Ab initio calculation of the phonon dispersion curve for lithium

G.J. Vázquez, L.F. Magaña

Classification
Physics Abstracts
63.20

Ab initio calculation of the phonon dispersion curve for lithium

G. J. Vázquez (*) and L. F. Magaña

Instituto de Física, Universidad Nacional Autónoma de México,
Apartado Postal 20-364, C.P. 01000, México, D. F. México

Résumé. — Nous avons réalisé un calcul *ab initio* pour le potentiel interionique du Li. A partir du potentiel calculé nous avons obtenu la courbe de dispersion des phonons en utilisant l'approximation harmonique self-consistante, et nous comparons les résultats avec l'expérience. Pour obtenir le potentiel interionique nous avons suivi une méthode basée sur le formalisme de la fonctionnelle de densité, qui est une extension de l'approche perturbative usuelle. Cette méthode a été appliquée auparavant seulement à l'hydrogène métallique. Les seuls paramètres nécessaires pour le calcul sont la charge du noyau et la densité électronique moyenne.

Abstract. — We have performed an *ab initio* calculation of the interionic potential of Li. From the calculated potential we have obtained the phonon dispersion curve using the self-consistent harmonic approximation and compared results with experiment. To obtain the interionic potential we have followed a method which is based on the density functional formalism and is an extension of the usual perturbative approach. This method had been applied previously only to metallic hydrogen. The only input parameters required to calculate the interionic potentials are the charge of the nucleus in the metal and the average electron density.

1. Introduction.

The knowledge of the interionic potential for solids is a very important ingredient for the investigation of their properties. Several methods have been used to find the interionic potential of metals [1-10]. Some of them are based on the use of empirical Morse or Lennard-Jones potentials. These potentials show no Friedel oscillations at all and decay very rapidly. Another often used approach for finding the interionic potential is by pseudopotentials. For this case the parameters used to define the pseudopotential are usually determined by fitting some electronic properties, predicted with the pseudopotential, to experimental information such as electrical resistivity of the liquid metal, the shape of the Fermi surface or spectroscopic data. The pseudopotentials may also be found from first principles. They show the presence of Friedel oscillations and may be local, non-local or energy dependent.

It is clear at present that a pseudopotential determined in an empirical way cannot always be regarded as weak [11], so that its use in getting the interionic potential is not justified.

On the other hand, the interionic potential can be constructed from first principles using the pseudopotential theory [7, 8, 9] for simple metals. This has been done using a non-linear response calculation of the induced charge density around an ion in an electron gas. A pseudopotential is chosen to reproduce the induced charge density in linear response, except in a region close to the ion. In this region a modelling of the induced charge density has to be done. This modelling is not unique. The non-linear effects are partly included in the pseudopotential in this way.

In this work we have followed the method which Magaña *et al.* applied to metallic hydrogen [1] to obtain the interionic potential.

This method is based on the Density Functional Formalism [13, 14] for calculating the density around an ion in an electron gas. The interionic potential is given in terms of the density and the direct interaction between two ions. There are no adjustable parameters, and no modelling of the density in the region close to the ion is needed.

From the resulting potential the phonons are obtained using the Self-Consistent Harmonic Approximation [15].

In section 2 we describe briefly the method for constructing the pair potential from the induced charge

---

(*) UNAM-PSPA Scholarship holder.

density around an ion in an electron gas. In section 3 we present the main results of the Hohenberg, Kohn and Sham Formalism or Density Functional Formalism for obtaining the induced charge densities. Section 4 is used to present the set of equations to be solved to obtain the phonon dispersion curve by the Self-Consistent Harmonic Approximation. Results and discussion are given in section 5.

2. The interatomic potential.

We have followed the method of Magaña et al. which is an extension of the usual perturbative approach for calculating interatomic potentials in simple metals and is based on the Density Functional Formalism and which we explain briefly. For more details the reader may see references [1, 12].

We start with an interacting and electrically neutral electron gas, represented by a Hamiltonian H and an average electronic density n_0. Two static charges of magnitude Z are added to this system and to preserve charge neutrality, $2 Z$ electrons are also added. One of the static charges is located at the origin and the other at $\mathbf{R}$. The average electron density is practically unchanged by the inclusion of the $2 Z$ electrons. The new total Hamiltonian for the electron gas H_T, is the sum $H + H'$, where

$$H^1 = - \int d^3r \, \psi^+(r) \left[\frac{Z}{|\mathbf{r}|} + \frac{Z}{|\mathbf{r} - \mathbf{R}|} \right] \psi(r) \quad (1)$$

and a sum over electron spin is implied and $\psi(\mathbf{r})$ and $\psi^+(\mathbf{r})$ are field operators.

We are using atomic units, $e = \hbar = m = 1$, where e and m are the electron charge and mass, $\hbar$ is Planck's constant divided by 2π.

The total energy change including the direct interaction Z^2/R between the external static charges and the differences between the ground state energies of the electrons described by H_T and H respectively can be written as

$$\Delta E_T = \frac{Z^2}{R} - Z \int_0^1 d\lambda \int d^3r \, \rho_\lambda(\mathbf{r}) \left[\frac{1}{|\mathbf{r}|} + \frac{Z}{|\mathbf{r} - \mathbf{R}|} \right] \quad (2)$$

where

$$\rho_\lambda(\mathbf{r}) = \langle \, \Psi(\lambda) \, | \, \psi^+(\mathbf{r}) \, \psi(\mathbf{r}) \, | \, \Psi(\lambda) \, \rangle \quad (3)$$

and $| \, \psi(\lambda) \, \rangle$ is the state vector for the ground state of the Hamiltonian $H(\lambda) = H + \lambda H'$, i.e.

$$H(\lambda) \, | \, \Psi(\lambda) \, \rangle = E_{el}(\lambda) \, | \, \Psi(\lambda) \, \rangle \quad (4)$$

and λ is such that $0 \leqslant \lambda \leqslant 1$.

The pair potential, $V(\mathbf{R})$, is given by the structure dependent part of ΔE_T.

We need to calculate the electron density, $\rho_\lambda(\mathbf{r})$, for each value of λ between zero and one.

Because of the numerical difficulty of performing the two centres calculation for each $\mathbf{R}$ and guided by the usual method, it is assumed that $\rho_\lambda(\mathbf{r})$ can be reasonably approximated by

$$\rho_\lambda(\mathbf{r}) \cong \Delta n_\lambda(\mathbf{r}) + \Delta n_\lambda(\mathbf{r} - \mathbf{R}) + n_0 \quad (5)$$

where $\Delta n_\lambda(\mathbf{r})$ is the displaced electron density around the charge at the origin and $\Delta n_\lambda(\mathbf{r} - \mathbf{R})$ is the displaced electron density around the charge at $\mathbf{R}$, n_0 is the unperturbed electron density.

Using equation (5) in equation (2), neglecting additive constants and terms which are $\mathbf{R}$ independent and using spherical symmetry, we get for the pair potential

$$V(\mathbf{R}) = \frac{Z^2}{R} - 2 Z \int_0^1 d\lambda [F_1(\lambda, R) + F_2(\lambda, R)] \quad (6)$$

where

$$F_1(\lambda, R) \equiv \int_0^R \frac{4 \pi r^2 \, \Delta n_\lambda(\mathbf{r})}{R} \, dr \quad (7)$$

and

$$F_2(\lambda, R) \equiv \int_R^\infty 4 \pi r \, \Delta n_\lambda(\mathbf{r}) \, dr . \quad (8)$$

Equation (6) is the form for the pair potential we use. We have to calculate $\Delta n_\lambda(\mathbf{r})$ in order to get $F_1(\lambda, R)$ and $F_2(\lambda, R)$. For this we use the Density Functional Formalism of Hohenberg, Kohn and Sham [13, 14].

This formalism considers the problem of obtaining, for the ground state, the density and the energy of an electron gas under the influence of an external static potential.

3. Electronic densities from non-linear screening.

The central result of the Hohenberg-Kohn-Sham formalism [13, 14] states that there exists a one-body local potential $V_{eff}(\mathbf{r})$ which, through the one-body Schrödinger equation given by

$$\left[-\frac{1}{2} \nabla^2 + V_{eff}(\mathbf{r}) \right] \psi_i(\mathbf{r}) = \varepsilon_i \, \psi_i(\mathbf{r}) , \quad (9)$$

generates the set of wave functions $\psi_i(\mathbf{r})$ and the exact ground state density of the system through the independent particle density expression :

$$n(\mathbf{r}) = \sum_{\varepsilon_i < \varepsilon_f} | \, \psi_i(\mathbf{r}) \, |^2 \quad (10)$$

where the sum extends up to the Fermi energy.

The effective potential is given by

$$V_{eff}(\mathbf{r}) = - \Phi(\mathbf{r}) + \frac{\delta E_{xc}[n(\mathbf{r})]}{\delta n(\mathbf{r})} \quad (11)$$

where $\Phi(\mathbf{r})$ is the total electrostatic potential of the

system, and $E_{xc}[n(\mathbf{r})]$ is the exchange-correlation energy of the system.

When we omit gradient corrections, we can write

$$\frac{\delta E_{xc}[n(\mathbf{r})]}{\delta n(\mathbf{r})} = \frac{d}{dn}\left[n(\mathbf{r})\,\varepsilon_{xc}(n(\mathbf{r}))\right] \tag{12}$$

where $\varepsilon_{xc}(n(\mathbf{r}))$ is the exchange-correlation energy per particle in a homogeneous electron gas of density n.

Using spherical symmetry, we write the equations to be solved for our case

$$\left(-\frac{1}{2}\frac{d^2}{dr^2} + V_{eff}(r) + \frac{l(l+1)}{r^2} - \varepsilon_k\right) r R_{lk}(r) = 0, \tag{13}$$

where $R_{lk}(r)$ is a solution to the radial Schrödinger equation of energy $\varepsilon_k = \frac{1}{2}k^2$.

Notice that the potential of the impurity in the electron gas is contained in $\Phi(\mathbf{r})$ and that, in the absence of the impurity, $R_{lk}(r)$ is proportional to the spherical Bessel function of the first kind, $J_l(kr)$.

From equation (10) we can obtain the electron displaced density around an ion in the electron gas :

$$\Delta n(\mathbf{r}) = \sum_{\varepsilon i < \varepsilon f} |\psi_i(\mathbf{r})|^2 - n_0 \tag{14}$$

or

$$\Delta n(\mathbf{r}) = \frac{1}{\pi^2}\sum_{l=0}^{\infty}(2l+1)\int_0^{k_F}dk\,k^2 \times$$

$$\times \left[|R_{lk}(r)|^2 - |J_l(kr)|^2\right] + 2\sum_b |\psi_b(r)|^2 \tag{15}$$

where $\psi_b(r)$ refers to the bound state wave functions.

For the exchange-correlation contribution to the effective potential, equation (12), we use the expression given by Hedin and Lundqvist [16], in atomic units :

$$V_{xc}(\mathbf{r}) \equiv \frac{\delta E_{xc}[n(r)]}{\delta n(r)} - 0.02909 \times$$

$$\times \left[\frac{21}{r_s} + 0.02734 \ln\left(1 + \frac{21}{r_s}\right)\right] \tag{16}$$

where $\frac{4}{3}\pi r_s^3 = \frac{1}{n_0}$.

The electrostatic potential obeys Poisson's equation

$$\nabla^2\Phi = -4\pi D(r) \tag{17}$$

where

$$D(\mathbf{r}) = Z\delta(\mathbf{r}) + n_0 - n(\mathbf{r}) \tag{18}$$

or

$$D(\mathbf{r}) = Z\delta(\mathbf{r}) - \Delta n(\mathbf{r}). \tag{19}$$

In order to have $V_{eff}(\mathbf{r})$ vanishing at large $\mathbf{r}$, the

exchange-correlation part is rescaled to :

$$V_{xc}(\mathbf{r}) \rightarrow V_{xc}[n(\mathbf{r})] - V_{xc}[n_0]. \tag{20}$$

We solved equations (13), (15), (16), (19) and (20) self-consistently. We carried out the calculation of the density following the method of Manninen et al. [17] to achieve automatic self-consistency. Notice that the calculation has to be done for each value of λ, using $Z = \lambda Z_0$, where Z_0 is the charge of the nucleus of the ion in the metal.

Once we had obtained the densities for the set of values of λ for the metal we used equations (6) to obtain the interionic potential. From this potential we obtained the phonon dispersion curve using the Self-Consistent Harmonic Approximation.

4. The phonons.

We followed the work of Boccara and Sarma [18] with the extensions given by Gillis et al. [19] and Cowley and Shukla [20].

This scheme contrasts with that of Born and Von Karman [21, 22] by making no initial hypothesis of smallness for the amplitude of atomic vibrations and hence no truncated Taylor series expansion of the interatomic potential energy.

A trial Harmonic Hamiltonian of the form

$$H_h = \sum_i\left(-\frac{1}{2M}\nabla_i^2\right) + \frac{1}{2}\sum_{ij}(\mathbf{u}_i - \mathbf{u}_j)\cdot\Phi_{ij}\cdot(\mathbf{u}_i - \mathbf{u}_j)$$

is adopted, where $\mathbf{u}_i$ are the dynamical displacement variables and the Φ_{ij} are determined by minimizing the free energy of the crystal and result given as a thermal average of the second derivatives of the ion pair potential.

The resulting set of self-consistent equations to solve in order to obtain the phonon dispersion curve is

$$\omega_\lambda^2(\mathbf{k})\,\varepsilon_\lambda^\alpha(\mathbf{k}) = \sum_\beta D_{\alpha\beta}(\mathbf{k})\,\varepsilon_\lambda^\beta(\mathbf{k}) \tag{21}$$

where $\varepsilon_\lambda^\alpha(\mathbf{k})$ is the component of the polarization vector $\varepsilon_\lambda(\mathbf{k})$ and the dynamical matrix is :

$$D_{\alpha\beta}(\mathbf{k}) = \frac{1}{M}\sum_l(1 - \cos(\mathbf{k}\cdot\mathbf{R}_l))\langle\Phi_{\alpha\beta}(\mathbf{R}_l)\rangle \tag{22}$$

with

$$\langle\Phi_{\alpha\beta}(\mathbf{R}_l)\rangle = \frac{1}{(8\pi^3\det\lambda l)^{1/2}} \times$$

$$\times \int d^3u\,\exp\left(-\frac{1}{2}\sum_{\gamma\delta}u_\gamma(\lambda_l^{-1})_{\gamma\delta}u_\delta\right)\Phi_{\alpha\beta}(\mathbf{R}_l + \mathbf{u}_l) \tag{23}$$

where M is the ion mass, $\mathbf{u}_l$ is the vector describing the displacement of atom l from its equilibrium position

$\mathbf{R}_l$ and $\Phi_{\alpha\beta}(\mathbf{R}_l + \mathbf{u}_l)$ is the tensor derivative of the interatomic potential evaluated at $\mathbf{R}_l + \mathbf{u}_l$.

Finally

$$(\lambda_l)_{\alpha\beta} = \frac{1}{MN} \sum_{\mathbf{k}\lambda} (1 - \cos(\mathbf{k} \cdot \mathbf{R}_1)) \, \varepsilon_\lambda^{*\alpha}(\mathbf{k}) \, \varepsilon_\lambda^\beta(\mathbf{k}) \times$$

$$\times \coth\left(\frac{1}{2} \beta\hbar\omega_\lambda(\mathbf{k})/\omega_\lambda(\mathbf{k})\right) \quad (24)$$

where N is the number of ions. The sum is over the first Brillouin zone, β is $1/k_B \, T$, k_B being the Boltzmann constant.

Notice that $\langle \Phi_{\alpha\beta}(\mathbf{R}_l + \mathbf{u}_l) \rangle$ which plays the same role as the $\Phi_{\alpha\beta}$ in the Harmonic Approximation is the tensor derivative of the potential averaged over the phonon states generated by the potential.

To solve the set of self-consistent equations (21), (22), (23) and (24) and get the phonon dispersion curve we start with the frequencies generated by the Harmonic Approximation as the first trial. Then the convergence procedure is followed.

5. Results and discussion.

We have applied the method to lithium.

First, we obtained the densities fully self-consistently. The calculation of the densities were performed solving the Schrödinger equation in steps of 0.01 a_0, where a_0 is the Bohr radius up to $R = 0.5 \, a_0$. For $0.5 \, a_0 \leqslant R \leqslant 2.5 \, a_0$, it was solved in steps of 0.02 a_0 and in steps of 0.04 a_0 up to 22.5 a_0, where the phase shifts were evaluated.

The sums over l in equation (15) were terminated at $l_{max} = 4$. The values of the phase shifts for $\lambda = 1$ are given in table I. The density is shown in figure 1 for $\lambda = 1$ too.

The step size in λ for performing the integral of equation (6) was 0.25/3.

Once we obtain the densities for the set of values of λ, we calculate the interionic potential using equation (6).

The interionic potential is shown in figure 2. After getting the potential we find the first and second derivatives as functions of R and use these derivatives to start the self-consistent calculation of the phonons.

The phonon dispersion curve is shown in figure 3, where comparison with experimental results [30] is made. It is possible to see that predicted phonons have
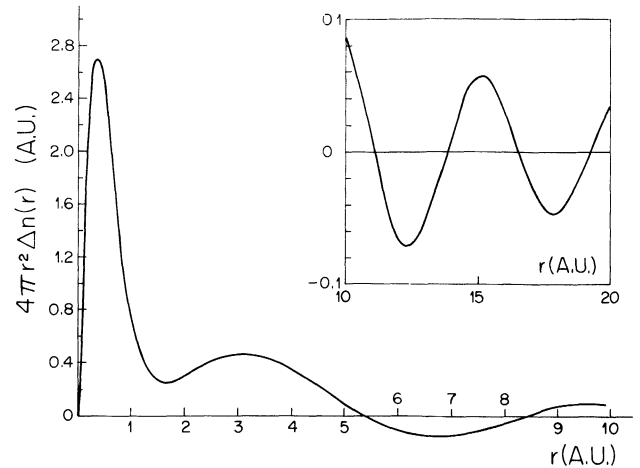

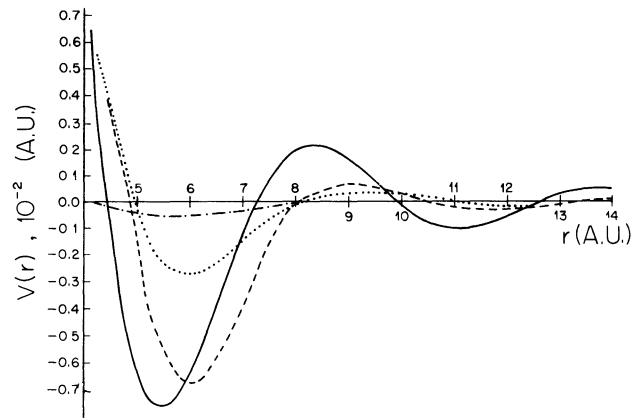Fig. 1. — Displaced electron density around a lithium ion.

Fig. 2. — Calculated interionic potential for lithium in this work : ——— ; From reference [23] : – – ; From reference [24] : –·– ; From reference [8] : . . . . .

the same overall shape as experimental results. The maximum frequency predicted is about 40 % bigger than the experimental one. The maximum frequency obtained with Harmonic Approximation was about 55 % that the corresponding experimental value.

The calculation of the phonons included 17 neighbouring shells. The frequencies were converged with respect to the number of shells to within one percent except for the Kohn anomalies. The temperature was taken with three different values : 0 K, 10 K and 300 K without any significant differences in the phonon dispersion curve.

Because of the nature of integration of equation (6) it is clear that the method is most easily applied to nuclei of small charges. We had to obtain the density numerically eleven times according of the step size in λ. But in this method we do not have any adjustable parameter for the interionic potential so that it is a very pure *ab initio* calculation. There is no ambiguity in the procedure for obtaining the potential. This is

Table I. — *Values of the phase shifts, n_l, for the metal we studied. The Friedel Sum Rule, FSR, resulting from the calculation and the value of r_s are also given.*

$r_s = 3.236 \, a_0$; $a_0 = 0.529$ Å
FSR = 2.9962
$n_0 = 3.2161$
$n_1 = 0.4867$
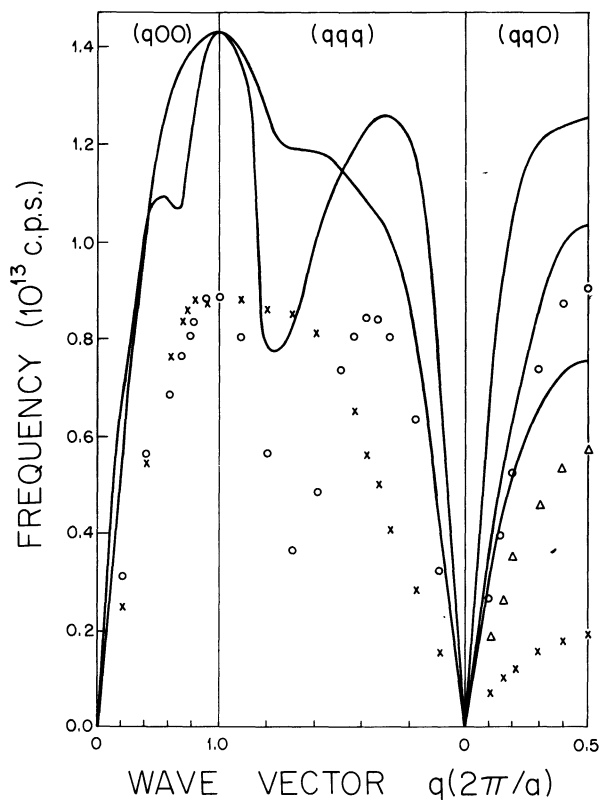$n_2 = 0.0102$
$n_3 = 0.0026$
$n_4 = 0.0003$

Fig. 3. — Calculated phonon dispersion curve for lithium :
——; Experimental phonon dispersion curve for lithium :
×, △, ○.

why we think the resulting potential should be close to the real one. The only input parameters we need to perform the calculation of the interionic potential are the nuclear charge and the average electronic density. To get the phonons we need the type of structure of the metal.

On the other hand, superposing the two displaced charge densities, at the origin and at **R** (Eq. (5)), is a major approximation but is common to the usual perturbation theory approach. It is clear that there was no guarantee that the method could work for metals with ions heavier than hydrogen ion, but it works reasonably well even with the assumption of

locality, and lithium is a material that presents the problem of being extremely non-local [8].

There have been other calculations of phonons for lithium (see, for example, Refs. [8] and [25]). They have been performed within the pseudopotential approach which has been discussed in the first part of this work. The calculations of phonons for lithium in references [8] and [25] were made using the Harmonic Approximation and show a difference of about 10 % with respect to the experimental results. In these references the pseudopotentials were chosen in order to fit a previously calculated non-linear response electron density around an ion embedded in an electron gas, except for a region close to the ion.

In figure 2 we show the interionic potential for lithium from reference [8] and from other calculations including ours. The authors of reference [25] did not give the interionic potential for lithium.

All the interionic potentials shown in figure 2, except ours, were obtained using pseudopotential theory. The authors of reference [23] reported force constants which are 2 or 3 times larger than experimental ones. They did not report phonon dispersion curves and they made the calculation using an empirical pseudopotential proposed by Heine-Abarenkov-Animalu [26, 27], which had been evaluated by Animalu [27] by fitting the shape of the Fermi surface. The same authors calculated again the force constants for lithium [28] using an Ashcroft pseudopotential [29] and this time they obtained a good agreement with the experimental results but they did not report phonons for lithium. The calculation in reference [24] was performed in an attempt by Torrens and Gerl to reproduce the interionic potential for lithium reported in reference [23] by taking the Fourier transform of screened Heine-Abarenkov-Animalu ion form factors. No force constants nor phonons were reported.

Finally we strongly feel that the method we have followed could be improved by taking a more realistic interionic charge density instead of equation (5). This could be done, perhaps, by finding the charge for two centres of force. The method would not have any adjustable parameter yet and should give an interionic potential very close to the real one.

References

[1] MAGAÑA, L. F., WHITMORE, M. D. and CARBOTTE, J. P., Can. J. Phys. **60** (1982) 424.

[2] JOHNSON, R. A., J. Phys. F **3** (1973) 295.

[3] POMUK, H. O. and HALICIOGLU, T., Phys. Status Solidi A **37** (1976) 694.

[4] LEE, J. K., BARKER, J. A., ABRAHAM, F. F., J. Chem. Phys. **58** (1973) 3166.

[5] BLASKES, M. I. and MELIUS, C. F., Phys. Rev. B **20** (1979) 3197.

[6] CARLSSON, A. E., KLEIN, M. L. and ENRENREICH, H., Philos. Mag. A **41** (1980) 241.

[7] RASOLT, M. and TAYLOR, R., Phys. Rev. B **11** (1975) 2717.

[8] DAGENS, L., RASOLT, M. and TAYLOR, R., Phys. Rev. B **11** (1975) 2726.

[9] MANNINEN, M., JENA, P., NIEMINEN, R. M., LEE, J. K., Phys. Rev. B **24** (1981) 7057.

[10] HARRISON, W. A., WILLS, J. M., Phys. Rev. B **25** (1982) 5007.

[11] GUPTA, A. K., JENA, P. and SINGWI, K. S., Phys. Rev. B **18** (1978) 2712.

[12] MAGAÑA, L. F., Phys. Lett. **80A** (1980) 193.

[13] HOHENBERG, H. and KOHN, W., *Phys. Rev.* **136** (1964) B964.

[14] KOHN, W. and SHAM, L. J., *Phys. Rev.* **140A** (1965) 1133.

[15] SHUKLA, R. C., *J. Chem. Phys.* **45** (1966) 4178.

[16] HEDING, L., LUNDQVIST, B. I., *J. Phys. C* **4** (1971) 2064.

[17] MANNINEN, M., NIEMINEN, R., HAUTOJARVI, P., ARPONNEN, J., *Phys. Rev.* **12** (1975) 4012.

[18] BOCCARA, N. and SARMA, G., *Physics* **1** (1965) 219.

[19] GILLIS, N. S., WERTHAMER, N. R. and KOCHLER, T. R., *Phys. Rev.* **3** (1968) 951.

[20] COWLEY, E. R. and SHUKLA, R. C., *Phys. Rev. B* **4** (1974) 1261.

[21] BORN, M., VON KARMAN, T., *Phys. Z.* **13** (1912) 297.

[22] BORN, M., VON KARMAN, T., *Phys. Z.* **14** (1913) 15.

[23] SHYU, W. M., GASPARI, G. D., *Phys. Rev.* **163** (1967) 667.

[24] TORRENS, I. M., *Interatomic Potentials* (Academic Press, New York) 1972, p. 119.

[25] PERDEW, J. P. and VOSKO, S. H., *J. Phys. F* **6** (1976) 1421.

[26] HEINE, V. and ABARENKOV, I., *Philos. Mag.* **9** (1964) 451.

[27] ANIMALU, A. O. E., *Proc. R. Soc.* A **294** (1966) 376.

[28] SHYU, W. M. and GASPARI, G. D., *Phys. Rev.* **170** (1968) 687.

[29] ASCHROFT, N. W., *Phys. Lett.* **23** (1966) 48.

[30] SMITH, H. G., DOLLING, G., NICKLOW, R. M., VIJAYARAGHAVAN, P. R. and WILKINSON, M. K., *Neutron Inelastic Scattering* (International Atomic Energy Authority, Vienna) 1968, vol. 1, p. 149.