

NEW CRITERIA FOR THE SELECTION OF EXCHANGE AND CORRELATION FUNCTION

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A model potential is proposed to calculate phonon frequencies of fcc Ca. A unique technique is suggested to determine the parameter of the potential and a new criterion for the selection of screening function is also suggested for the first time to incorporate the effect of exchange and correlation in the pseudopotential form factor. Excellent agreement is found between theoretical phonon dispersion curves and experimental findings.

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Various theoretical studies on simple, noble and transition metals [1-5] have been made based on pseudopotential theory but relatively few attempts [6-11] have been made on alkaline earth metals. Phonon spectrum is the lattice characteristics which reflects the peculiarities of the inter atomic interaction in a crystal. Many authors tried to obtain phonon frequencies of alkaline earth metals within the framework of pseudopotential theory but limited efforts are made for the calculation of phonon dispersion of calcium [6-10]. The results obtained by Animalu [6], Taut et al [7] and Prasad [8] are found very poor with the experimental values. The result obtained by Moriarty [9] has the discrepancy of 17% with the experimental values near the zone boundary. Wang et al [10] used pseudo-ion model potential for the calculation of phonon dispersion of fcc calcium and found good agreement with the experiment results but they used two fitting parameters R_c and R_s to minimize the mean square deviation at the Brillouin zone. Singh et al [11] used the Heine-Abrenkov model potential for the calculation of phonon frequencies of fcc calcium. They considered s-d hybridization effect along with d state radius of Ca equal to Sc. They obtained the potential parameter D and r_c by matching the calculated values of phonon frequencies with experimental results of the transverse mode in [100] direction. The maximum discrepancy found in the results is 11% in T_2 [110] direction at the zone boundary. Looking to the earlier work it is felt worthwhile to study the phonon dispersion of calcium on the basis of pseudopotential theory.

In any pseudopotential formalism local and nonlocal approach have been used for the calculation of metallic properties [1,12,13]. A nonlocal pseudopotential is complicated to tackle so most of the people preferred to work on local pseudopotential. In the present note a local form of pseudopotential which retains some features of nonlocality has been proposed. In real space the potential is of the form,

$$W(r) = -\frac{2Z}{r_c^2} \left[2 - \exp\left(1 - \frac{r}{r_c}\right) \right] \cdot r \quad r < r_c \quad = -\frac{2Z}{r} \quad r \geq r_c \quad (1)$$

In the wave number space (q-space) the potential takes the form as (in Ryd.),

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$$W_B(q) = -\frac{8\pi Z}{\Omega_0 q^2} \left\{ \begin{aligned} & \frac{4(\cos qr_c - 1)}{q^2 r_c^2} + \frac{4 \sin qr_c}{qr_c} + \frac{\sin qr_c}{(1+q^2 r_c^2)^3} [5qr_c - 4q^3 r_c^3 - q^5 r_c^5] \\ & + \frac{\cos qr_c}{(1+q^2 r_c^2)^3} [11q^2 r_c^2 + 4q^4 r_c^4 + q^6 r_c^6] + \frac{2eq^2 r_c^2 (q^2 r_c^2 - 3)}{(1+q^2 r_c^2)^3} - \cos qr_c \end{aligned} \right\} \quad (2)$$

where Z is the valency, Ω_0 the volume per ion, q the wave vector, and e is the base of natural logarithm. It is evident that the potential contains only one parameter r_c and it has also the characteristics of exhibiting varying cancellation within the core. In addition the potential is continuous at $r = r_c$ and its strength goes on decreasing as $r \rightarrow 0$.

The parameter of the potential plays an important role in the calculation of metallic properties so it is necessary to determine it in a proper and logical way. In the present work we propose a novel approach for estimating the parameter r_c . This is accomplished by making parameter l , R_a and Z_A dependent in the following manner,

$$r_c = \left(\frac{l(l+1)}{Z_A} \right)^{1/2} \frac{R_a}{2} \quad (3)$$

where l , R_a and Z_A are orbital angular momentum quantum number (maximum value for the system), atomic radius and atomic number respectively. We note here that as within the core there is varying cancellation and potential is l -dependent; in this sense it may takes non-local character of the potential up to certain extent.

The form factor of pseudopotential is characterized by its q_0 value (the q_0 values are the values at which the form factor takes first zero) [14-16]. Hence by using the above value of r_c we have calculated the q_0 values for several metals. Table 1 shows the values of r_c and q_0 obtained in the present work along with other values of q_0 [1]. It is found that our q_0 values are very close to other values.

Table 1. Parameter r_c (a.u.) and wave vector q_0

Metal	r_c (a.u.)	q_0 Present Work	q_0 Other values [1]
Li	1.8812	0.92	0.67, 0.77, 1.13, 1.26
Na	2.0530	1.02	0.866, 0.89, 0.96, 0.97, 0.98, 0.99
K	2.7322	0.94	0.93, 0.94
Rb	2.7017	1.02	0.78, 0.82, 0.94, 1.0
Cs	2.9375	1.02	0.79, 1.07
Cu	1.2128	1.22	1.36, 0.62
Ag	1.3931	1.20	1.52, 0.60
Au	1.3130	1.27	1.52, 0.60
Mg	1.6694	0.84	0.75, 0.78, 0.83, 0.90
Zn	1.2962	0.94	0.78, 0.83, 0.85, 0.87, 0.95
Hg	1.4516	0.97	0.67, 0.88, 0.92, 0.93, 1.19
Al	1.4335	0.77	0.73, 0.75, 0.76
Ga	1.3875	0.84	0.876, 0.916, 0.899, 0.944
In	1.5684	0.81	0.75, 0.83, 0.88, 0.90, 0.931, 0.956
Sn	1.5708	0.75	0.77, 0.83, 0.846
Pb	1.5606	0.78	0.64, 0.84, 0.88, 0.92
Ca	2.2581	0.77	-
Sr	2.3054	0.82	-
Ba	2.4122	0.81	-

There have been number of dielectric functions [3,17-25] tried to obtain the pseudopotential screened form factor but there is no concrete way of selecting proper screening function. The choice of the screening function is the most important factor for the successful application and calculation of metallic properties. In the present study a new criterion on the selection of proper screening function is investigated. The energy-volume relation has been studied for Ca using different screening functions. Finally, the screening function, which gives lowest energy, is adopted for the further calculations. Table 2 gives the lowest energies derived from figure 1 for Ca using different screening functions. It is interesting to point out that for Ca, Taylor screening function gives lowest energy. We then used this particular combination of r_c and screening function to calculate the phonon dispersion of Ca as test case study.

Table 2. Lowest energies for Ca using different screening functions (Ryd.).

Metal	Energy (Ryd.)					
	Hartree [3]	Sham [3]	Taylor [17]	Hubbard-Sham[18]	Ichimaru-Utsumi [20]	Sarkar et al [21]
Ca	-1.607010	-1.64755	-1.64924	-1.61829	-1.62717	-1.607010

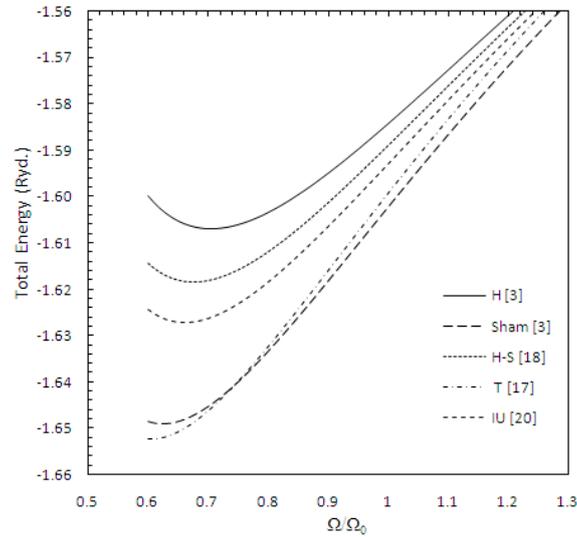


Fig. 1. Energy-Volume relation for Ca

The dynamical matrix from which phonon energies and polarization vectors are calculated may be obtained either by summing real-space force constants or by performing a sum in reciprocal space. It is known that the real space sum converges faster than the more common reciprocal space sum and is more justifiable for the calculation of thermal properties and integral properties of the electron-phonon interactions. We have used the real space sum method for calculating the phonon dispersion relation of Calcium using our model potential.

In the case of Ca, the following data have been used in atomic units,

$$\Omega_0 = 293.5, \quad a = 2.745, \quad r_c = 2.258, \quad Z = 2.0$$

Computations of the phonon frequencies along three major symmetry directions have been carried out by solving the secular determinant for 37 nearest neighbors. The calculated phonon dispersion curves in three principle symmetry directions have been drawn and compared with the

experimental results of Stassis et al [26] as in Fig. 2. Excellent agreement is found between theoretical phonon dispersion curves and experimental findings.

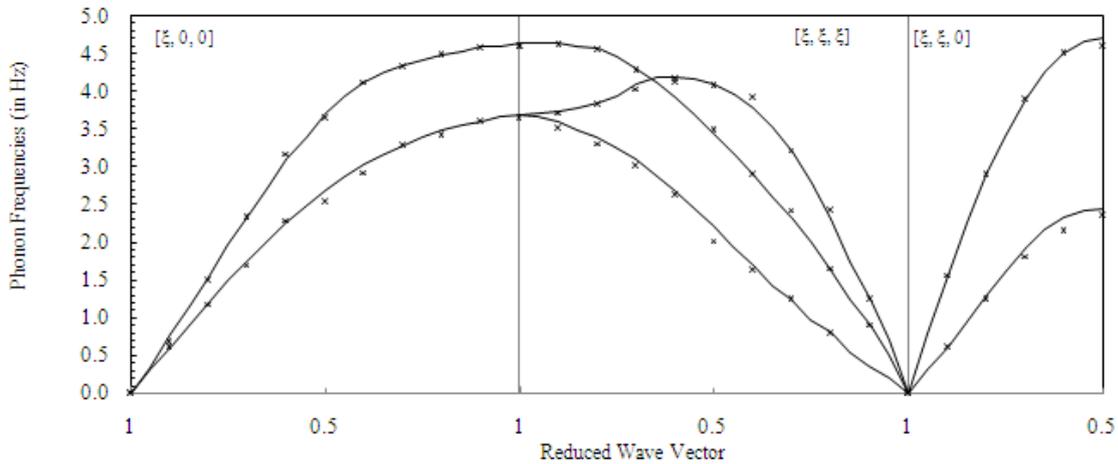


Fig. 2. Phonon dispersion curve of fcc Ca, continuous line shows present calculated values of phonon frequencies while x shows experimental values of Stassis et al [26].

To the best of our knowledge we note here that no such pseudopotential approach has been reported so far based on above criterion. The successful application of present study confirms the formalism of the pseudopotential developed in the present work. We further point out that by making potential parameter l , R_a and Z_A dependent it should be possible to pick up the trend of pseudopotential in the periodic table. This is highly desirable in any formalism of the local pseudopotential.

From the success of our results we believe that it would be interesting to analyze all the model potentials reported so far on the line of the above criterion for the selection of screening function, which may leads to the best result.

The study of other properties of metals, liquid metals and alloys by employing the potential proposed in the present work is in progress and results would be published in due course of time.

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