DENSITY FUNCTIONAL MODELLING OF ELASTIC PROPERTIES OF ELEMENTAL SEMICONDUCTORS

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The expressions for bulk modulus, its first and second pressure derivatives for elemental semiconductors are derived using the ab initio pseudopotential approach to the total crystal energy within the framework of local Density Functional formalism. The expression for the second pressure derivative of the bulk modulus for four-fold crystal structures are derived for the first time within the pseudopotential framework. The computed results for the semiconductors under study are very close to the available experimental data and will be useful in the study of equation of states.

Keywords: AB INITIO CALCULATIONS, PSEUDOPOTENTIAL, ELASTIC PROPERTIES, ELEMENTAL SEMICONDUCTORS.

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1. INTRODUCTION

The study of the isothermal bulk modulus and its pressure derivatives of the binary compounds is an important tool for the study of various physical properties [1, 2], thermal properties [3, 4] and the Equation Of States (EOS) [5-8]. The reason being that the bulk modulus is defined as the derivative of volume therefore it is more sensitive to the variation in EOS than the volume itself. This provides a basis for studying the Earth's deep interior [9]. In the past few years, it has become possible [10] to compute lattice constants, bulk moduli, cohesive energies, phonon spectra and other static properties knowing only the atomic numbers and masses of the atoms composing the materials. An empirical relation for the bulk moduli was obtained by Cohen [11] using scaling arguments for the relevant energy and volume. Later on Lam et al. [12] have explored the microscopic origin of the above empirical relation excluding correlation effects.

The purpose of this paper is to derive the expressions for bulk modulus, its first and second pressure derivatives for elemental semiconductors within the pseudopotential framework. For this in part – 2, the *ab initio* pseudopotential approach to the total crystal energy is presented and the resulting expression for total crystal energy is written as a function of the Seitz-Wigner radius. In part – 3, using the above expression for total crystal energy, the relations for bulk modulus and its pressure derivatives are worked out. The results of numerical calculation based on above derived relations are very close to the available data.

2. PSEUDOPOTENTIAL APPROACH TO TOTAL CRYSTAL ENERGY

The ab initio pseudopotential approach to the total crystal energy calculation is presented. Using this approach the expression for the total crystal energy will be derived from the variationally determined valence electron eigen values and charge densities. The large and geometry-insensitive core contributions are explicitly projected out of the energy expression by using a pseudopotential formalism. The local Density Functional (DF) formalism for the exchange and correlation potential is self consistently employed in the derivation.

Most importantly, a drastic simplification of the energy expression is made by formulating the relevant expression for the total crystal energy in momentum space. The virtue of the momentum space formalism rests on its simplicity. Any real space integral is replaced by a simple summation over reciprocal vectors. The convergence of the summation is very rapid because of the smooth pseudopotential used in place of the real potential, which is singular at the origin.

This expression is particularly designed to be applied with the pseudo-potential method and a plane-wave basis set. A plane wave basis set is used to represent the (pseudo) valence wave functions. Such a basis set describes the charge density in the valence region to the same degree of accuracy for different crystal structures. In other words, the basis is not biased toward a particular crystal structure, which is usually difficult to achieve in other choices of basis sets. Furthermore, the angular dependence of the charge density is well accounted for, and there is no need for a spherical averaging procedure of the charge density which may introduce appreciable error in describing highly directional covalent bonds [13-16]. The present formalism, however, is readily applicable to calculations with mixed basis sets (e.g. plane wave plus Gaussian) as well. This enables one to extend the calculations to the case of transition metals.

Within the pseudopotential framework [17], following the conventional DF formalism [18, 19] the total crystal energy (E); defined as the total energy difference between the solid and isolated cores or the negative of the sum of ionization potentials of the valence electrons plus the cohesive energy; is given by:

$$E = T_e + V_{e-e} + V_{e-ion} + V_{ion-ion} + E_{XC} \qquad (1)$$

The individual contributions are interpreted as the kinetic energy of electrons, the Coulomb energy due to electron-electron interaction, the energy due to electron-ion interaction, the Coulomb energy due to the ion-ion interaction and the electronic exchange-correlation energy. Since the effect of core electrons is included in the pseudopotentials, the term 'electrons' used in this paper refers to the valence electrons only. The Slaters X_α method [20] is used in deriving E_{xc}.

To obtain the total crystal energy (E) as a function of the Seitz-Wigner radius (R) it is useful to write $\bar{\varepsilon} = \bar{\varepsilon}_o + \bar{\varepsilon}'$ for systems where the band structure is not too far from the free-electron dispersion, with $\bar{\varepsilon}_o$ being the average eigenvalue from the free-electron dispersion and $\bar{\varepsilon}'$ is the correction term. Then the final expression for total crystal energy becomes:

$$E = \frac{B}{R^2} - \frac{A}{R} + \frac{C}{R^3} - DR^2 - \frac{f}{gR + h} \qquad (2)$$

where $A = \left(3 / 2\pi\right)\left(9\pi / 4\right)^{1/3} Z^{4/3} + F_S Z^2 \approx 0.9163 Z^{4/3} + F_S Z^2$ with F_S being the structure dependent Ewald constant and for diamond structure $F_S = 1.671$, $B = \left(3 / 5\right)\left(9\pi / 4\right)^{2/3} Z^{5/3} \approx 2.2099 Z^{5/3}$,

$C = \left(3 / 4\pi\right) Z U_{PS}\left(\bar{G} = \bar{0}\right) \approx 0.2387 Z U_{PS}\left(\bar{G} = \bar{0}\right)$ $D \propto \left|V\left(\bar{G}\right)\right|^2$ is a positive number, with $V\left(\bar{G}\right)$ being the screened pseudopotential form factor and the last term is the correlation term with $f = 0.88Z$, $g = Z^{1/3}$ and $h = 7.80$.

3. RELATIONS FOR BULK MODULUS AND ITS PRESSURE DERIVATIVES

On using equation (2) for the total crystal energy along with the equilibrium relation:

$$AR_o^2 - 2BR_o - 3C - 2DR_o^5 + \frac{fgR^4}{\left(gR + h\right)^2} = 0 \tag{3}$$

The bulk modulus can readily be calculated using the following relation:

$$K_0 = \Omega_{a,0} E'' = \frac{1}{9\Omega_{a,0}}\left[\frac{8B}{R_0^2} - \frac{3A}{R_0} + \frac{15C}{R_0^3} - \frac{fgR_0\left(3gR_0 + h\right)}{\left(gR_0 + h\right)^3}\right] \tag{4}$$

where R_0 and $\Omega_{a,0}$ are the equilibrium Seitz-Wigner radius and equilibrium volume respectively. Here the prime denotes differentiation w.r.t. atomic volume. The equilibrium condition (3) is used either to eliminate the dependence on C or D.

The first and second pressure derivatives K_o' and K_o'' respectively are then given by:

$$K_0' = \left[\frac{dK}{dP}\right]_{P=0} = -\left[1 + \Omega_{a,0}\frac{E'''}{E''}\right]$$

$$K_0'' = \left[\frac{d^2K}{dP^2}\right]_{P=0} = \frac{E'''}{\left(E''\right)^2} + \Omega_{a,0}\frac{E''''}{\left(E''\right)^2} - \Omega_{a,0}\frac{\left(E'''\right)^2}{\left(E''\right)^3}$$

Using equations (2)-(3) in the above definitions:

$$K_0' = \frac{7}{3} + \frac{2}{9\Omega_{a,0}K_0}\left[\frac{A}{R_0} - \frac{4B}{3R_0^2} + \frac{fgR_0\left(3g^2R_0^2 + 8ghR_0 + 2h^2\right)}{3\left(gR_0 + h\right)^4}\right] \tag{5}$$

$$K_0'' = \frac{1}{K_0}\left[\begin{array}{c} \dfrac{124}{9} - \left(1 + K_0'\right)\left(2 + K_0'\right) + \dfrac{8}{27\Omega_{a,0}K_0} \\[2ex] \left\{\dfrac{5A}{R_0} - \dfrac{7B}{R_0^2} + \dfrac{fgR_0\left(5g^3R_0^3 + 18g^2hR_0^2 + 15gh^2R_0 + 3h^3\right)}{\left(gR_0 + h\right)^5}\right\} \end{array}\right] \tag{6}$$

The last term in equations (**4, 5** and **6**) containing constants f, g and h represents the effect of correlation on K_0, K_0' and K_0''.

4. RESULTS AND DISCUSSION

Analytic expressions for the bulk modulus, its first and second pressure derivatives are derived from the ab initio pseudopotential total energy formalism. These expressions are written explicitly as a function of equilibrium Seitz-Wigner radius alone. In these expressions we have included the contribution due to correlation term, which was omitted by Lam et al. [12]. The agreement (Tables 1 and 2) between the numerical and experimental values is very good.

Table 1 − *Comparison of calculated and experimental values of bulk modulus K_0. The bulk moduli are calculated using equation (4)*

COMPOUNDS	R_0 in a.u.	K_0 in GPa	
		Exp. [21]	Calc.
C	2.09	442.0	444.3
Si	3.18	98.0	100.1
Ge	3.32	77.2	87.4
α-Sn	3.81	53.0	55.8

Table 1 − *Comparison of calculated and experimental values of first pressure derivative K_0' and second pressure derivative K_0'' of bulk modulus. The first pressure derivatives of bulk modulus are calculated with equation (5) using the experimental value for K_0. The second pressure derivatives of bulk modulus are calculated with equation (6) using the experimental value for K_0 and experimental/calculated value for K_0'.*

COMPOUNDS	K_0'		K_0'' in GPa^{-1}
	Exp. [21]	Calc.	Calc.
C	4.69	4.04	− 0.030
Si	4.24	4.16	− 0.072
Ge	4.55	4.31	− 0.125
α-Sn		4.08	− 0.106

The calculated values of K_0', first pressure derivatives of bulk modulus, are found to be greater than 4 for all the semiconductor binary compounds under study. These values are in accordance with the experimental values of K_0' which remain between 4 and 6 for most of the crystals studied so far. It is worth noticing that the magnitude of the values of K_0'', second pressure derivatives of bulk modulus, are less than the values of K_0' in all the semiconductor binary compounds under study. Moreover for all the semiconductors under study the values of K_0', K_0'' are negative which is consistent with the study of Anderson et al. [6]. Thus these values of K_0' will be much helpful in the study of EOS and to understand the elastic properties of these semiconductors.

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