

# The Cohesive Energy Calculations of Some FCC (LiCl, NaCl, RbBr, KI) Lattices Using Density Functional Theory

E. A. Joseph<sup>1\*</sup>, M. F. Haque<sup>2</sup>

<sup>1,2</sup>Department of physics, Abubakar Tafawa Balewa University, Bauchi, P.M.B. 0248, Bauchi, Nigeria

**Abstract:** *The cohesive energies of lithium chloride (LiCl), sodium chloride (NaCl), rubidium bromide (RbBr) and potassium iodide (KI) 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 LiCl, NaCl, RbBr and KI were calculated within Perdew Wang local density approximations (LDA) of DFT; the results obtained from the calculations of cohesive energies of LiCl, NaCl, RbBr and KI were approximately 7.69eV, 7.23eV, 6.65eV, and 6.50eV respectively. These results obtained are in the neighborhood of experimentally found values of 8.85eV, 8.18eV, 6.90eV and 6.74 for LiCl, NaCl, RbBr and KI respectively within reasonable percentage errors.*

**Keywords:** FCC; cohesive energy, DFT, ground state, lattice constant, total energy

## 1. Introduction

Density functional theory (DFT) is one of the most popular and quantum-mechanical approaches to many-body systems and are applied to computations of ground-state properties of molecules and the band structure of solids in physics. Calculation of the bulk ground state properties, such as lattice constant, bulk modulus, cohesive energy, and atomic positions, play an important role in the physics of condensed matter [1]. Bulk calculations help us to understand, characterize, and predict mechanical properties of materials in surroundings, under extreme conditions.

In this computational research work, some selected face-centered cubic (FCC) lattices or crystals were investigated using DFT based FHI-aims code as a tool to calculate the cohesive energies of LiCl, NaCl, RbBr and KI.

The FHI-aims code uses DFT as a main production technique to determine electronic and structural properties of molecular or solid condensed matter in its ground state within the local and semi-local approximations [2, 16].

In this study of ionic compounds, each ion is surrounded by six ions of the opposite charge as expected on electrostatic grounds. Halites or rocksalt crystals as these ionic compounds are called can be represented as a face-centred cubic (FCC) lattice with a two-atom basis or as two interpenetrating face centered cubic lattices. The first atom is located half way between lattice points along the FCC unit cell edge. Ionic compounds/crystals are composed of pairs of atoms, in which one member of the pairs donates an electron to the other, and vast number of such pairs is held together by dipoles forces. Because of the strong electrostatic forces between their ions; they tend to have high melting and boiling points. It is of great deal of energy to separate positive and negative ions in a crystal lattice. Ionic compounds have a wide variety of uses and applications.

A recent study used bovine cartilage samples exposed to inflammatory molecules to mimic the effects of arthritis and then treated the tissue with lithium chloride [3]. Molten LiCl is used for the preparation of carbon nanotubes, graphenes and lithium niobate. On the other hand, Large, pure sodium chloride crystals are used to make infrared or ultraviolet optical windows, lenses and prisms; particularly in infrared applications where silicate glasses are not transparent to electromagnetic radiation.

RbBr is used as a nerve sedative while KI is a component in the electrolyte of dye sensitive solar cells (DSSC) along with iodine. 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  $E_{\text{coh}}$  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 [4, 5]. 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 [6].

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, Augmented 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

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method mentioned above with the electron density as the basis quantity [7].

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 [8]. In this research, the cohesive energies of LiCl, NaCl, RbBr and KI were computed based on DFT package FHI-aims code in the range between 6.50eV and 7.67eV which is in reasonable agreement with experimental data in the range between 6.74eV and 8.85eV.

## 2. Theoretical Framework

Density functional theory (DFT) is a quantum mechanical technique used in physics, chemistry and material science to investigate the structural and electronic properties of many body systems. 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 [9, 10, 16].

Traditional methods in electronic structure theory, in particular Hartree-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 [16].

### 2.1 The Hohenberg-Kohn Theorem

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.

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:

$$E[n(r)] = \langle \psi | T + U + V | \psi \rangle = \langle \psi | T + U | \psi \rangle + \langle \psi | V | \psi \rangle = F[n(r)] + \int n(r)V(r)dr \quad (2.7)$$

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 [12]. 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-dimensional function  $n(r)$  which minimizes a functional  $E[n(r)]$ . Unfortunately, this is of little use as  $F[n(r)]$  is not known [9, 16].

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,  $\psi$ . 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

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

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:  $V - V' \neq \text{constant}$ . Assuming that the ground state charge densities are the same:  $n[V] = n[V']$ . The following inequality holds [9, 16]:

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

$$E < E' + \langle \psi' | T + U + V - T - U - V' | \psi' \rangle \quad (2.3)$$

That is

$$E < E' + \int n(r) \{V - V'\} dr \quad (2.4)$$

Conversely,

$$E' < E - \int n(r) \{V - V'\} dr \quad (2.5)$$

Adding (4) and (5) gives

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

The inequality is strict because  $\psi$  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 [11]. We can write that:

### 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 fictitious or 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 represented as a sum over one-electron orbitals (the KS orbitals)  $\psi_i$  [9, 13]:

$$n(r) = 2 \sum_i |\psi_i(r)|^2 \quad (2.8)$$

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:

$$\left( -\frac{\hbar^2}{2m} \nabla^2 + V_{KS}(r) \right) \psi_i(r) = \epsilon_i \psi_i(r) \quad (2.9)$$

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:

$$n(\uparrow)(r) = n(\downarrow)(r) = \frac{1}{2} n(r) \quad (2.10)$$

Therefore, we only need  $N/2$  Kohn-Sham orbitals, to each of which we assign an occupation number of  $f=2$ . These orbitals satisfy the orthogonality condition [12]:

$$\int \psi_i^* \psi_j(r) dr = \delta_{ij} \quad (2.11)$$

Again the density can also be written as:

$$n(r) = \sum_{i=1}^{N/2} |\psi_i(r)|^2 \quad (2.12)$$

And the kinetic energy as

$$T_S = -\frac{1}{2} \sum_{i=1}^{N/2} \langle \psi_i | \nabla^2 | \psi_i \rangle \quad (2.13)$$

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

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

$$V_{KS} = V(r) + V_H + V_{xc} \quad (2.17)$$

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

Equation (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 [11].

### 3. Methodology

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 [2].

To calculate the cohesive energies, we first compute the ground state total energies of LiCl, NaCl, RbBr and KI for

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  $n(r)$ . To solve this problem it is convenient to rewrite the energy functionals as:

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

The first term is the kinetic energy of non-interacting electrons. The second term called the Hartree 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  $E_{xc}$  [9, 16]. 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:

$$\frac{\delta E}{\delta \psi_i^*(r)} = \frac{\delta T_S}{\delta \psi_i^*(r)} + \left[ \frac{\delta E_{ext}}{\delta n(r)} + \frac{\delta E_H}{\delta n(r)} + \frac{\delta E_{xc}}{\delta n(r)} \right] \frac{\delta n(r)}{\delta \psi_i^*(r)} = \epsilon_i \psi_i(r) \quad (2.15)$$

Finally,

single free atom and their bulk. The energies are then converted to the cohesive energies using the equation:

$$E_{coh} = -\frac{E_{bulk} - NE_{atom}}{N} = -\left[ \frac{E_{bulk}}{N} - E_{atom} \right] \quad (3.1)$$

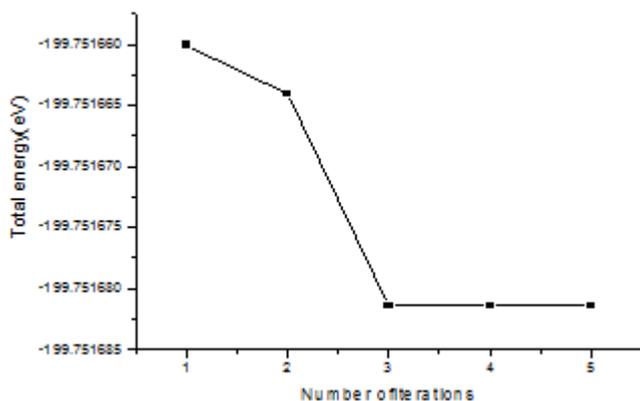
All calculations were carried out using FHI-aims code upgrade 6 (released on 17<sup>th</sup> July, 2011; version 071711\_6). It works on any Linux based operating system. Computations can only be carried out after building an executable binary file. FHI-aims package is distributed in a source code form 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. FHI-aims require two input files: Control.in:- which contains all run time-specific information and Geometry.in:- which contains

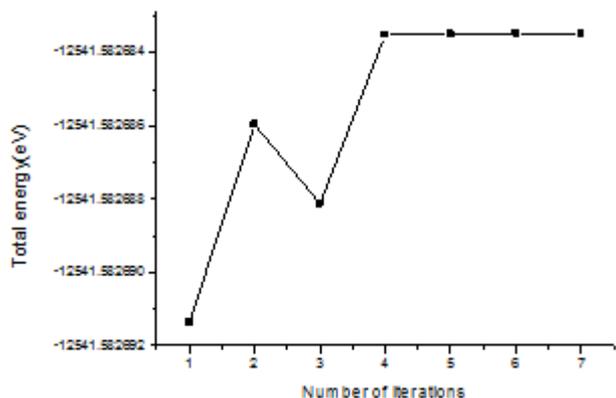
information directly related to the atomic structure for a given calculation. The two input files must be placed in the same directory where FHI-aims binary file is invoked at the terminal [16]. The FHI-aims input files are constructed and production run are made to give results in the output files.

#### 4. Results and Discussion

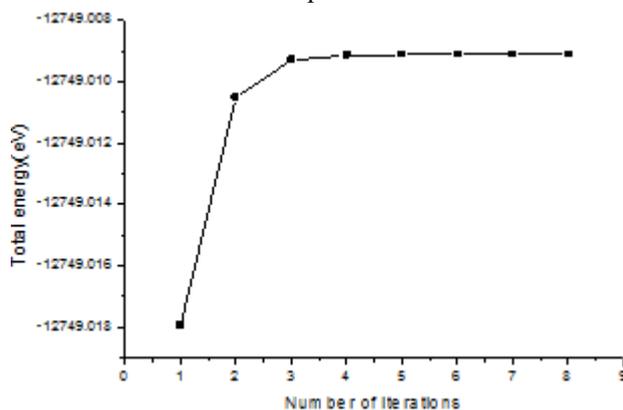
The results of the total energy and the number of iterations from the output file of the FHI-aims code were used to plot graphs to obtain the optimized parameters for LiCl, NaCl, RbBr and KI using LDA as the exchange-correlation functional. The total energies of each compound and their corresponding constituent atoms were used to calculate the cohesive energies of LiCl, NaCl, RbBr and KI. The results obtained are discussed as follows:



**Figure 4.1:** Binding curve of total energy against no. of iterations for pw-lda Li atom



**Figure 4.2:** Binding curve of total energy against no. of iterations for pw-lda Cl atom



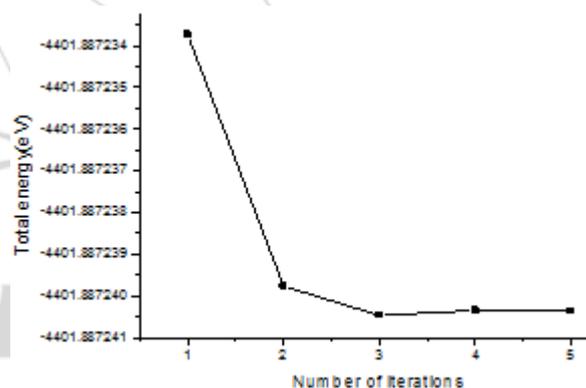
**Figure 4.3:** Binding curve of total energy against no. of iterations for pw-lda LiCl

The resulting binding curves in fig.4.1 and fig.4.4 show how the total energy lowered significantly after the 1<sup>st</sup> and 2<sup>nd</sup> iterations implying instability as a result of low ionization energy of cations (Li and Na ions) before converging through the rest of the iterations.

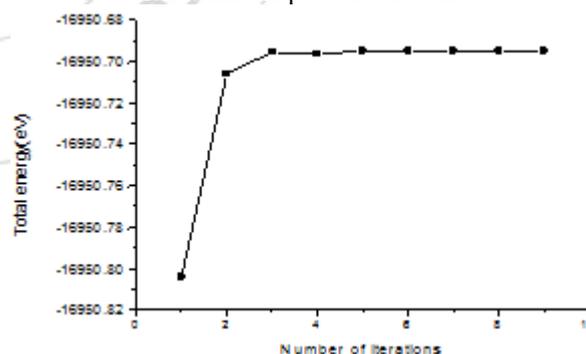
Fig.4.2 shows an opposite trend as the total energy rises in an unstable manner before attaining stability from the 4<sup>th</sup> iteration through the remaining iterations as a result of high electron affinity of anion.

The binding curves in fig.4.3 and fig.4.5 show that the total energy is stable and more converged. This implies that crystals of LiCl and NaCl are more stable than a collection of free Li and Cl atoms, and also Na and Cl atoms. This implies that the corresponding atoms attract each other, that is, there exist a stronger attractive intermolecular force that hold the atoms together thus the energy of the crystals is lower than the energy of their corresponding free atoms[14].

The cohesive energy of LiCl and NaCl was calculated to be approximately 7.67eV and 7.23eV respectively which is in reasonable agreement with experimental values of 8.85eV and 8.18eV respectively [15].



**Figure 4.4:** Binding curve of total energy against no. of iterations for pw-lda Na atom



**Figure 4.5:** Binding curve of total energy against no. of iterations for pw-lda NaCl

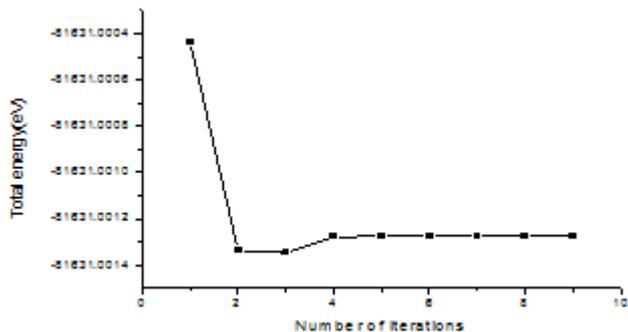


Figure 4.6: Binding curve of total energy against no. of iterations for pw-lda Rb atom

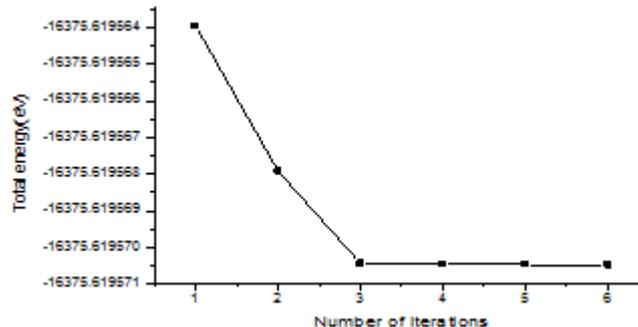


Figure 4.9: Binding curve of total energy against no. of iterations for pw-lda K atom

Fig.4.6 begins fixed iteration at 4<sup>th</sup> iteration to the last iteration while fig.4.9 begins fixed iteration at 3<sup>rd</sup> iteration through the last iteration. The total energy in both cases show instability until the 4<sup>th</sup> and 3<sup>rd</sup> iterations respectively as a result of low ionization energy of cations (Rb and K ions) before converging through the rest of the iterations. The resulting binding curve in Fig.4.7 and fig.4.10 also show an opposite trend as the total energy rises in an unstable manner before attaining stability from the 5<sup>th</sup> iteration through the remaining iterations as a result of high electron affinity of anions (Br and I ions).

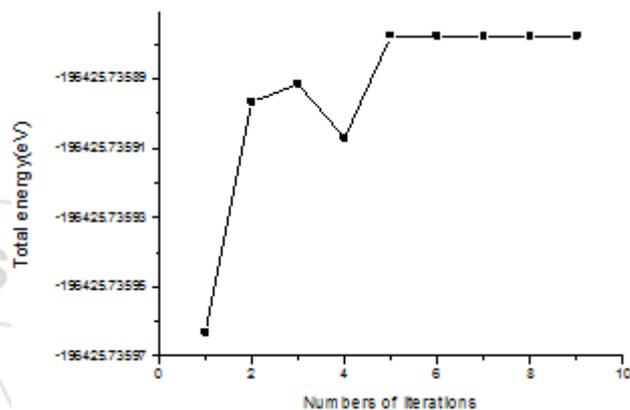


Figure 4.10: Binding curve of total energy against no. of iterations for pw-lda I atom

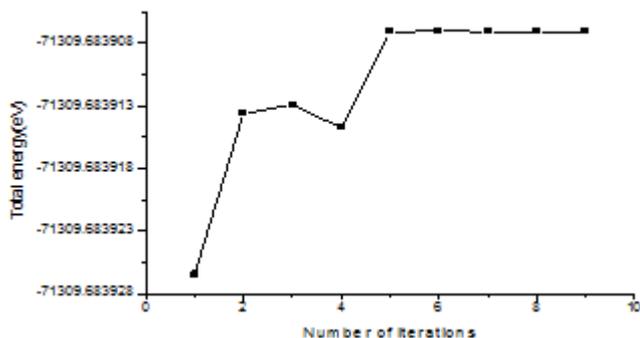


Figure 4.7: Binding curve of total energy against no. of iterations for pw-lda Br atom

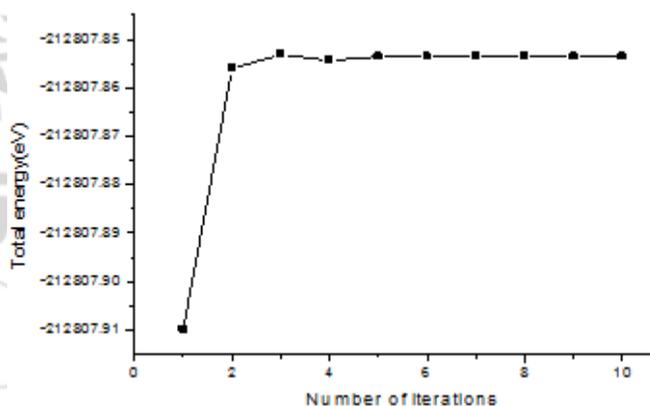


Figure 4.11: Binding curve of total energy against no. of iterations for pw-lda KI

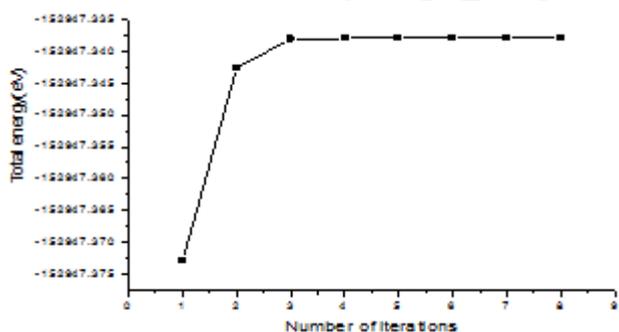


Figure 4.8: Binding curve of total energy against no. of iterations for pw-lda RbBr

The resulting binding curves in fig.4.8 and fig.4.11 show that the total energy is stable and more converged. This implies that crystals of RbBr and KI are more stable than a collection of free Rb and Br atoms; and K and I atoms. Similarly, this implies that the corresponding atoms attract each other, that is, there exist a stronger attractive intermolecular force that hold the atoms together thus the energy of the crystals is lower than the energy of their corresponding free atoms [14].

The cohesive energy of RbBr and KI was calculated to be approximately 6.65eV and 6.50eV respectively which is in good agreement with experimental values of 6.90eV and 6.74eV respectively [15].

## 5. Conclusion

The total energies of the fcc lattices were calculated with grids of 12x12x12 for all compounds; a setting which gives a good compromise of computational times and physical accuracy within LDA of the FHI-aims code. The cohesive energies of FCC LiCl, NaCl, RbBr and KI were calculated with the values underestimated within LDA. The lattice constants of these ionic crystals are inversely proportional to their respective cohesive energies. The cohesive energies calculated for LiCl, NaCl, RbBr and KI vary from experiment by 13.3%, 11.6%, 3.6%, and 3.6%. The values obtained are in agreement with experimental values and literature reports within some reasonable percentage error.

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