Computation of the Cohesive Energies of NaCl, SiO$_2$ and Al Using Density Functional Theory

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Authors' contributions

This work was carried out in collaboration between all authors. Authors AF and SGA designed the study, author AF undertook the experimental work, performed the analysis, wrote the protocol, wrote the first draft of the manuscript and managed literature searches. Author AH managed the analyses of the study and literature searches. Author ED managed literature searches. All authors read and approved the final manuscript.

Original Research Article

ABSTRACT

In this paper, the cohesive energies of Sodium Chloride (NaCl), Silicon dioxide (SiO$_2$) and Aluminum (Al) based on computer code FHI-aims were calculated using Density Functional Theory. The code has several input parameters in which some of the variables were optimized. The cohesive energies of NaCl, SiO$_2$ and Al were calculated within Local Density Approximation (LDA) of Perdew Wang of the density functional theory. The results obtained from the computation of the cohesive energies of NaCl, SiO$_2$ and Al were 8.38 eV, 12.32 eV and 3.64 eV respectively which is in good agreement when compared to the experimental values of 8.18,12.94 and 3.39eV for NaCl, SiO$_2$ and Al respectively. These energies are within reasonable percentage errors of 2.4%, 4.8% and 6.9% respectively.

Keywords: Total and cohesive energy; DFT; lattice constant; bulk modulus; ground state; LDA.

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1. INTRODUCTION

Total and Cohesive Energy calculations employing density-functional theory represent a reliable tool in condensed matter physics, material science, and physical chemistry. A large variety of applications such as in molecules, bulk materials and surfaces have proven the power of these methods in analyzing as well as predicting non-equilibrium and equilibrium properties. Density-functional theory (DFT) is one of the most popular and successful quantum mechanical approaches to matter. It is nowadays routinely applied for computations of ground state properties of molecules and solids such as the binding energy of molecules and the band structure of solids in physics. This is a computational material science research work in which the Cohesive Energies of NaCl, SiO_2 and Al were calculated using DFT based code FHI-aims as a tool. The different compounds or materials were selected to enable the author carry out a comparative analysis in solids with different cohesion.

In computational nanoscience, focus is made on atoms, molecules and solids, based on their structure and cohesive properties, and how they interact with each other. Emphasis are employed on the properties of specific materials rather than universal properties of all, and our interest on the structure and binding, means that, cohesive energy E_{coh} of a system is very important. Cohesive energy of a system is seen as the energy that must be added to a crystal to separate its components into neutral free atoms at rest, at infinite separation, with some electronic configuration [1,2]. 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 about the stability and chemical reactivity of solids. Eventually, it is the quantity which determines the structure, because different possible structures would have different cohesive energies [3]. The cohesive energy of a solid is commonly referred to as the energy required in disassembling it into constituent atoms or molecules. The determination of cohesive energy therefore helps us to understand the nature and magnitude of interactions that exist among constituent parts of solids. In solid compounds and transition metals, the description of cohesive energy involves the fundamental different types of interaction and bulk modules of diatomic solid. For any given element its surface energy is a fraction of its cohesive [4].

In condensed state, atoms are held together by cohesive forces which are the total forces exerted by an atom on its nearest neighbours. In most cases, it is very difficult to measure forces because ultimate strength and elastic limit depend on the imperfections of samples in mechanical tests. Therefore, various physical properties associated with the cohesive forces characterizing in a way, the strength of interaction bonds in a crystal are used as measure of these forces among atom in a crystal lattice.

Many powerful methods for solving Schrodinger's equation have been developed during decades of struggling with the many-body problem. The methods are Nearly-Free-Electron Approximation, Cellular Method, Augmented Plane Wave Method, Scattering Matrix and Green's Function Method, Orthorgonolized Plane Wave Method, Pseudopotential Method, Green's Function Cellular Method. These methods are time consuming, bulky or cumbersome posing problems to researchers in this field. In the light of the above, DFT a powerful tool that replace the many-body electronic wave function used in placed of the above mentioned methods with the electronic density as the basic quantity used in this research work to calculate the cohesive energies of NaCl, SiO_2 and Al.

In this research work, the cohesive energies of NaCl, SiO_2, and Al were computed based on the DFT package FHI-aims code as developed by Fritz Haber Institute. From the results obtained, it shows that the cohesive energies ranges from 3.64 eV to 12.32 eV which is in agreement with the experimental values that ranged from 3.39 eV to 12.94 eV.

2. THEORETICAL FRAME WORK

DFT is one of the most widely used methods for calculations of the structure of atoms, molecules, crystals, surfaces, and their interactions [5]. It is one of the most popular and robust theoretical approaches currently available for solving the electronic structures of solids and their surfaces [6]. Although, no other theoretical approach has provided as much basic understanding of the electronic structures of surfaces in general and solid compounds in particular, DFT has proven capable of computing a host of properties of condensed matter and their surfaces to

reasonable accuracy. For these reasons DFT has become a common tool in first principles calculation aimed at describing or even predicting the properties of molecules and condensed matter system [7].

The central theme of DFT, i.e. the notion that it is possible and beneficial to replace the dependence on the external potential $V(r)$ by a dependence on the density distribution $n(r)$, is presented as a straight forward generalization of the familiar Legendre transform from the chemical potential, μ ,to the number of particles N. This approach is used here to introduce the Hohenberg–Kohn energy functional and to obtain the corresponding theorems, using classical non uniform fluids as simple examples. The energy functional for electronic systems is considered next, and the Kohn–Sham equations are derived [5].

2.1 The Hohenberg-Kohn Theorem

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 degradable ground state, it is obvious that there is only one ground state charge density $n(r)$ that corresponds to a given $V(r)$. Hohenberg and kohn demonstrated the opposite, far less obvious result with only one potential $V(r)$ that yields a given ground-state charge density $n(r)$[7].

If we consider a 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 the external potential. The charge density $n(r)$ is defined by Hohenberg and Kohn as [7]:

$$n(r) = N \int \left| \psi(r_1, r_2, r_3, ..., r_N) \right|^2 dr_2 ... dr_N \quad (2.1)$$

Now considering a differential Hamiltonian $H' = T' + U' + V'$ (V and V' do not differ simply by a constant: $V - V' \neq$ constant), with ground state wave function ψ' .Assuming that the ground state charge densities are the same:

$n[V] = n'[V']$. The following inequality holds:

$$E = \langle \psi' | H' | \psi' \rangle < \langle \psi | H' | \psi \rangle = \\ \langle \psi | H + V' - V | \psi \rangle \quad (2.2)$$

That is,

$$E' < E + \int (V(r) - V'(r)) n(r) dx \quad (2.3)$$

The inequality is strict because ψ and ψ' are different being Eigen state of different Hamiltonians. By reversing the primed and unprimed quantities, one obtains a contradictory result. This demonstrates that no two potentials can have the same density.

The first Hohenberg and Kohn theorem that has a straightforward consequence is that of the ground state energy E and is also uniquely determined by the ground state charge density. In mathematical terms E is a functional $E[n(r)]$ of $n(r)$ can be written as;

$$E[n(r)] = (\psi | T + U + V | \psi) = \\ (\psi | T + U | \psi) + (\psi | V | \psi) = F[n(r)] + \int n(r) V(r) dr \quad (2.4)$$

Where $F[n(r)]$ is a universal functional of the charged density $n(r)$ (and of $V(r)$). For this functional a variational principle holds; the ground state energy is minimized by the ground state charge density. In this way, DFT exactly reduces the N -body problem to the determination of a 3-dimensional function $n(r)$ which minimizes a functional $E[n(r)]$ Unfortunately, this is of little use as $F[n(r)]$ is not known.

2.2 The Kohn-Sham Equations

In 1965, Kohn and Sham reformulated the problem in a more familiar form and opened the way to practical application of DFT [8]. The system of interacting electrons is mapped onto an auxiliary 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 representable as

a sum over one-electron orbital (the KS orbitals) $\psi_i(r)$.

$$n(r) = 2\sum_i \left|\psi_i(r)\right|^2 \qquad (2.5)$$

Where i runs from 1 to $\dfrac{N}{2}$. If we assume double occupancy of all states and the Kohn-Sham orbital are the solutions to the Schrodinger equation

$$\left(-\frac{\hbar^2}{2m}\nabla^2 + V_{KS}(r)\right)\psi_i(r) = \in_i \psi_i(r) \quad (2.6)$$

(m is the electron mass) obeying orthogonality constraints;

$$\int \psi_i^*(r)\psi_j(r)dr = \delta_{ij} \qquad (2.7)$$

The existence of a unique potential $V_{ks}(r)$ having $n(r)$ as its ground state charge density is a consequence of the Hohenberg and Kohn theorem which holds irrespective of the form of the electron-electron interaction U.

3. MATERIALS AND METHODS

This research is based on computer package program FHI-aims (Fritz Haber Institute ab-initio molecular simulations) for computational materials science based on quantum-mechanical first principles. The program uses DFT as a main production technique to compute the total energy and derived quantities of molecules and solids of condensed matter in its electronic ground state within the local or semi-local approximations [9]. The program allows to describe electronic in single-quasiparticle excitations in molecules using different self–energy formalisms, and wave function based molecular total energy calculation based on Hartree-Fock and many-body perturbation theory [10].

All calculations were carried out using FHI-aims code upgrade 6 (released on 17th July, 2011; version 071711_6). It only 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, a working Linux-based operating system (Ubuntu 11.10 in this case) and a

working FORTRAN 95 (or later) compiler was installed. In this case we use x86 type computer and therefore intel's ifort compiler (specifically Composerxe 2011.6.233) was installed for this work. A compiled version of lapack library, and a library providing optimized linier 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 and the executable program was successfully build.

FHI-aims requires two input files: **control.in:-** which contains all runtime-specific informations and **geometry.in**:- which contains information directly related to the atomic structure for a given calculation. The two input files must be places in the same directly from where the FHI-aims binary file is invoked at the terminal.

4. RESULTS AND DISCUSSION

The results obtained are based on the output files from the FHI-aims code used for the computations. This is used to obtain the total energies and the number of iterations. Graphs were plotted to obtain the optimized parameters for NaCl, SiO_2 and Al within Local Density Approximation. These solids crystal were optimized and its parameters were then used to calculate the cohesive energies of NaCl, SiO_2 and Al. The result obtained for the computations of the cohesive energies of NaCl, SiO_2 and Al solids are presented and discussed below:

The resulting binding curve in Fig. 4.1 indicates a stable total energy and also the best converged energy of -16882.40709414eV for NaCl. This means that a crystal of sodium Chloride is more stable than a collection of free Na and Cl atoms. This also implies that the Na and Cl atoms attract each other i.e there exist a stronger attractive interatomic force that holds the atoms together thus the energy of the crystal is lower than the energy of the free atoms.

The cohesive energy of NaCl were calculated and the result obtained for the cohesive energy gives 8.38 eV which is in agreement when compared to the experimental value of 8.18 eV [11]. This result shows that the computation of NaCl within the used k-grid for the local density approximation converges, and the calculated cohesive energy varies from the experimental
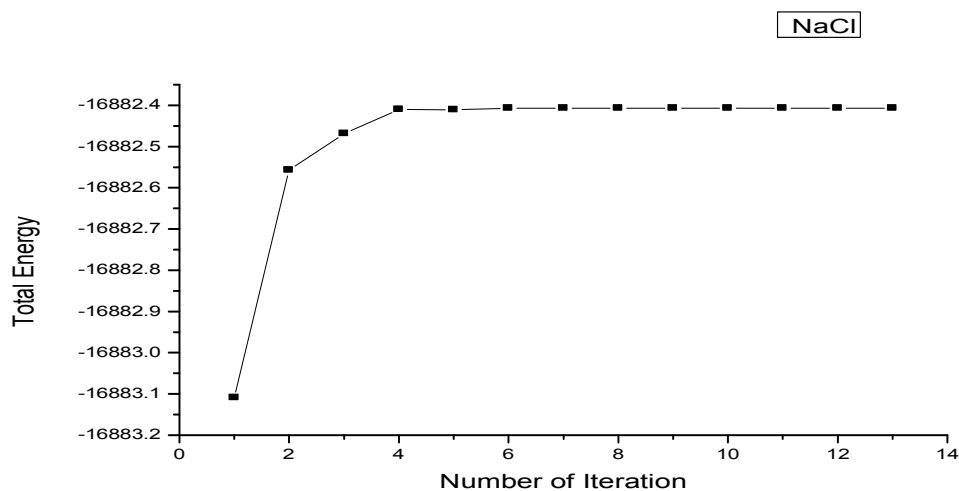
Fig. 4.1. NaCl pw-lda binding curve for total energy

value by 2.4% which can be said to be due to deviations for the atoms used in the DFT calculations rather than the solid [12].

The binding curve in Fig. 4.2 shows that as the total energy increases there is a stepwise increase in the number of iterations. The increase becomes gradual between the 4th and 5th numbers of iteration until a stable energy is reached at -4393.08794679eV where its stability remains fixed all through the rest of the iterations. This large negative total energy is due to the nature of Na ionization energy to be too small and highly accurate in the LDA due largely to error cancellation in the attraction of the valence electron to the core of the atom of Na [13].

Fig. 4.3 shows the graph for the total energy of Cl which decreases linearly with total energy as the number of iteration increases until it reaches the third number of iteration and becomes fixed all through the remaining iterations. This indicate a reverse to what is obtainable in Fig. 4.2 in that the convergence stable trends of Cl shows its ability for electron affinity faster and accurate with lesser number of iteration in the computation of the LDA. This calculation is obtained for only a single atom of Na and Cl which was used in calculating the cohesive energy of NaCl compound.

The resulting binding curve in Fig. 4.4 shows a slow gradual increase until a stable total energy converges at -9899.04372613eV for SiO_2. This
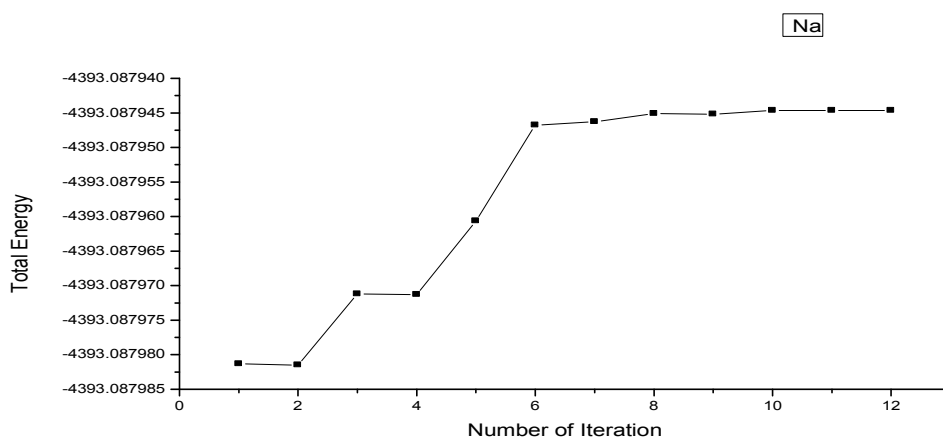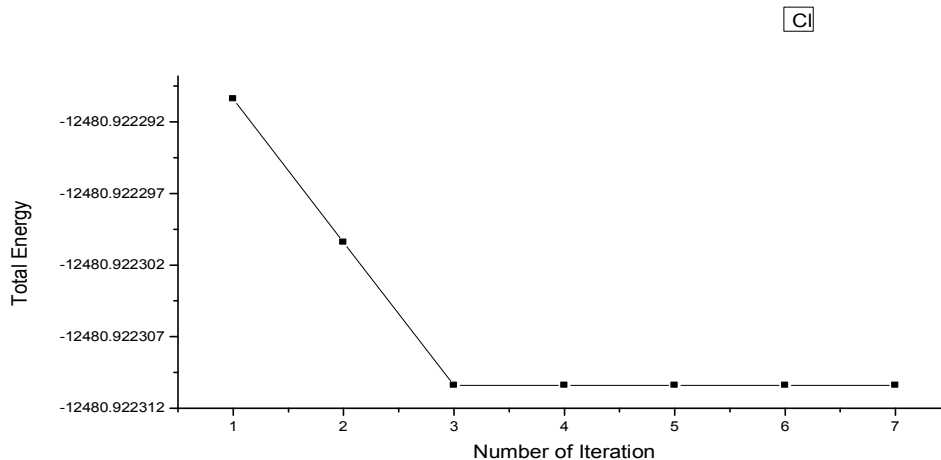

Fig. 4.2. Na pw-lda binding curve for total energy

5

Cl

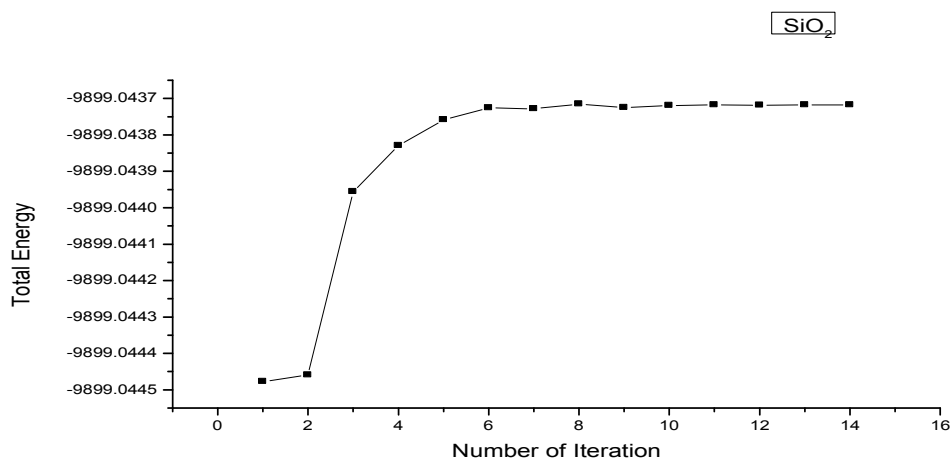**Fig. 4.3. Cl pw-lda binding curve for total energy**

SiO_2

Fig. 4.4. SiO_2 pw-lda binding curve for total energy

means that a crystal of Silicon dioxide is more stable than a collection of free Si and O_2 atoms and the existence of a strong attractive interatomic force that holds the atoms of SiO_2 together thus the energy of the crystal is lesser than the energy of the free atoms.

The calculated value obtained for the cohesive energy of SiO_2 gives 12.32352 eV which is in good agreement when compared to the experimental value of 12.94190 eV [13]. The calculated cohesive energy for SiO_2 is observed to be different from the experiment by a factor of 4.8%.

The trend in Fig. 4.5 decreases downwardly to create a curve pattern until it becomes stable at

the 4th, 5th and 6th, iterations this can be attributed to the covalent bonding that exist in the bulk atom of silicon. The resulting value of the total energy were then used to calculate the cohesive energy of SiO_2.

The binding curve in Fig. 4.6 increases initially as the number of iterations increases and decreases to become stable for a shortwhile before picking up and finally the stable energy converges at the 6th number of iteration for -2044.91989906 eV of energy. The flip-flop nature of the oxygen atom shows oxygen to be barely stable at molecular level and metastable at atomic level owing to high electronegativity of the valence electron of oxygen atom [14]. This correlation converges in LDA.

6

The binding curve in Fig. 4.7 shows that the total energy of the bulk element of aluminum increases as the number of iteration increases and converges steadily this unique nature of the stability of aluminum with respect to free atoms is due to the lowering of the energy of the highest occupied bloch orbital with k=0 in the crystal compared to the electronic of the free atom [15]. This interaction of the cohesive energy within the bulk atom of aluminum is responsible for its high conducting property in electronics and optical devices [16].

The cohesive energy obtained for the bulk Al was calculated and the result is 3.64eV which is also in good agreement when compared to the experimental value of 3.39eV [15]. The calculated difference observed is 6.9% from the experimental value obtained from the work in [17].

The resulting binding curve in Fig. 4.8 shows the decrease in the total energy to create a curve pattern until it becomes stable at the 4th, 5th and 6th iterations, this can be signifies to the metallic bonding that exist in the bulk atom of aluminum. The resulting value of the total energy were then used to calculate the cohesive energy of Al bulk.
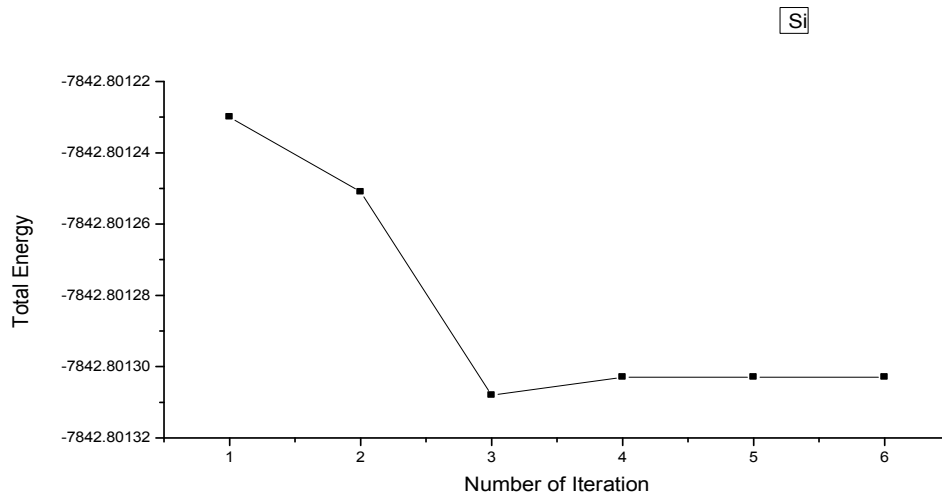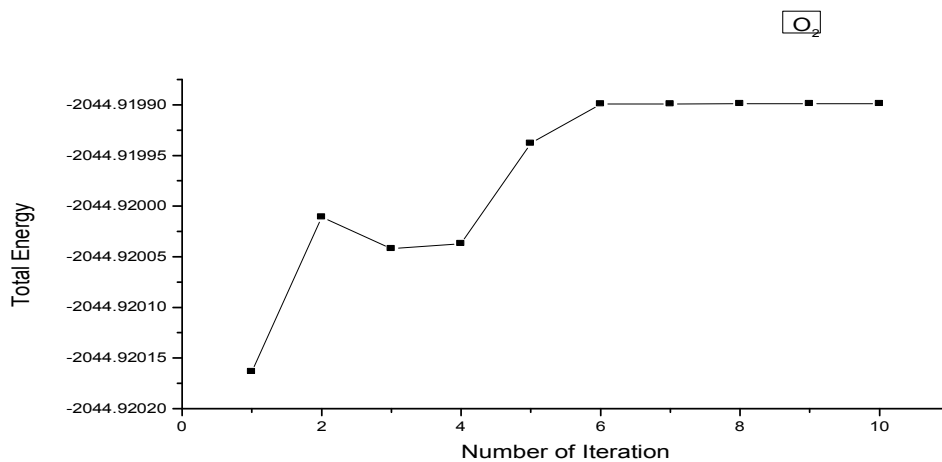

Fig. 4.5. Si pw-lda binding curve for total energy

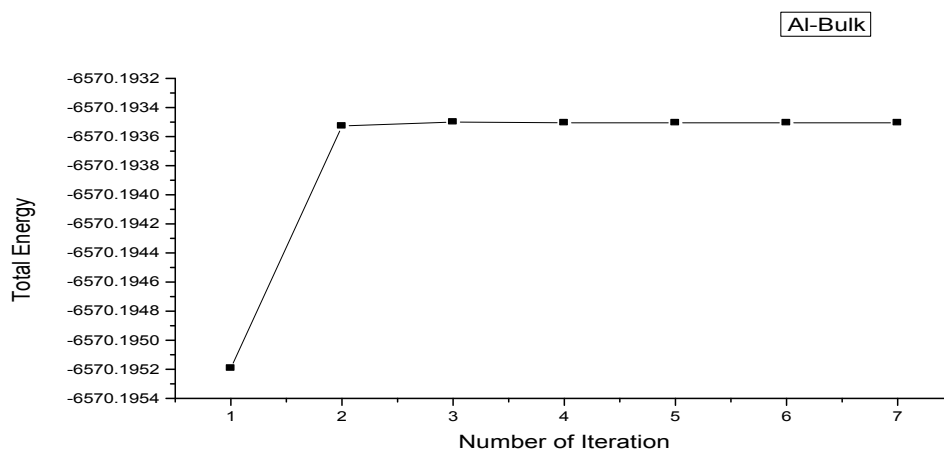
Fig. 4.6. O_2 pw-lda binding curve for total energy

Al-Bulk

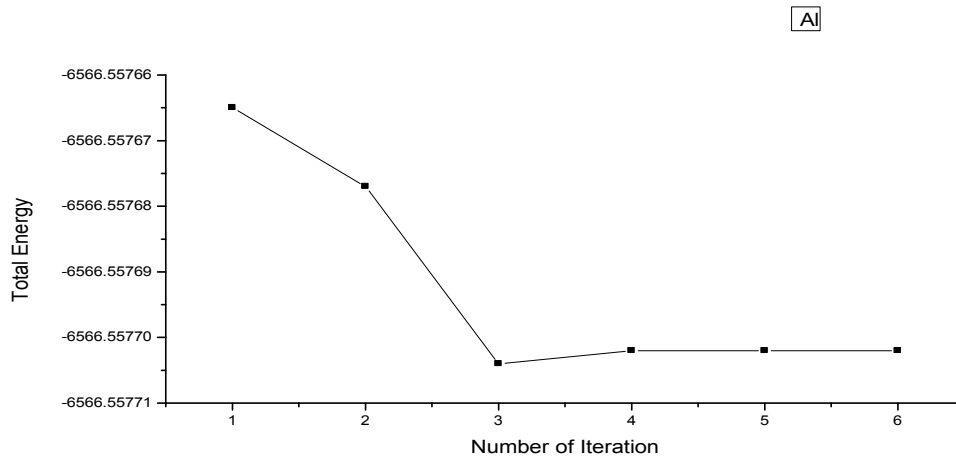**Fig. 4.7. Al Bulk pw-lda binding curve for total energy**

Al

Fig. 4.8. Al pw-lda binding curve for total energy

5. CONCLUSION

The cohesive energies of NaCl for fcc, SiO_2 for hcp and Al for fcc crystal within LDA were calculated. The results of the total energy required for separating the condensed compound during the optimized process is found to converge faster with the 12x12x12 k-grid points in the Brillioun zone of the FHI-aim code. The result presented above have confirmed a faster and more accurate study of the solid considered when compared to literature report of other studies reporting higher iterations before convergence. The values obtained are in agreement with the experimental values reported within some reasonable percentage errors. The calculated cohesive energies for NaCl, SiO_2 and Al are observed to be different from the experiment by 2.4%, 4.8% and 6.9% respectively

for LDA. The major source of this deviation comes from the present DFT calculations of the solid rather than the atom.

COMPETING INTERESTS

Authors have declared that no competing interests exist.

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