Original Research Article

THE COHESIVE ENERGY CALCULATIONS OF SOME BCC (Li, Cr, Fe, Mo) LATTICES USING DENSITY FUNCTIONAL THEORY

ABSTRACT

The cohesive energies of lithium (Li), chromium (Cr), iron (Fe) and molybdenum (Mo) were computed using density functional theory (DFT). DFT based Fritz Haber Institute-ab initio molecular simulation (FHI-aims) computer code has several input parameters in which some of the variables were optimized. The cohesive energies of Li, Cr, Fe and Mo were calculated within Perdew Wang local density approximations (LDA) of DFT. The results obtained from the calculations of cohesive energies of Li, Cr, Fe and Mo were approximately 1.82eV, 5.33eV, 5.35eV, and 8.02eV respectively. These results obtained are in the neighborhood of experimentally found values of 1.63eV, 4.10eV, 4.28eV and 6.82eV respectively, within reasonable percentage errors.

*keywords**:** bcc; cohesive energy, DFT, ground state, lattice constant, total energy.*

1. INTRODUCTION

Cohesive energy calculations vis-à-vis the first principle total energy calculations using DFT is considered satisfactory in the physics of condensed matter systems, material science and physical chemistry. DFT has a wide application in atoms, molecules and bulk structures; and the method can be used to predict properties of atomic and bulk systems.

DFT being one of the most popular and quantum-mechanical approaches to many-body systems are applied to computations of ground-state properties of molecules and the band structure of solids in physics [5]. This research work involves some body-centered cubic (BCC) lattices or crystals that were investigated using DFT based FHI-aims code as a tool to calculate the cohesive energies of Li, Cr, Fe and Mo.

This research puts into perspective a single alkaline metal, Li and three transition metals Cr, Fe and Mo. This choice is based on comparative study and practical applications of these materials for modern technology.

Electrochemical batteries as of today are the most (or one of the most) promising energy storage technology in grid integration of renewables, electric vehicles, and electronics devices [12]. The batteries have relatively high energy and efficiency and specific example of such batteries is Li-ion battery. Also, lithium has been found effective in assisting the perfection of silicon nano welds in electronic components for electrical batteries and other devices.

Stainless steel and chromium plating (electroplating with chromium) have high commercial use. Iron as well as molybdenum is used in steel alloys, including high strength alloys and superalloys. Indeed these materials have high industrial use and demands. Hence, the needs to further study the cohesive energies of these materials using FHI-aims.

Our interest on structure and binding imply that the cohesive energy E_{coh} of a system is very important. It is useful for studying binding strength in crystal structures and can help to gain information about structural preferences of solids.

Cohesive energy is the energy that must be supplied to a solid or crystal to separate its constituents into free atoms at rest and at infinite separation with the same electronic configuration [6, 11]. Cohesive energy is one of the parameters used to understand the nature of chemical bonding and several important parameters can be predicted using it. Its magnitude tells us the stability and chemical reactivity of solids. Eventually, it is the quantity which determines the structure of solids, because different possible structures would have different cohesive energies [19].

Many powerful methods for solving schrodinger's equation have been developed during decades of struggling with the many-body problem. These methods are Nearly-Free-Electron Approximation, Cellular Method, Augumented Plane-Wave method, Scattering Matrix Method, Pseudopotential Method; and other methods. These methods are time-consuming, cumbersome and pose problems to researchers in this field. Hence, DFT as a powerful tool replaces the many-body electronic wave function used in the method mentioned above with the electron density as the basis quantity [4].

In calculating basic properties of solids like cohesive energy, lattice constants, band structures and density of state, we use DFT as the most popular and successful quantum-mechanical approaches to matter [20].

In this research, the cohesive energies of Li, Cr, Fe and Mo were computed based on DFT package FHI-aims code in the range between 1.82eV and 8.02eV which is in reasonable agreement with experimental data in the range between 1.63eV and 6.82eV.

2. THEORETICAL FRAMEWORK

Density functional theory (DFT) is a quantum mechanical modelling method used in physics, chemistry to investigate the electronic structure or ground state of many body systems, in particular atoms, molecules, and the condensed phases [16]. The principles of DFT are conveniently expounded by making reference to conventional wave-function theory. Any problem in the electronic structure of matter (atom and molecules) is covered by Schrödinger's equation. DFT has proved to be highly successful in describing structural and electronic properties in a vast class of materials, ranging from atoms and molecules to simple crystals and complex extended systems (including gases and liquids). DFT has become a common tool in first-principle calculations aimed at molecular and condensed matter systems [8, 14].

Traditional methods in electronic structure theory, in particular Hatree-Fock theory and its descendants are based on the complicated many-electron wave function. The main objective of DFT is to replace the many-body electronic wave function with the electronic density as the basis quantity. Whereas many-body wave function is dependent on 3N variables, three special variables for each of the N electrons, the density is only a function of three variables and is a simpler quantity to deal with both conceptually and practically. [5]

2.1 THE HOHENBERG-KOHN THEOREM

It was Hohenberg and Kohn who stated a theorem that tells us that the electron density is very useful. The Hohenberg-Kohn (H-K) theorem asserts that the electron density of any system determines all ground-state properties of the system. In this case the total ground state energy of a many-electron system is a functional of the density.

Let us consider a system of N interacting (spinless) electrons under an external potential V(r) (usually the coulomb potential of the nuclei). If the system has a non-degenerate ground state, it is obvious that there is only one ground state charge density that corresponds to a given V(r). In 1964, Hohenberg and Kohn demonstrated the opposite, far less obvious result: there is only one external potential V(r) that yields a given ground-state charge density n(r). The demonstration is very simple and involves the disproof of a proposition by showing that it leads to absurdity.

For many-electron Hamiltonian $H=T+U+V$, with ground state wave function, ψ. T is the kinetic energy, U is the electron-electron interaction. V is the external potential. The charge density $n(r)$ as defined by Hohenberg-Kohn is

$$n(r) = N\int \left|\psi\left(r_1, r_2, r_3, \ldots, r_N\right)\right|^2 dr_2 \ldots dr_N$$

(2.1)

Now considering a differential Hamiltonian $H^{'} = T^{'} + U^{'} + V^{'}$, with the ground state wave function $\psi^{'}$. V and $V^{'}$ do not differ simply by a constant: $V - V^{'} \neq$ constant.

Assuming that the ground state charge densities are the same: $n[V] = n^{'}[V^{'}]$. The following inequality holds[5, 8] :

$$E < \left\langle \psi^{'} \middle| H \middle| \psi^{'} \right\rangle = \left\langle \psi^{'} \middle| H^{'} \middle| \psi^{'} \right\rangle + \left\langle \psi^{'} \middle| H - H^{'} \middle| \psi^{'} \right\rangle$$

(2.2)

$$E < E^{'} + \left\langle \psi^{'} \middle| T + U + V - T - U - V^{'} \middle| \psi^{'} \right\rangle$$

(2.3)

That is

$$E < E^{'} + \int n(r)\left\{V - V^{'}\right\}dr$$

(2.4)

Conversely,

$$E^{'} < E - \int n(r)\left\{V - V^{'}\right\}dr$$

(2.5)

Adding (4) and (5) gives

$$E + E^{'} < E^{'} + E \qquad \text{Contradiction!} \qquad (2.6)$$

The inequality is strict because ψ and $\psi^{'}$ are different, being eigen state of different Hamiltonians. By reversing the primed and unprimed quantities, one obtains an absurd result. This demonstrates that no two potentials can have the same density. The first Hohenberg-Kohn (*H-K*) theorem demonstrate the existence of a one-to-one mapping between the ground state electron density and the ground state wave function of a many-particle system. A straight forward consequence is that the ground state energy E is also uniquely determined by the ground-state charge density. In mathematical terms, *E* is a functional *E [n(r)]* of *n(r)*. This is why this field is known as density functional theory [5, 8]. We can write that:

$$E[n(r)] = (\psi|T + U + V|\psi) = (\psi|T + U|\psi) + (\psi|V|\psi) = F[n(r)] + \int n(r)V(r)dr$$

(2.7)

Where *F [n(r)]* is a universal functional of the charged density *n(r)* (and not of *V(r)*) also known as the *H-K* functional [18]. For this functional a variation principle holds: the ground state energy is minimized by the ground state charge density; this is the *H-K* second theorem. In this way, DFT exactly reduces the *N*-body problem to the determination of a 3-dimentional function *n(r)* which minimizes a functional *E [n(r)].* Unfortunately, this is of little use as *F [n(r)]* is not known.[5; 8]

2.2 THE KOHN-SHAM (KS) EQUATIONS

In 1965, Walter Kohn and Lu Sham proposed an educated guess that later yielded results in which they reformulated the problem in a more familiar form and opened the way to practical application of DFT. The system of interacting electrons is mapped onto a ficticious or auxillary system of non-interacting electrons having the same ground state charge density *n(r).* For a system of non-interacting electrons the ground-state charge density is represented as a sum over one-electron orbitals (the KS orbitals) ψ_i:

$$n(r)=2\sum_i\left|\psi_i(r)\right|^2$$

(2.8)

Where i runs from 1 to N/2. If we assume double occupancy of all states, and the Kohn-Sham orbitals are the solution to the Schrödinger equation [5, 8]:

$$\left(-\frac{\hbar^2}{2m}\nabla^2+V_{KS}(r)\right)\psi_i(r)=\in_i\psi_i(r)$$

(2.9)

In closed systems, suppose there is an even number of electrons, so that they all can be paired up and the external potential V(r) is independent of spin. Spin-up and spin-down contribute equally to the total density:

$$n^{(\uparrow)}(r)=n^{(\downarrow)}=\frac{1}{2}n(r)$$

(2.10)

Therefore, we only need $N_e/2$ Kohn-Sham orbitals, to each of which we assign an occupation number of f=2. These orbitals satisfy the orthogonality condition [18]:

$$\int\psi_i^*\psi_j(r)dr=\delta_{ij}$$

(2.11)

Again the density can also be written as:

$$n(r)=\sum_{i=1}^{Ne/2}\left|\psi_i(r)\right|^2$$

(2.12)

And the kinetic energy as

$$T_S=-\frac{1}{2}\sum_{i=1}^{Ne/2}\langle\psi_i|(r)|\nabla^2|\psi_i(r)\rangle$$

(2.13)

The existence of a unique potential V_{KS} in equation (2.9) having *n(r)* as its ground state charge density is a consequence of the *H-K* theorem, which holds irrespective of the form of electron-electron interaction, *U*. The problem is now to determine $V_{KS}(r)$ for a given *n(r) [6].* To solve this problem, it is convenient to rewrite the energy functionals as:

$$E = T[n(r)] + E_H[n(r)] + E_{xc}[n(r)] + \int n(r)V(r)dr \qquad (2.14)$$

The first term is the kinetic energy of non-interacting electrons. The second term called the Hatree energy contains the electrostatic interactions between clouds of charges. The third, called the exchange-correlation energy, contains all the remaining terms. The logic behind such procedures is to subtract out easily computable terms which accounts for a large fraction of the total energy. The only term for which no explicit form can be given is E_{xc} *[5, 8]*.

Utilizing the *H-K* theorem, we minimize the total energy with respect to the orbitals in order to obtain the orbitals that give rise to the ground state energy. While performing the minimization, we prefer to minimize with respect to $\psi_i^*(r)$ and $\psi_i(r)$. One can prove that both yield the same result.

Just like regular differentiation, we can employ chain rule for the functional derivatives. This of course works for all the terms except for kinetic energy. Kinetic energy may be differentiated directly with respect to the orbital. We thus have:

$$\frac{\delta E}{\delta \psi_i^*(r)} = \frac{\delta T_S}{\delta \psi_i^*(r)} + \left[\frac{\delta E_{ext}}{\delta n(r)} + \frac{\delta E_H}{\delta n(r)} + \frac{\delta E_{xc}}{\delta n(r)}\right]\frac{\delta n(r)}{\delta \psi_i^*(r)} = \in_i \psi_i(r)$$

(2.15)

Finally,

$$-\frac{1}{2}\nabla^2\psi_i(r) + \left[V(r) + \int dr'\frac{n(r')}{|r-r'|} + \{\in_{xc}(r) + n(r)\frac{\delta \in_{xc}[n]}{\delta n(r)}\}\right]\psi_i(r) = \in_i \psi_i \qquad (2.16)$$

Where the first, second and third terms in the large brackets gives the KS potential:

$$V_{ks} = V(r) + V_H + V_{xc}$$

(2.17)

Where V_H is introduced as the Hatree potential, and the exchange-correlation potential, V_{xc}.

Equation (2.16) is a system of equations, which when solved simultaneously represents the many system in terms of single-particle orbitals.

So far, the entire field of DFT rest on two-fundamental mathematical theorems proved by kohn and Hohenberg and the derivation of a set of equations by KS in the mid-1960's [17].

3. METHODOLOGY

In this research, the main production method is DFT to compute the total energy and derived quantities of molecules and solids of condensed matter in its electronic ground state [1]. DFT in the LDA is used here. An all-electron full-potential treatment that is both computationally efficient and accurate is achieved for periodic and cluster geometries on equal footing, including relaxation and ab-initio molecular dynamics [5, 9].

To calculate the cohesive energies, we first compute the total energies of Li, Cr, Fe and Mo for single free atom and their bulk structures. The cohesive energies can be calculated from the total energies using the equation: $E_{coh} = -\frac{E_{bulk} - NE_{atom}}{N} = -\left[\frac{E_{bulk}}{N} - E_{atom}\right]$

(3.1)

FHI-aims code upgrade 6 (released on 17th July, 2011; version 071711_6) was used for calculations. It works on any Linux based operating system. Computations can only be carried out after building an executable binary file. FHI-aims package is distributed in a source code form and requires: a working Linux based operating system (ubuntu 11.10 in this case), a working FORTRAN 95(or later) compiler. In this case we use x86 type computer and therefore intel's ifort (specifically composerxe 2011.6.233) was installed for this work, and also a compiler version of lapack library, and a library providing optimized basic linear algebra subroutines (BLAS). Standard libraries such as intel's mkl or IBM's essl provide both lapack and BLAS support. Intel's composerxe 2011.6.233 comes with mkl.

All necessary adjustment were made for building the executable binary file for running the code [1, 5]. FHI-aims require two input files: Control.in:- which contains all run time-specific information and Geometry.in:- which contains information directly related to the atomic structure for a given calculation. The two input files must be placed in the same directory where FHI-aims binary file is invoked at the terminal [1, 5].

LDA is a known widely used approximation that works for materials with slowly varying or homogeneous electron density but in practice demonstrate surprisingly accurate results for a wide range of ionic, covalent and metallic materials.

LDA is requested as the approximation to the exchange-correlation energy functional in the code. This is because LDA is convenient and simple in calculation of atomic and molecular structures. The functional depends only on the density at the coordinate where the functional is evaluated. The FHI-aims input files are constructed and production run are made to give results in the output files.

4. RESULTS AND DISCUSSION

The results from the output files were used to generate tables of values which were in turn used to plot graphs of total energies against number of iterations in order to obtain optimized parameters for BCC (Li, Cr, Fe and Mo) lattices within LDA. The optimized parameters were then used to obtain the cohesive energies of the BCC lattices.

Below are results obtained for the calculations of cohesive energies and their discussion:

Table 1: input and output parameters for BCC metals

Metals	Input parameter	Output parameters	
	Lattice constant, a (Ǻ)	Total energy(atom) (eV/atom)	Total energy(bulk) (eV/atom)
Li	3.49	-199.82087698	-201.63742548
Cr	2.89	-28629.40409260	-28634.73682541
Fe	2.87	-34699.31049185	-34704.66534706
Mo	3.15	-111111.31729126	-111119.34204722

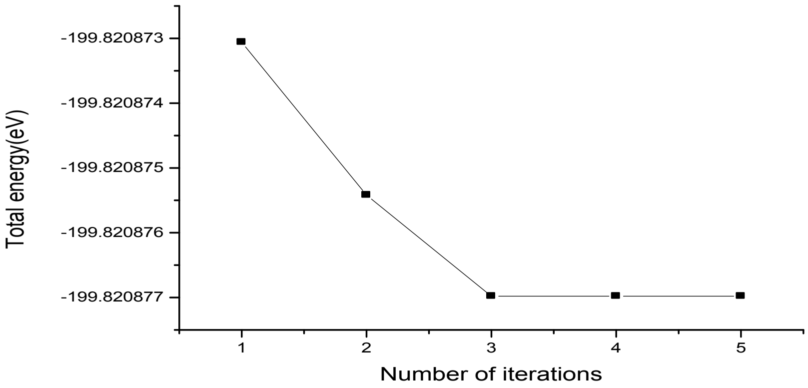

Fig.1. Binding curve of total energy against no. of iterations for pw-lda Li atom

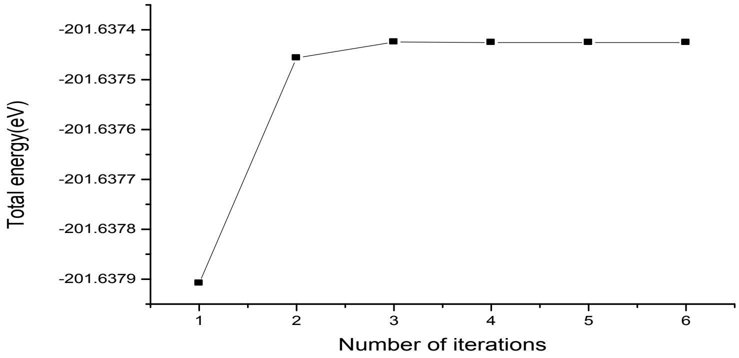

Fig.2. Binding curve of total energy against no. of iterations for pw-lda Li bulk

Fig.1. shows that the total energy decreases while number of iterations increases and converges faster with stability from 3rd iteration to the last iteration because the electrons of lithium atom are pulled closer to the positive charged nucleus(since they are physically closer to the atom and thus less reactive than the other alkali metals. Fig.2. on the other hand shows that the total energy tends towards stability as the number of iterations increases, taking more computational time and yielding more stable total energy than Li atom owing to metallic bonding in lithium bulk.

The cohesive energy obtained for bcc lithium was calculated to be approximately 1.82eV. This result is in good agreement as compared to experimental value of 1.63eV [3]. Other result is 0.124Ry, equivalently 1.70eV [2].

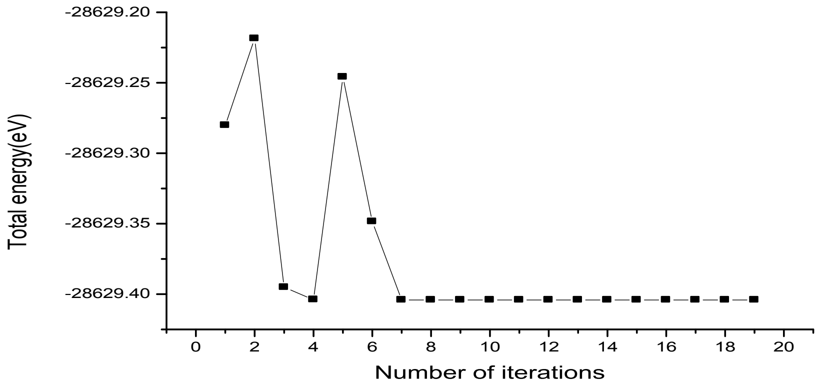

Fig.3. Binding curve of total energy against no. of iterations for pw-lda Cr atom

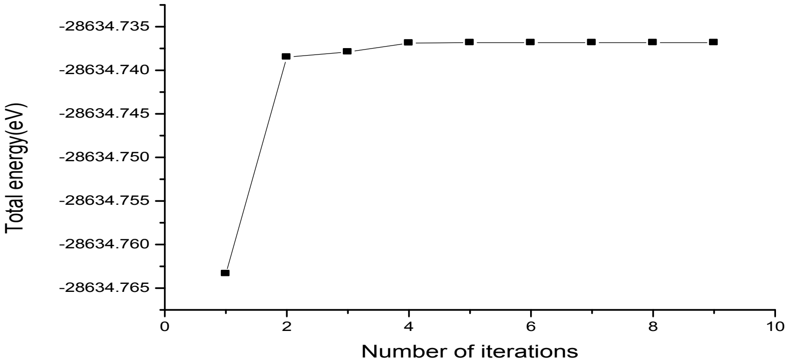

Fig.4. Binding curve of total energy against no. of iterations for pw-lda Cr bulk

From Fig.3, clearly the total energy for single chromium atom is unstable at early iterations due to half-filled and unpaired d-orbital electrons and its eagerness to bond but becomes stable from the 7th iteration. However, the total energy of Cr bulk in Fig.4 becomes stable and converges with fewer numbers of iterations after a sharp rise from 1st iteration to the 2nd iteration.

The cohesive energy of bcc chromium is calculated to be approximately 5.33eV which is in reasonable agreement with experimental value of 4.10eV [10]. Other result by P.H.T. Philipsen et al is 5.22eV [15]

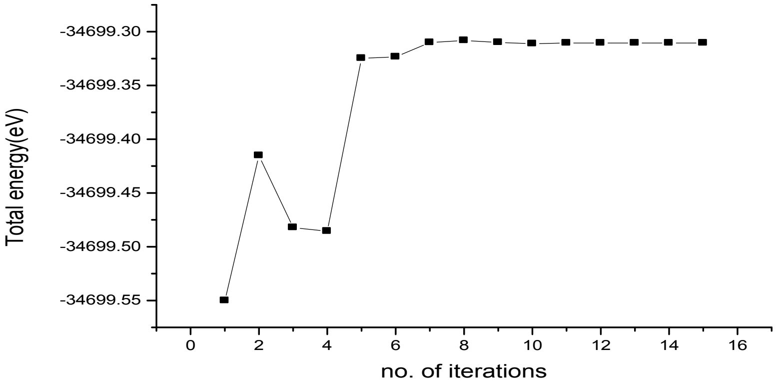

Fig.5. Binding curve of total energy against no. of iterations for pw-lda Fe atom

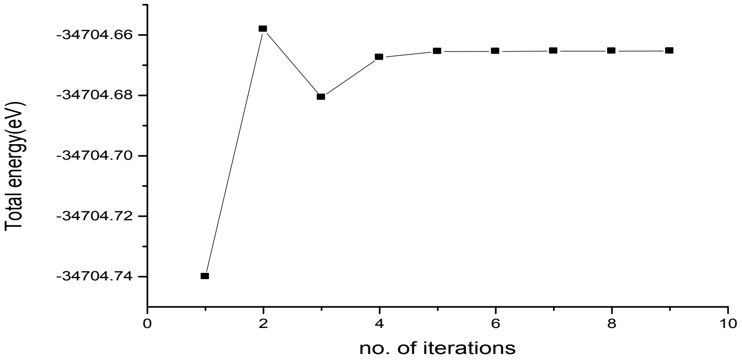

Fig.6. Binding curve of total energy against no. of iterations for pw-lda Fe bulk

Fig.5 shows that the total energy for single iron atom is unstable at early iterations due to unpaired d-orbital electrons and its eagerness to bond but becomes stable from the 7th iteration. In fig.6, the total energy of iron bulk significantly rises from the 1st iteration to the 2nd iteration before a stepwise fall and rise to the 4th iteration to become stable and converged. To attain efficient convergence the linear mixing parameter and broader smearing were chosen carefully since magnetic metals are hard to converge [20]

The cohesive energy was calculated to be approximately 5.35eV which is in reasonable agreement with experimental value of 4.28eV [10]. Other result shows cohesive energy of Fe to be 6.25eV [15].

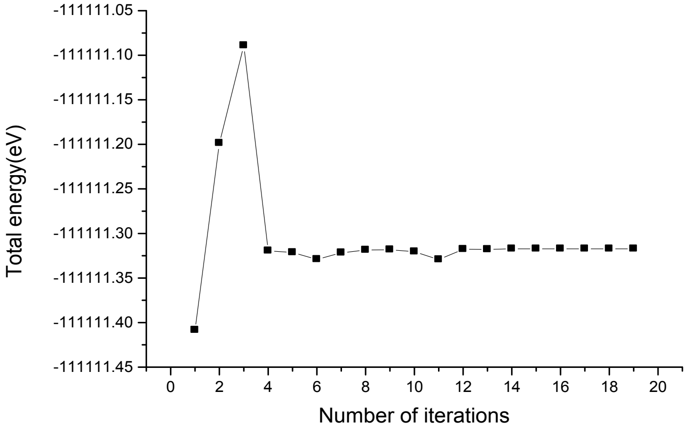

Fig.7. Binding curve of total energy against no. of iterations for pw-lda Mo atom

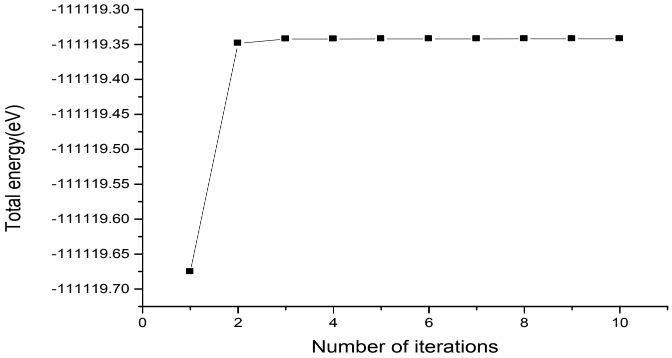

Fig.8. Binding curve of total energy against no. of iterations for pw-lda Mo bulk

Fig.7. shows that the total energy of Mo atom is unstable also due to half-filled d- orbitals and unpaired valence electrons just as chromium discussed above until the 12th iteration when it becomes stable for the rest of the convergence cycles. Fig.8. on the other hand shows that the total energy makes a sharp rise and immediately begins to converge from the 2nd iteration to the last iteration. Mo bulk clearly shows more stability with less number of iterations than Mo atom.

The calculated value for cohesive energy bcc molybdenum is approximately 8.02eV which is in reasonable agreement with experimental value of 6.82eV [10]. LAPW calculation of cohesive energy of Mo is 7.782eV [13].

5 CONCLUSIONS

The contribution of a constituent atom to the total energy E_{tot} might be variationally improved by basis functions sitting on adjacent atoms, thus leading to an overestimating of E_{coh}. Using atomic states, however, the total energy is already converged at the level of the minimal basis, and neighboring basis functions have no effects [7].

The cohesive energies of the bcc lattices were calculated with grids of 12x12x12 for all metals except iron with 16x16x16; a setting which gives a good compromise of computational times and physical accuracy within LDA of the FHI-aims code. The values obtained are in agreement with experimental values and literature reports within some reasonable percentage error. The overestimation observed in Cr, Fe as well as Mo is likely from the exchange correlation contribution to the cohesive energy. The overbinding of the LDA appears to be related to a not sufficiently repulsive exchange contribution to the cohesive energy . Also, the large overbinding for Iron can be partly ascribed to the unphysical spherical restriction on the density of the iron atom [15]. The cohesive energies calculated for Li, Cr, Fe and Mo vary from experiment by 11.4%, 30.0%, 25.0%, and 17.6%.

REFERENCES

[1] Blum, V., Gehrke R, Hanke F, Havu P, Havu V, Ren X, Reuter K, Scheffler M. Ab initio molecular simulations with numeric atom-centered orbitals. Computer Physics Communications, 180, (2009), 2175-2196.

[2] Ching W.Y. and Callaway J. Band Structure, Cohesive energy, and Compton profile of Lithium, Department of Physics and Astronomy, Louisiana State University, Baton Rouge, Louisiana 70803. Phys. Rev. B 9, 5115 (1974).

[3] Dean L. The elements handbook (Available online at https://www.knowlegdedoor.com/2/elements_handbook/cohesive energy.html. (Accessed on 30/08/2016).

[4] Francis A., S.G. Abdu, Ali Haruna and Danladi E. Computation of the cohesive energies of NaCl, SiO_2 and Al using density functional theory, Phys. Sc. Int. Journal 11(3), 2016.

[5]Galadanci, G.S.M and Garba B. Computations of the Ground State Cohesive properties Of Alas Crystalline Structure Using Fhi-Aims Code, Department of Physics, Bayero University, Kano, Nigeria. IOSR-JAP, vol 4, Issue 5 (sep. -oct. 2013), PP 85-95.

[6] Galperin, Y. Introduction to modern solid state physics, (2002). Available @ http://wwwgradinetti.org/teaching/chem 121/assests/. (Accessed on 18/08/2016).

[7] Gehrke R. First Principle Basin-Hopping for the Structure Determination of Atomic clusters, 2008.

[8] Giannozzi, p. Density functional theory for electronic structure calculations struttura della material Vol. I, (2005).

[9] Havu V., Blum V., Havu P., and Scheffler M. Efficient O(N) integration for all-electron electronic structure calculation using numeric basis functions. J. Comp. Phys., (2009).

[10] Jian-Min Zhang, Yan-Ni Wen, Ke-Wei Xu. Atomic Simulation of the vacancies in BCC metals MAEAM", Central European journal of physics, CEJP 4(4) 2006 481-493.

[11] Kittel, C. Introduction to solid state physics 7th edition, John Willey, Newyork. (1996).

[12] Legrain, F.C.G. Comparative studies of Li, Na, Mg insertion in elemental group IV materials and oxides: material choices for post-lithium batteries, National university of Singapore, (2016).

[13] L.F. Matheiss and D.R. Hamann Linear Augumented-Plane-Wave Calculations of the Structural Properties of bulk Cr, Mo, and W", AT&T Bell Laboratories, Murray Hill, New Jersey 07974. Phys Rev. B 33, 823 (1986).

[14] Parr, R. G., Yang,W. Density functional theory of atoms and molecules (oxford university press, Newyork), (1989).

[15] P.H.T. Philipsen and E.J.Baerends, Cohesive energy of 3d transition metals: Density Functional Theory of atomic and bulk calculations. Theoretical Chemistry Department, Vrije Universiteit, De Boelelaan 1083,1081 HV Amsterdam, The Netherlands. Phys. Rev. B vol. 54 No.8, (1996)

[16] Shahriar G. and Farzane Y. Structural properties, Theory Functional Calculations (DFT), Natural Bond Orbital and Energies For The N-(3-CHLORO-1H-INDAZOLE-5-YL)-4-METHOXYBENZENE SULFONAMIDE, Department of chemistry, Faculty of science, Imam Khomeini international University, Qazvin, Iran. Asian Jounal of Basic and Applied Sciences, Vol. 1, No. 1, 2014.

[17] Sholl, D. S., Steckel, J. A. Density functional theory: A practical introduction (A John Willey & sons, inc., publication), (2009).

[18] Tuckerman M. Intoduction to DFT. Maria Currie Tutorial Series: Modelling Biomolecules. Dec. 6-11, 2004.

[19] Verma, A.S., Sarkar, B.K. and Jindal V.K. Cohesive Energy of Zincblende(AIIIBv and AIIBVI) structured solids, pramana journal of physics, India Academy of Science (2010),Vol.74, No.5 pp.85855.

[20] Wieferink, J., Nemec, I., Blum, V. Tutorial II periodic systems manuscript for exercise problems presented at the hands –on tutorial workshop on ab-initio molecular simulation at Friz-Haber Institute der max-planck-Gesellschaft Berlin, July 14, 2011.