

Unified study of lead: Energy-dependent pseudopotential calculation

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Abstract. A Unified study of lattice-mechanical properties of lead using energy-dependent pseudopotential is carried out. Energy dependence in pseudopotential is considered through the effective mass approximation; the pseudopotential model chosen is the local Heine-Abarenkov model potential. Properties studied include cohesive energy, equilibrium lattice parameter, second-order elastic constants, pressure derivative of second-order elastic constants, equation of state (at $T = 0$ K), phonon-dispersion and effective two-body interaction. The results show fairly good agreement with experiment especially with a modified Heine-Abarenkov potential.

Keywords. Effective mass; pseudopotential; unified study; non-locality; lead.

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1. Introduction

Being one of the most complicated member of the simple metal group, lead offers a challenge in the theoretical investigation of its lattice mechanical properties. In a previous paper (Sen and Sarkar 1981, to be referred to as I henceforth), we have discussed the various difficulties and reviewed the existing literature which showed the absence of a unified study of static and dynamic properties of Pb even with a local pseudopotential. The results of the study undertaken in I shows that it is possible to carry out a unified calculation of some significance using a local Heine-Abarenkov pseudopotential. The major shortcomings of the previous study in the second order theory are (i) the difficulty in explaining both static and dynamic properties simultaneously; (ii) the underestimation of crystal energy magnitude—a feature common in most of the existing calculations (Suzuki 1971; Gupta and Tripathy 1971; Ashcroft and Langreth 1967); (iii) the inability to reproduce some peculiarities of phonon spectra.

The importance of higher order terms in electron-ion pseudopotential has been pointed out (Bertoni *et al* 1974; Schmuck and Quittner 1968; Brovman and Kagan 1974), non-locality (Hafner 1974) and the spin orbit interaction (So *et al* 1978; Animalu 1966). But the existing literature also indicates that the inclusion of higher-order terms or the spin orbit interaction are of little or no avail in generating good agreement even for lattice dynamics alone.

Bortolani and Ottaviani (1969) demonstrated that a second-order description of lattice dynamics of lead is phenomenologically valid and some isolated studies (Harrison 1965; Kachhava 1973) provide a somewhat reasonable description of the phonon dispersion of Pb. Harrison used the two-parameter modified point-ion model

for a fair analysis of lattice vibration, but the use of the Hartree dielectric function makes the results which were obtained not very reliable. Incidentally, a unified study of Pb using point-ion potential is difficult for the hypersensitiveness of its parameters (I). The unified study attempted at by Kachhava with Ashcroft pseudopotential using effective mass correction gave a good description of the phonon spectra of Pb, but the calculated static properties were in good agreement with experiment. Moreover, the effective mass correction was not properly used in the theoretical formulation. However, this work inspired the present investigation of the importance of energy dependence of pseudopotential via the effective mass and orthogonality hole correction in the unified study of Pb.

Non-locality and energy dependence are general features of any pseudopotential approach. But relatively little is known about how important they are in a specific case. In semi-empirical studies non-locality can generally be ignored (Cohen and Heine 1970) while in theoretical analysis one can define a good local approximation by the choice of appropriate matrix elements. The non-locality of diagonal matrix elements is not covered by this argument, but may be absorbed into an effective mass (m_K) correction factor which usually differs only slightly from unity (Cohen and Heine 1970; Shaw and Pynn 1969; Weaire 1967).

Some of the model pseudopotential calculations (Animalu and Heine 1965; Weaire 1967) retains the energy dependence explicitly, while some of the effects may be simulated by an effective mass (m_E) correction (Cohen and Heine 1970). The orthogonality hole is also a general feature of any pseudopotential approach and it seems always to be connected with energy dependence (Shaw and Harrison 1967). However, when energy dependence is neglected altogether, orthogonality hole arises differently (Pick and Sarma 1964; Pendry 1968). How these factors affect expressions for the total cohesive energy and phonon spectra will be specified in § 2.

The present study shows how a vastly improved unified description of lattice mechanics of Pb may be obtained through the effective mass and orthogonality hole corrections, especially with a modified Heine-Abarenkov potential.

In § 2, we briefly discuss the modifications in the framework of second order theory with an energy-dependent pseudopotential. The calculational procedure of various metallic properties was described earlier (Sarkar and Sen, 1981; Sen *et al* 1981; Sarkar *et al* 1983). The results obtained are discussed in § 3.

2. Theory

A possible refinement of the theory regarding the non-locality and the energy dependence of pseudopotential is the use of effective mass corrections (Shaw and Pynn 1969; Cohen and Heine 1970). Let us define

$$m_K = 1 + K^{-1} [\partial / \partial K (\langle \hat{K} | W | \hat{K} \rangle)]^{-1}, \quad (1)$$

and

$$m_E = 1 - \partial / \partial E (\langle \hat{K} | W | \hat{K} \rangle), \quad (2)$$

where W is the non-local part of the total pseudopotential, apart from local terms which are independent of K and E . Then m_K and m_E may be taken as the component of the total effective mass defined by

$$m^* = m_E m_K. \quad (3)$$

If m_κ and m_E are treated as constants (evaluated say at the Fermi level) the effective mass factor appear in the band structure energy through the energy denominator. Consequently the energy-wave number characteristics (EWNC) function of the second order pseudopotential theory should be amended (Shaw 1969; Weaire 1968) to read

$$F_q = (m_\kappa/m_E) [w_q^{\text{ion}}]^2 \chi_q/\epsilon_q \quad (4)$$

where w_q^{ion} is the local ionic pseudopotential χ_q is the linear density response function (Hartree) and ϵ_q is the electronic dielectric function.

Connected with this effective mass correction is the correction due to orthogonality hole. Because of the orthogonality of this valence electron wave function with the core states, the net electronic density in the core region will be zero. The electronic charge depleted from the region will effectively augment the charge density in other region to a value which we write as $(1 + \alpha) Ze/\Omega$, where α is treated as a constant. Since the orthogonality hole moves around with the ion, it is convenient to treat the total charge density as a uniform negative background of $(1 + \alpha) Ze/\Omega$ into which are planted ions carrying a positive charge of Z^*e , where $Z^* = (1 + \alpha)Z$ is the effective valence to be used in all the first and higher order energy terms. The charge Z^* must be used in the Ewald term and the electrostatic field due to the orthogonality hole is, of course, felt by electrons and therefore, enters in w_q^{ion} as an extra charge spread over the core so that

$$w_q^{\text{ion}} \rightarrow 4\pi Z(1 + \alpha)e^2/\Omega q^2 \quad \text{as } q \rightarrow 0. \quad (5)$$

The electron gas between the ions also has a correspondingly enhanced density and its screening behaviour is complicated (Shaw 1969). We may approximate it by writing

$$\epsilon_q = 1 - (8\pi e^2/\Omega q^2) (1 - f_q) \chi_q (1 + \alpha) m_\kappa \quad (6)$$

where f_q describes the correction due to exchange and correlation.

The cancellation between the band structure and the Ewald terms in the limit $q \rightarrow 0$ demands the relation

$$(1 + \alpha)^{-1} = m_E, \quad (7)$$

which is the same as obtained by Shaw and Harrison (1967) to the lowest order in α . The values of m_κ and m_E are given in a table by Cohen and Heine (1970) but the values are not very reliable since the screening in the model potential used is not wholly consistent with recent theories.

Following the suggestion of Cohen and Heine (1970) we put $m_\kappa = 1$ and define α from (7) using m_E as a free parameter but so adjusted as to give a reasonable value for α .

Finally we modify the local Heine-Abarenkov potential

$$w_q^{\text{ion}} = (4\pi Z^*e^2/\Omega q^2) [(1 + U) \cos qr_c - U \sin qr_c/qr_c] \quad (8)$$

by introducing a q -dependence in the potential depth parameter U in the form

$$U_q = U_1 + (U_2 - U_1) [1 - \exp(-q^2/q_0^2)], \quad (9)$$

where U_1 and U_2 are the two parameters of modified potential and q_0 is a fixed arbitrary small parameter, the value for which in the present calculation is chosen to be $10^{-2}\pi/a$, $2a$ being the lattice constant. It may be pointed out that the calculated properties are insensitive to the chosen values of q_0 .

This modification is made in the light of the observation that agreement with the experimental values for both static and dynamic properties of Pb demands two different values of the same parameter. Following a similar observation Das *et al* (1981) modified the Ashcroft potential through a similar q -dependence in the lone model parameter r_c . But here we introduce the wave-vector dependence in the potential depth which seems to be more physical and it appears that this modification in a way simulates some features of the general Heine-Abarenkov potential. In our study we have used Taylor's (1978) exchange and correlation correction factor f_q in the screening function.

3. Results and discussion

The properties investigated include cohesive energy, equilibrium lattice parameter, second order elastic constants, equation of state (at $T = 0$ K) effective ion-ion interaction and phonon dispersion. All calculations are performed by considering terms upto the second-order in the electron-ion pseudopotential using a modified Heine-Abarenkov model potential coupled with Taylor's dielectric function in effective-mass formalism. An exponential cut-off in the form $\exp(-\eta/2 (q/2k_f)^2)$ is used to suppress tail-end oscillation of the pseudopotential form factor. The results are independent of the choice of the arbitrary parameter η .

In table 1 the calculated static properties are compared with experimental values.

The calculated crystal energy is in very good agreement with the experimental value. This is important because most of the existing calculations (Suzuki 1971; Gupta and Tripathy 1971; Ashcroft and Langreth 1967) underestimate the crystal energy. In the case of elastic constants the discrepancy is maximum (21 %) for C_{44} , 6.3 % for C_{11} and 12 % for C_{12} . However, the pressure derivatives of elastic constants namely dC_{11}/dp and dC_{44}/dp have discrepancies of only 3 % and 1 % respectively, but at dC_{12}/dp the error is large and equal to 35 %. Figure 2 shows that the calculated equation of state (at $T = 0$ K) compares well with extrapolated experimental results. The calculation of elastic constants and equation of state may, however, be regarded as satisfactory compared to the existing theoretical results and more so considering the fact that we are trying to make a unified study of both static and dynamic properties using the same set of parameters.

Table 1. Calculated static properties.

Crystal Energy (Ryd/atom)	Equilibrium lattice constant	Second order elastic constants (10^{12} dyne/cm ²)						
		C_{11}	C_{44}	C_{44}	dC_{11}/dp	dC_{12}/dp	dC_{44}/dp	
Theor	-7.45	9.2783	0.525	0.400	0.155	6.28	2.76	2.94
Expt.	-7.58 [†]	9.2783 ^{††}	0.560 ^{††}	0.457 ^{††}	0.169 ^{††}	6.82*	4.26*	2.97*

Model parameters $r_c = 2.00$; $U_1 = -0.808$; $U_2 = -0.870$; $\eta = 0.1$; $m_E = 0.910$

[†]Weast (1975); ^{††}Waldrof and Alers (1962); *Miller and Schuele (1969)

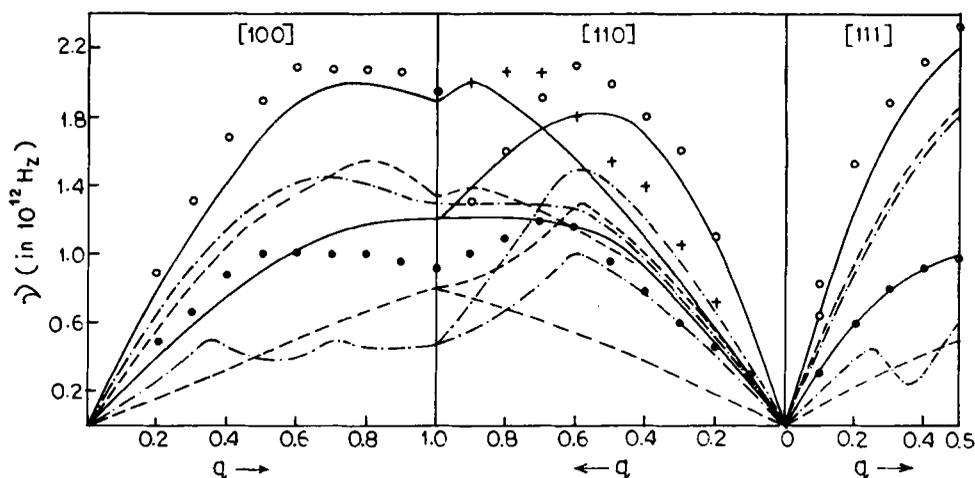


Figure 1. Phonon dispersion curves for Pb. at 100 K. — corresponds to present study, - - - phonon curves calculated by Kachhava (1973); - · - · corresponds calculated curve by Hafner (1974). Experimental points are taken from Brockhouse *et al* (1962) and are indicated by ○, ● and + for the longitudinal and two transverse branches respectively.

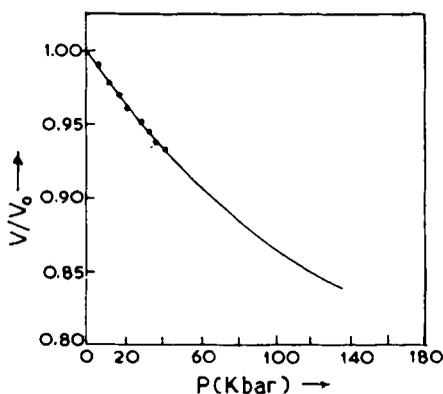


Figure 2. Equation of states for Pb, full curve corresponds to the present calculation Open dots are the experimental points taken from Vaidya and Kennedy (1970).

Besides the very pronounced Kohn anomalies the phonon dispersion curves of Pb shows many peculiarities which have been discussed in detail in paper 1. The dispersion values obtained in the present calculation are better than those obtained by Harrison's point ion model (paper 1) where parameters are only fitted to the dispersion curve. The calculated phonon spectrum (figure 1) is quite satisfactory and reproduces the softening of the (100) longitudinal branch before reaching the zone boundary. In figure 1 the calculated dispersion curves are compared with experimental results as also with the calculation of Kachhava (1973) and Hafner (1974). The improvement in the results of the present study is amply clear. Figure 3 shows the effective interaction of lead and it is

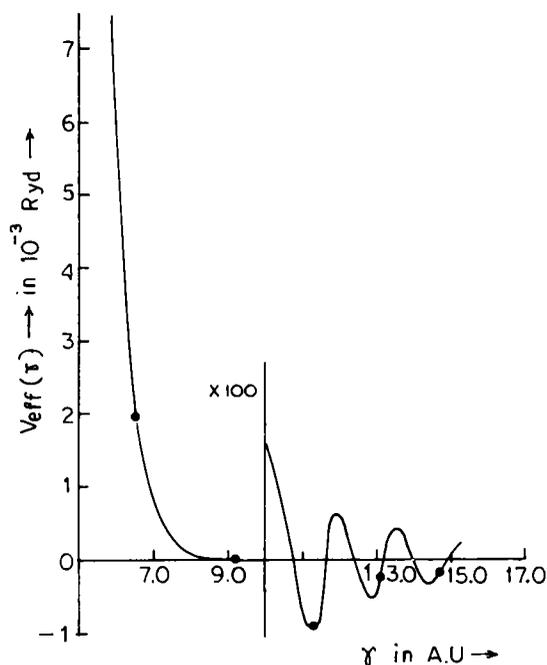


Figure 3. The effective ion-ion potential $V_{\text{eff}}(r)$ for Pb. The neighbour positions are shown in figure by solid circles.

seen that the interaction between the nearest neighbours is strongly repulsive. The results show that the present model works fairly well and the effective mass correction is quite important in lead, particularly in producing the aforesaid “softening” which is in accordance with the observation of Animalu (1973) regarding the energy dependence of pseudopotential.

The remaining discrepancies in the elastic constants and other properties perhaps indicate that other effects have also to be included for further improvement in specific problems. Despite the fact that the role of dielectric function in the case of a polyvalent metal is very crucial, our previous work (paper 1) showed more or less similar results for both Taylor (1978) and Vashishta-Singwi (1972) screening functions. Also, the effect of polarizability due to a possible polarizable quasicore of tetravalent simple metal like Pb was emphasized in the previous paper. However, preliminary calculation carried by us subsequently, shows that with a reasonable value of core polarizability, the effect on phonon frequencies is negligibly small.

The present literature does not provide a clear understanding of the importance of higher order perturbation terms or the non-local effect etc in the study of lead. Bertoni *et al* (1974) emphasized the importance of the third-order perturbation term in lead—a conclusion based on a study of a single property only and as such is liable to uncertainties. Brovman and Kagan (1974) also discussed the significant role of non-pairwise forces specially in the dynamics of polyvalent metals which lead to the appearance of forces of covalent type. This aspect of the problem demands the inclusion of higher order terms. But Cohen *et al* (1982) argued that in lead the effective

overall scattering strength is too weak to produce covalent bond and is truly metallic. Nevertheless, William and Appapillai (1973) questioned the validity of linear screening inherent in the usual pseudopotential theory in the case of polyvalent metals.

The importance of non-locality of the pseudopotential in the case of lead is also not clearly assessed. To what extent the remaining discrepancies of the present study can be removed by including these effects requires a detailed study.

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