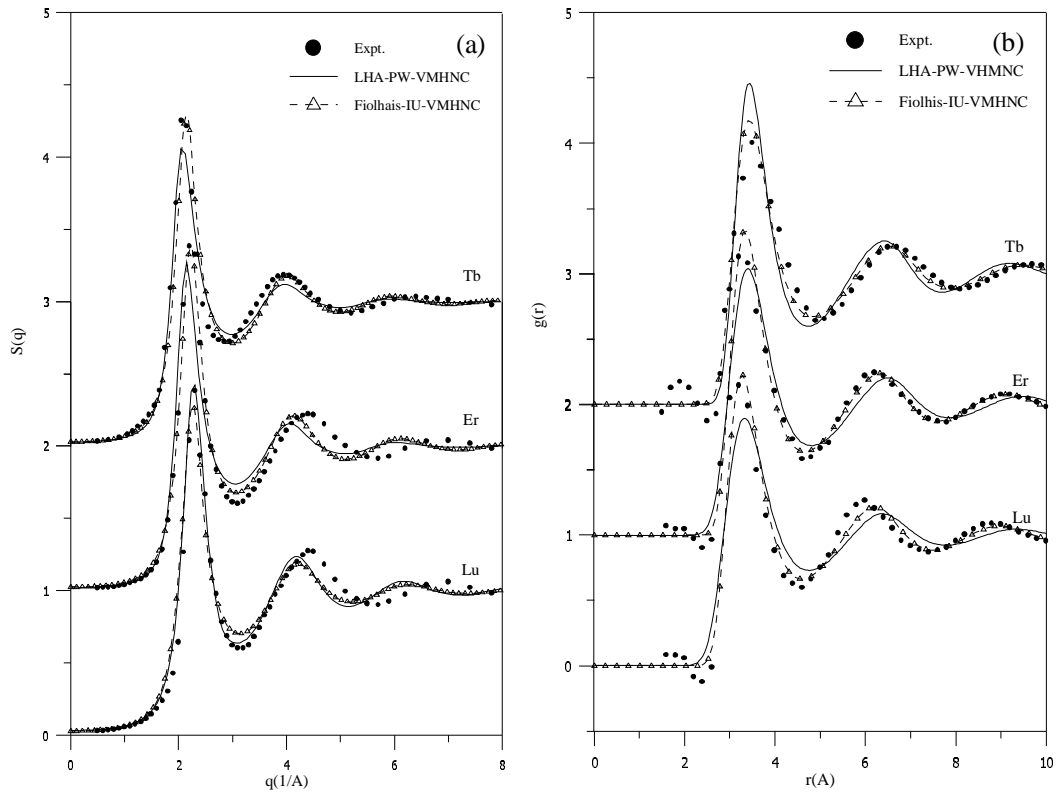


Fig. 5. Calculated a) structure factors  $S(q)$  and b) pair distribution functions  $g(r)$  with VMHNC approximation using simple metal theory.

As can be seen from these figures, both  $S(q)$  and  $g(r)$  are rather well described by these potentials, namely PW and Fiolhais' pair potentials for s-p bonded metals. There are some discrepancies in detail, such as the second peak region in  $S(q)$ , height of the first peak of  $g(r)$  and distinct Friedel oscillations in large  $q$  region are less than experimental data [1] and those obtained by others [15]. The positions of the second peak of  $S(q)$  have shifted to the right relative to those of the experimental data. The calculated values of  $S(q)$  from Fiolhais' pair potential correctly reproduce the position and height of experimental first peak for Tb and Er. We believe that  $Z_{\text{eff}}$  increases the height of the peaks of  $S(q)$  and  $g(r)$  without altering their positions. Also, there are some phase differences between  $S(q)$  that are obtained by LHA and Fiolhais' potentials and experimental results. But, these phase differences do not appear between calculated  $g(r)$  and experimental data. It is clear that calculated  $S(q)$  using LHA pseudopotential has smaller oscillations than obtained  $S(q)$  using Fiolhais' pseudopotential and experimental values.

The static structure factors  $S(q)$  and the pair distribution functions  $g(r)$  obtained by using KJ and Singh forms of WH model potential in conjunction with VMHNC approximation are shown in Figs. 6a and 6b. The same set of parameters are seen to produce reasonable structure properties.

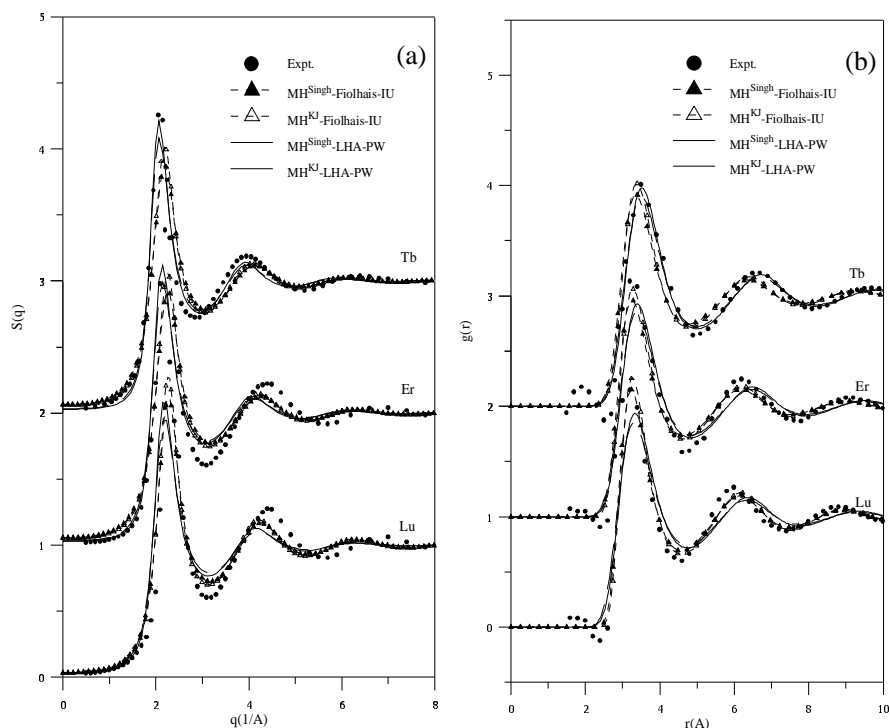


Fig. 6. Calculated a) structure factors  $S(q)$  and b) pair distribution functions  $g(r)$  with VMHNC approximation using MH model potential.

#### 4. Conclusions

In this study, we have calculated the pair potentials for some liquid rare-earth metals using the standard pseudopotential theory and MH model potential method. We have analysed the structure of some liquid rare-earths using the VMHNC liquid state theory. We have also check the validity of VMHNC in structural calculations using PW and MH potentials. A good agreement of our calculated structural properties the isothermal compressibility, static structure factor  $S(q)$  and the pair distribution function  $g(r)$  show that PW potentials using standard pseudopotential theory can be applicable for other liquid rare-earth metals namely actinides and we also consider to progress on this line in the future. On the other hand, it has been noted that regardless of the parameterization used the VMHNC theory which has previously proven to be successful for simple liquids and alkali metals, transition metals, always converges the solution. We show that the universal choice of Fiolhais' potential predicts more reasonable structural properties for liquids.

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