

Bulk modulus of metals according to structureless pseudopotential model

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Abstract

The method for calculating the bulk modulus of metals based on the structureless pseudopotential model was fully developed. The developed method was used to calculate the bulk modulus and kinetic energy contribution to the bulk modulus of 46 elemental metals. The results obtained were compared with experimental values and their variation with electron density parameter was studied. The results obtained revealed that the calculated and experimental bulk modulus of metals varies in the same manner with the electron density parameter. The calculated bulk modulus of metals was in very good agreement with experimental values for the simple metals in the low-density limit and the agreement between the calculated and experimental bulk modulus of metals decreases towards the high-density limit where we have the transition and the noble metals. The results further revealed that the kinetic energy contributes significantly to the bulk modulus of metals and varies in the same manner with the electron density parameter as the bulk modulus. The agreement between the calculated and experimental bulk modulus of metals shows that the structureless pseudopotential model is promising for predicting metallic properties.

Keywords

Metals, bulk modulus, pseudopotential, kinetic energy and electron density parameter

1.0 Introduction

The pseudopotential formalism provides a conceptual justification of nearly free electron model of solids and simultaneously, pseudopotentials provide a computational tool that substantially increases the range of problems that can be brought within computational reach. The pseudopotential approach for the study of the properties of solids is a way of organizing experimental and computational information about conduction electrons in a compact and physical form. In the pseudopotential approach for the study of properties of solids, with just a few fitting parameters obtained from experiments or calculations, it is possible to get a good estimate of different properties of solids [1].

The goal of pseudopotential theory is to obtain the key physical properties of atoms, molecules and solids by dealing only with the valence electrons. To avoid a complicated all-electron problem, an effective weaker potential between valence electrons and the atomic core is introduced. Interactions among the valence electrons are often described by density functional theory.

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In the pseudopotential formalism, tremendous simplification of computational effort is achieved by treating core electrons differently from valence electrons. Deep core electrons are considered as “frozen” in space and independent of the atom’s valence environment. Also, the core electrons are treated differently from valence electrons; however, the valence states are constructed under boundary conditions reflecting the surroundings of the atoms in the crystal environment and the core states are rectified to the.

Pseudopotential models have been used to calculate different properties of solids. Ling and Gelatt [2] used a local pseudopotential constructed from the bulk stability condition alone to calculate the shear and bulk moduli of 19 simple metals. They also studied the chemical trends in the elastic modulus of the simple metals and calculated the ratio of shear modulus to bulk modulus, which gave a result that was in good agreement with experimental value. Fiolhais et al.,[3] developed a local pseudopotential whose input parameters are valence, electron density parameter and equilibrium number of valence electrons. They used the pseudopotential to calculate binding energy, bulk modulus and its pressure derivative for some simple metals. The results they got were in good agreement with experimental values for the simple metals. Vackar et al.,[4] developed the all-electron pseudopotential, a pseudopotential technique that takes into account all electrons (core and valence) interactions of an atom in a bond and generate “all electron” pseudopotential with the relaxed core. The all electron pseudopotential is a functional of the charge density and does not correspond to any choice of occupation numbers of any atomic configuration. The potential revealed that the relaxation of the core could be quantitatively treated within the pseudopotential approach. The all electron pseudopotential was used to calculate the lattice constant and bulk modulus of silicon, diamond, non-magnetic cobalt, cubic TiC and hexagonal TiS₂. The results they got were in satisfactory agreement with experimental values. Lee et al., [5] described a semi empirical method for constructing pseudopotentials for correlated-electron calculations. They used a combination of calculated quantities and experimental ionization energies for a single electron in the field of an isolated ion. The pseudopotential obeys a norm-conservation condition, core-polarization effects were included in a consistent manner, and an accurate representation of the Hartree and exchange potentials outside the core was included. The pseudopotential worked very well for silicon but not satisfactorily well for titanium.

The structureless pseudopotential model evolved from the variational-consistent treatment of the ground state properties of metals. The structureless pseudopotential model modifies the jellium model, such that zero forces acts on the positive background in the uniform state [6]. In the structureless pseudopotential model, the input parameters are valence, electron density parameter and the Ashcroft core radius, which are not obtained from experimental values. The structureless pseudopotential model requires mechanical stability, neglects the crystal structure of metals. Its advantages over other pseudopotential models is that it possesses physical transparency, can be used with the density functional theory and it requires less computational resources.

In this work, the structureless pseudopotential model is used to calculate the bulk modulus of metals in order to test the strength of model in predicting metallic properties. Also, the kinetic energy contribution to the bulk modulus of solids is studied in order to know how the kinetic energy of the solids affects their bulk modulus and hence provide a better understanding of the bulk modulus of metals.

2.0 Theory and calculation

The energy functional of a system of interacting electrons in an external potential arising from the interaction with ions represented by a local pseudopotential, Φ can be expressed as a functional of the electronic density $n(r)$ as:

$$E[n] = T_s[n] + E_{xc}[n] + \frac{1}{2} \int dr dr' \frac{n(r)n(r')}{|r-r'|} + \int dr \Phi(|r-R_i|)n(r) + \frac{1}{2} \sum_{ij} \frac{Z^2}{|R_i-R_j|} \quad (2.1)$$

where the first three terms represents respectively the kinetic, exchange-correlation and electrostatic energy of the interacting system. The last two terms describes the interaction of electrons with the ions at site R_i via a pseudopotential, Φ and the Coulomb interaction between the ions.

To improve the convergence of the individual Coulomb term appearing in equation (2.1) above, the neutralizing positive background of the jellium is added and subtracted, hence

$$E[n] = T_s[n] + E_{xc}[n] + \frac{1}{2} \int dr \Phi([n]; r) [n(r) - n_+(r)] + \int dr \delta V(r) [n(r) - n_+(r)] + \int dr \sum_i \Phi(|r - R_i|) n_+(r) \quad (2.2)$$

$$+ \frac{1}{2} \int dr dr' \frac{n_+(r) n_+(r')}{|r - r'|} - \int dr \sum_i \frac{Z}{|r - R_i|} n_+(r) + \frac{1}{2} \sum_{ij} \frac{Z^2}{|R_i - R_j|}$$

with $\delta V(r) = \sum_i \Phi(|r - R_i|) + \int \frac{dr' n_+(r')}{|r - r'|}$ and $\Phi([n]; r) = \int dr' \frac{n(r') - n_+(r')}{|r - r'|}$

According to the density functional theory, the correct electronic density $n(r)$ can be obtained by minimizing the energy functional in equation (2.2) since only the first terms depends on $n(r)$, then

$$E[n] = T_s + E_{xc}[n] + \frac{1}{2} \int dr \Phi([n]; r) [n(r) - n_+(r)] + \int dr \delta V(r) [n(r) - n_+(r)] \quad (2.3)$$

The self-consistent electron density may be obtained from the Schrodinger equation

$$\left[-\frac{1}{2} \nabla^2 + V_{eff}(n, r) \right] \psi_i(r) = E_i \psi_i(r) \quad (2.4)$$

with the effective potential $V_{eff}(n, r) = \Phi(n, r) + \delta V(r) + V_{xc}(n, r)$ (2.5)

where $\delta V_{xc}(n, r) = \frac{\delta E_{xc}}{\delta n(r)}$. The last term in equation (2.3) is the Madelung energy of the neutralized

lattice. The total energy required to assemble the valence electrons and ions to form the solid, which is the binding energy is

$$E = T_s(n) + E_{ac} + W_R + E_m \quad (2.6)$$

where T_s is the kinetic energy, E_{xc} is the sum of the exchange and correlation energies, W_R is the average value of the non-Coulombic part of the pseudopotential and E_m is the average Madelung or electrostatic energy of point ions embedded in a uniform negative background of density n

In the density functional theory, in the low-density limit, the kinetic and exchange energies are given [7] as

$$T_s = \frac{1 \cdot 105}{r_s^2} \text{ and } T_x = -\frac{0 \cdot 458}{r_s} \quad (2.7)$$

where E_x is the average exchange energy and r_s is the electron density parameter connected with the electron density by the formula where ρ is the electron density and a_0 is Bohr's radius.

The correlation energy used in this work is that Carperley and Alder as parameterized by Perdew and Zunger [8] and is given as

$$r_s = \left(\frac{3}{4\pi\rho} \right)^{1/3} \frac{1}{a_0} \quad (2.8)$$

$$E_c = -\frac{0 \cdot 1423}{1 + 1 \cdot 0529 r_s^{1/2} + 0 \cdot 3339 r_s} \quad (2.9)$$

From equation (2.6), the binding energy is

$$T_s = \frac{1 \cdot 105}{r_s^2} - \frac{0 \cdot 458}{r_s} - \frac{0 \cdot 1423}{1 + 1 \cdot 0529 r_s^{1/2} + 0 \cdot 3339 r_s} + W_R + E_{sc} \quad (2.10)$$

The ionic potential Φ has a long-range attractive Coulomb part and a short-range repulsive part W_R due to the core orthogonalization and it is

$$\Phi = -\frac{z}{r} + W_R(z) \quad (2.11)$$

The potential may be represented by a simple form of the Ashcroft empty core pseudopotential such that the potential compensates $-z/r$ with a radius r_c

$$W_R(z) = \frac{z}{r} \Phi(r_c - r) \quad (2.12)$$

where $\Phi(r_c - r)$ is a step function which is equal to unity in the cell and zero outside. The average value of the repulsive part of the pseudopotential is

$$\bar{W} = \frac{n}{2} \int dr W_R(r) = \frac{n_{av}}{2} \int_0^{r_c} 4\pi r^2 \frac{z}{r} = 2\pi n_{av} r_c \quad (2.13)$$

where n_{av} is the average density of the electrons. In the structureless pseudopotential model, it is assumed that the ionic charges are assumed to be smeared to a uniform sphere background density with a spherical hole in it such that its potential is of the form [9]

$$V(r) = \begin{cases} \frac{z}{r} \left(\frac{3}{2} - \frac{r^2}{2r_0^2} \right), & r < r_0 \\ \frac{z}{r}, & r > 0 \end{cases} \quad (2.14)$$

The self-energy of the electrostatic interaction averaged over the whole Winger-Seitz sphere is

$$E_{es} = \frac{\frac{1}{2} \int_0^{r_0} V(r) 4\pi r^2 dr}{4\pi \frac{r_0^3}{3}} = \frac{3z}{5r_0} \quad (2.15)$$

The factor of half is to avoid double counting. The positive contributions are compensated by the negative energy of the electrons interacting with the uniform positive background.

The Madelung energy for a jellium system is given [8]

$$E_m = -\frac{3z}{2r_0} + E_{es} = -\frac{9z}{10r_0} \quad (2.16)$$

where $r_0 = z^{1/3} r_s$. Substituting equations (2.13) and (2.16) into (2.10) we obtain the binding energy according to the structureless pseudopotential model as

$$E = \frac{1 \cdot 105}{r_s^2} - \frac{0 \cdot 458}{r_s} - \frac{0 \cdot 1423}{1 + 1 \cdot 0529 r_s^{1/2} + 0 \cdot 3339 r_s} + 2\pi n r_c - \frac{9z}{10r_0} \quad (2.17)$$

but $r_0 = z^{1/3} r_s$ and $n = 4\pi r_s/3$, hence

$$E = \frac{1 \cdot 105}{r_s^2} - \frac{0 \cdot 458}{r_s} - \frac{0 \cdot 1423}{1 + 1 \cdot 0529 r_s^{1/2} + 0 \cdot 3339 r_s} + \frac{3r_c^2}{2r_s^3} - \frac{9z^{2/3}}{r_s} \quad (2.18)$$

where r_s is the electron density parameter which is between 2 and 6 for metals [10] and r_c is the Ashcroft core radius obtained from the bulk stability condition and it is given [9] as

$$r_c = \left[\frac{-2 \left(\frac{9\pi}{4} \right)^{2/3}}{15} r_s + \frac{1}{6\pi} \left(\frac{9\pi}{4} \right)^{1/3} r_s^2 + \frac{1}{5} z^{2/3} r_s^2 + \frac{2}{9r} r_s^4 \frac{dE_c}{dr_s} \right]^{1/2} \quad (2.19)$$

and E_c is the correlation energy.

The bulk modulus, which measures resistance to structure-preserving volume-changing deformations [2] is

$$B = -V \left(\frac{\partial P}{\partial V} \right)_N = \frac{1}{12\pi} \left(\frac{1}{r_s^2} \frac{\partial^2 E}{\partial r_s^2} - \frac{2}{r_s^2} \frac{\partial E}{\partial r_s} \right) \quad (2.20)$$

where pressure, P is

$$P = -\left(\frac{\partial E}{\partial V}\right)_N = \frac{1}{4\pi r_s^2} \frac{\partial E}{\partial r_s} \quad (2.21)$$

The kinetic energy contribution to the bulk modulus is [11]

$$KE_c = \Omega \frac{d^2 E_{kinetic}}{d\Omega^2} = \frac{3}{4\pi r_s} \frac{1}{9dr^2} \frac{1 \cdot 105}{r_s^2} \quad (2.22)$$

In this paper, the bulk modulus, of different metals were calculated based on the structureless pseudopotential model using equation (2.20) above. Also, the kinetic energy contribution to the bulk modulus of the metals was calculated using equation (2.22). The variation of the calculated bulk modulus of different metals and kinetic energy contribution to the bulk modulus of metals with electron density parameter was investigated. The calculated bulk modulus of metals was compared with experimental values in order to see how the bulk modulus of metals calculated using the structureless pseudopotential model agrees with experimental values. .

3.0 Results and Discussion

Figure 3.1 and Table 3.1 show the variation of the calculated and experimental bulk modulus of different metals with electron gas parameter. As shown in figure 3.1, both the calculated and experimental bulk modulus of different metals varies inversely with the electron density parameter. Also, in the low-density limit, ($r_s > 2.5$), the calculated bulk modulus of the metals were in very satisfactory agreement with experimental values, but in the high-density limit ($r_s < 2.5$), the calculated bulk modulus of the metals were not in satisfactory agreement with experimental values as the structureless pseudopotential model gave bulk modulus of metals in the high-density limit that are higher than experimental values. This shows that the higher the values of the electron density parameter of a metal, the closer its bulk modulus calculated using the structureless pseudopotential model is to experimental value. Simple metals such as *Na, K, Rb, Li, Cs*, are found in the low-density region and the calculated bulk modulus of these metals are in good agreement with experimental values. This is quite satisfying as the alkalis are often used as examples of “free-electron” metals [12]. But the transition and noble metals such as *Mn, Fe, Ti, Hg, Pd, Pb* etc are found in the high-density limit and the structureless pseudopotential model could not give bulk modulus of these metals that are in good agreement with experimental values. For the transition and noble metals, apart from *Fe, Cr, Co, Ni* and *Pd*, the structureless pseudopotential model overestimates the bulk modulus of transition and noble metals. Since r_s is a measure of effective interaction between electrons in the metal, the results in figure 3.1 shows that the bulk modulus of a metal varies inversely with the effective interaction between the electrons in the metal. The inability of the structureless pseudopotential model to give bulk modulus of transition and noble metals that are in good agreement with experimental values may be due to contribution of the core electrons which the structureless pseudopotential model does not take into consideration. This

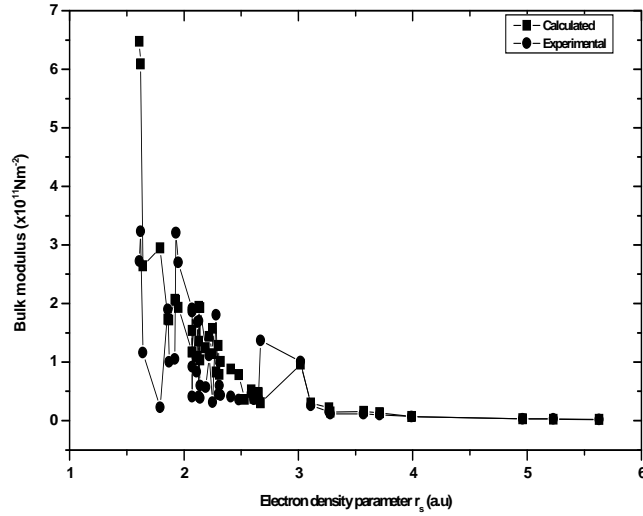


Figure 3.1: Variation of calculated and experimental bulk modulus of metals with electron density parameter.

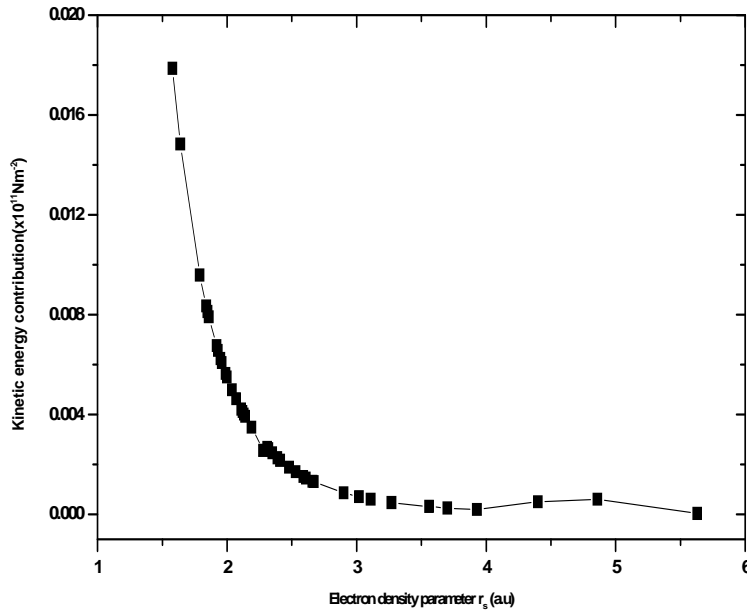


Figure 3.2: Variation of kinetic energy contribution to bulk modulus of metals with electron density parameter for different metals

may also be due to the band-structure contribution to the bulk modulus, which is crucial [3] in the calculation of bulk modulus of metals. Also, the neglect of the crystal structure, which plays a vital role in the properties of the transition metals [13] may be responsible for this. This may also be due to the volume-energy contribution to the bulk modulus, which dominates for the transition metals [6].

Table 3.1: Metals, electron density parameter r_s , calculated and experimental bulk modulus of metals. The experimental values were taken from [13].

Metals	$r_s(a.u)$	Calculated bulk modulus ($\times 10^{11}N/m^2$)	Experimental bulk modulus ($\times 10^{11}N/m^2$)
<i>Li</i>	3.28	0.146	0.116
<i>Na</i>	3.99	0.069	0.068
<i>K</i>	4.96	0.031	0.032
<i>Rb</i>	5.23	0.025	0.031
<i>Cs</i>	5.63	0.019	0.020
<i>Cu</i>	2.67	0.304	1.370
<i>At</i>	2.53	0.361	-----
<i>Ag</i>	3.02	0.961	1.007
<i>Au</i>	3.01	0.196	1.732
<i>Be</i>	1.87	1.717	1.003
<i>Mg</i>	2.65	0.481	0.354
<i>Ca</i>	3.27	0.217	0.152
<i>Ba</i>	3.71	0.135	0.103
<i>Po</i>	3.11	0.300	0.260
<i>V</i>	1.64	2.644	1.162
<i>Cr</i>	1.86	1.730	1.901
<i>Mn</i>	2.14	1.038	0.596
<i>Fe</i>	2.12	1.092	1.683
<i>Co</i>	2.07	1.169	1.914
<i>Ni</i>	2.07	1.169	1.860
<i>Zn</i>	2.31	0.787	0.598
<i>Zr</i>	2.11	1.098	0.833
<i>Sr</i>	3.57	0.158	0.116
<i>Pd</i>	2.28	0.828	1.808
<i>Cd</i>	2.59	0.526	0.467
<i>Hg</i>	2.65	0.465	0.382
<i>Al</i>	2.07	1.539	0.922
<i>Ga</i>	2.19	1.244	0.569
<i>In</i>	2.41	0.881	0.411
<i>Tl</i>	2.48	0.785	0.359
<i>Bi</i>	2.25	1.143	0.315
<i>Sc</i>	2.32	1.009	0.435
<i>Ti</i>	1.92	2.073	1.051
<i>Y</i>	2.61	0.376	0.366
<i>Ru</i>	1.93	2.053	3.207
<i>Rh</i>	1.95	1.934	2.704
<i>Lu</i>	2.13	1.356	0.411
<i>Sn</i>	2.22	1.438	1.110
<i>Pb</i>	2.30	1.281	0.450
<i>Te</i>	1.79	2.950	0.230
<i>Nb</i>	2.13	1.952	1.702
<i>Sb</i>	2.14	1.927	0.383
<i>Bi</i>	2.25	1.573	0.315
<i>Mo</i>	1.61	6.475	2.725
<i>W</i>	1.62	6.092	3.232

Figure 3.2 shows the variation of the kinetic energy contribution to the bulk modulus of metals. As shown in figure 3.2, the kinetic energy varies in the same manner with the electron gas parameter as the bulk modulus of metals. Figure 3.2 further revealed that metals with having high bulk modulus have high kinetic energy contribution to the bulk modulus. Metals in the low-density limit having small values of bulk modulus have small kinetic energy contribution.

These shows that kinetic energy contributes significantly to the bulk modulus of metals and the kinetic energy contribution is of the right magnitude for materials ranging from sp-bonded metals to strongly bonded metals [11].

The results obtained in this study compares very well with experimental values and followed the same trend just like the results obtained for the bulk modulus of sixteen metals calculated by Pollack et al., [14]. Also, the results obtained in this work for simple metals (*Li, Na, K, Cs, Mg, Ca, Be, Ba, Sn, Pb, In, Tl* and *Al*) compares favourably well with the ones obtained by Fiolhais et al., [3] that calculated some binding energy, chemical potential and bulk modulus of simple metals using a local pseudopotential.

4.0 Conclusion

In this work, the bulk modulus of different metals has been calculated using the structureless pseudopotential model. The structureless pseudopotential model gave bulk modulus of simple metals that are in good agreement with experimental values while it overestimates the bulk modulus of most transition and noble metals. The disagreement between calculated and experimental bulk modulus of metals increases with a decrease in the electron density parameter of the metals. The kinetic energy of metals contributes significantly to the bulk modulus of metals. The agreement between the calculated bulk modulus of metals and experimental values shows that the structureless pseudopotential model is quite promising in predicting the properties of metals.

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