Original Research Article

Cohesive Energies Computation of BCC and FCC Crystals Using Density Functional Theory

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ARTICLE INFO	ABSTRACT
	The cohesive energies of BCC (Li, Cr, Fe, Mo), and FCC (LiCl, NaCl, RbBr, KI) solid crystals lattices have been calculated 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 all the elements and compounds under study were calculated within Perdew Wang local density approximation (LDA) of DFT, all the results are in reasonable agreement with experimental measurements. The measurement of cohesive energy should give an idea about lattice interatomic spacing which in turn gives the stability of the crystal.

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 (Galadanci and Garba, 2013) 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 (Galperin 2002). 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 (Verma *et. al.,* 2010). In metallic crystals, atoms are joined together by metallic bond. Metallic crystals are very hard and forms bonds that are most common in metal elements and alloys. Examples of some metals are: lithium (Li), chromium (Cr), iron (Fe) molybdenum (Mo), beryllium (Be), titanium (Ti), zinc, and zirconium. Ionic crystals formed of alkali halides are simply a collection of impenetrable charged spheres, glued together by electrostatic interaction. Apart from the influence on the specific crystalline arrangement chosen for sodium chloride and the other ionic compounds in our case study, the dominant contribution to the cohesive energy comes in any case from the electrostatic interaction (also often called madelung energy E^{mad}). Ionic crystals are simply the binding between electronegative and electropositive elements. Generally, Solids are classified due to their cohesion. There are Van der Waal, metallic, covalent and ionic crystals. In condensed state, atoms are held together by cohesive forces which are the total forces exerted by an atom on its nearest neighbors. The forces responsible for cohesion of solids include: coulomb, magnetic and gravitational forces. But Coulomb force has the major contribution to the cohesion of a solid. In calculating basic properties of solids like cohesive energy, lattice constants, band structures, and density of states, we use DFT as the most popular and successful quantum mechanical approaches to matter (Wieferink 2011). DFT computational codes are used in practice to investigate the structural, magnetic and electronic properties of molecules and defects. This is a computational

material science research in which the ground state property (cohesive energy) of body-centred cubic(BCC) lattices - lithium(Li), chromium(Cr), iron(Fe), molybdenum(Mo) and face-centred cubic (FCC) lattices -Lithium Chloride(LiCl), sodium chloride(NaCl), rubidium bromide(RbBr), potassium iodide (KI) is the subject of this paper.

2. Methods
2.1 Setting up Geometry In and Control.In
In setting up the geometry.in file of a periodic structure in FHI-aims, all three lattice vectors as well as the atomic positions in the unit cell must be specified. The lattice vectors are specified by the keyword lattice_ vector, with a lattice constant 'a' in Å is defined. Also, the same for the geometry.in for FCC. Similarly, the geometry.in for all other structures in BCC and FCC are also created, including geometry.in for all single atom and compounds.

In control.in, the input files for bulk LiCl, NaCl, RbBr, KI, were created with the following settings: Physical settings, SCF settings and k-grid settings.

Also, in control.in, the input files for single atom Li, Cr, Fe, Mo, Cl, Na, Rb, Br, K, I. Both settings for control.in are followed by a copy and paste of the default "tight" species settings for Li, Fe, Mo, as supplied with code: species_defaults/tight/atomic number_atomic symbol_faults.

A bash script named run.sh will be created to calculate total energies of some elements and solid compounds as a function of lattice constant, a. Note that the grid factors refers to the reciprocal lattice vectors in geometry.in. If there are inequivalent lattice vectors, their order in geometry.in determines the ordering of reciprocal lattice vectors in the code. The total energy per atom of each of the structures was plotted as a function of the number of iterations using "Origin" software. From such plots the most stable structure is determined.

2.2 K-Grod Convergence
The total energies of Li, Cr, Fe, Mo, NaCl, LiCl, RbBr and KI, were calculated as a function of the lattice constant for k-grid of 12x12x12. K-point sampling were performed on a 12x12x12 grid for all bulk structures exception of Fe bulk structure for which a 16x16x16 grid were used. All structures were relaxed so as to obtain converged total energy. A graph of all the total energies against the number of iterations is then plotted.

2.3 Calculation of Cohesive Energies
The total energy of a free atom, say fcc, NaCl unit cell is calculated, for the single atom energy, special care has to be taken. First, the free atom is of course spin polarized and we use "spin collinear" instead of "spin none" as well as properly initialize the magnetization with " default_initial_moment hund". Second, we use a more converged basis in particular, we use all basis functions up to "tier 3", the cutting potential is set to "cut_pot 8.3.1.", and the basis dependent confining potentials is turned off with "basis_dep_cutoff 0". The cohesive energy (E_{coh}) of a crystal is the energy per atom needed to separate it into its constituent atoms (E_{coh}) and is defined as;

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

(1)

Where E_{bulk} is the bulk total energy per unit cell and N the number of atoms in the unit cell. E_{atom} is the energy of the isolated atom calculated.

3. Results and Discussion
3.1 Results
Table 1. Pw- LDA Li atom

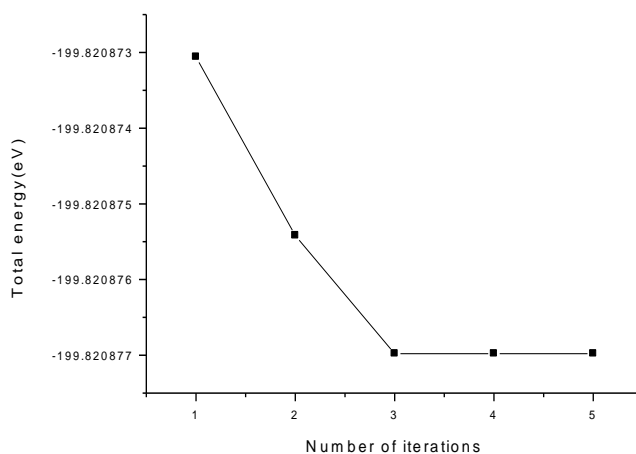| No. of iteration	Total Energy(eV)
1	-199.82087306
2	-199.82087542
3	-199.82087698
4	-199.82087698
5	-199.82087698

Fig. 1. Binding curve of total energy against no. of iteration for pw- LDA Li atom

Table 2. Pw- LDA Li bulk

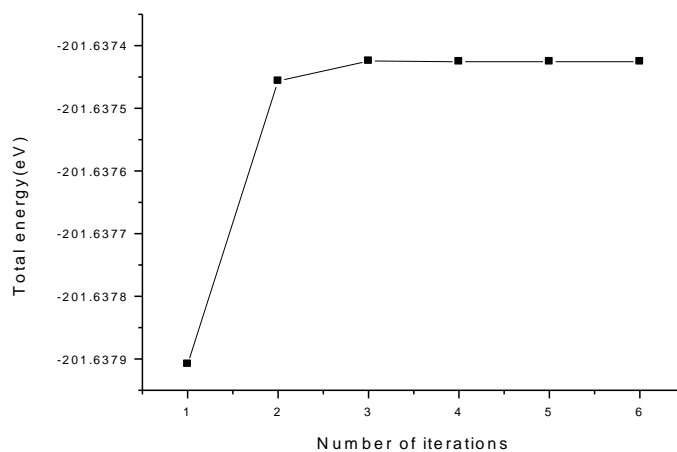| No. of iteration	Total Energy(eV)
1	-201.63790819
2	-201.63745648
3	-201.63742433
4	-201.63742557
5	-201.63742555
6	-201.63742548

Fig. 2. Binding curve of total energy against no. of iteration 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. 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. (Dean 2016). other result is 0.124Ry, equivalently 1.70eV (Ching and Callaway, 1974).

Table 3 Pw- LDA Cr atom

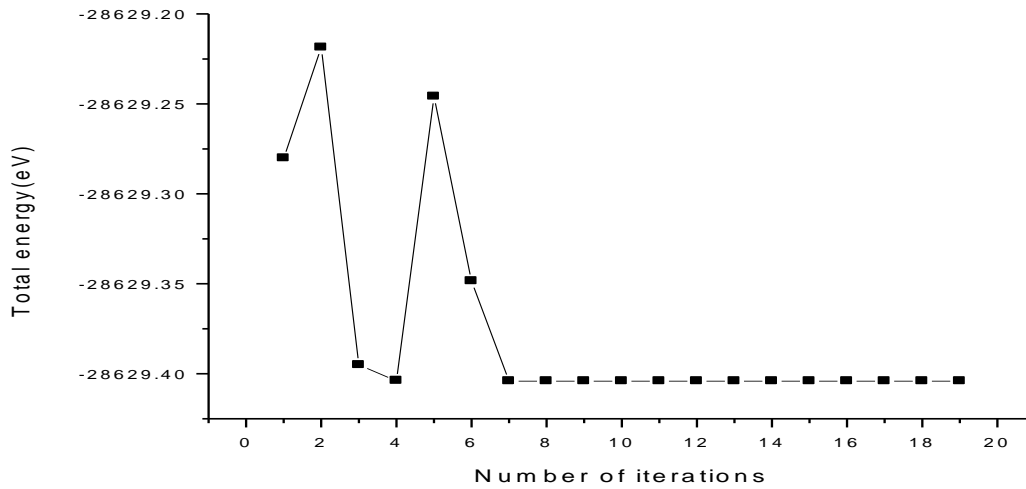| No. of iteration	Total Energy(eV)
1	-28629.28021
2	-28629.21864
3	-28629.39513
4	-28629.40391
5	-28629.24592
6	-28629.34853
7	-28629.40413
8	-28629.4041
9	-28629.40411
10	-28629.4041
11	-28629.4041
12	-28629.4041
13	-28629.4041
14	-28629.40409
15	-28629.40409
16	-28629.40409
17	-28629.40409
18	-28629.40409
19	-28629.40409

Fig. 3. Binding curve of total energy against no. of iteration for Pw- LDA Cr atom

Table 4 Pw- LDA Cr bulk

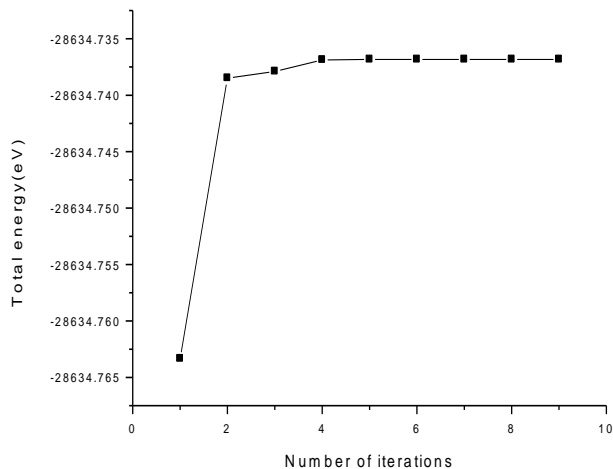| No. of iteration	Total Energy(eV)
1	-28634.76334
2	-28634.73849
3	-28634.7379
4	-28634.73687
5	-28634.73684
6	-28634.73682
7	-28634.73683
8	-28634.73683
9	-28634.73683

Fig. 4. Binding curve of total energy against no. of iteration 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 (Jian *et al.,* 2006). Other result by Philipsen, and Baerends, 1996, is 5.22eV.

Table 5 Pw- LDA Fe atom

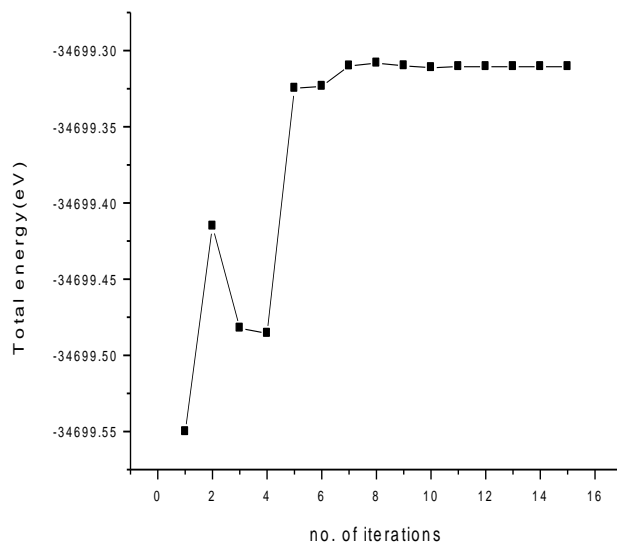| No. of iteration	Total Energy(eV)
1	-34699.55016
2	-34699.41519
3	-34699.48219
4	-34699.48564
5	-34699.3247
6	-34699.32338
7	-34699.31005
8	-34699.30819
9	-34699.31
10	-34699.31116
11	-34699.31057
12	-34699.31053
13	-34699.31049
14	-34699.31049
15	-34699.31049

Fig. 5. Binding curve of total energy against no. of iterations for Pw- LDA Fe atom

Table 6 Pw- LDA Fe bulk

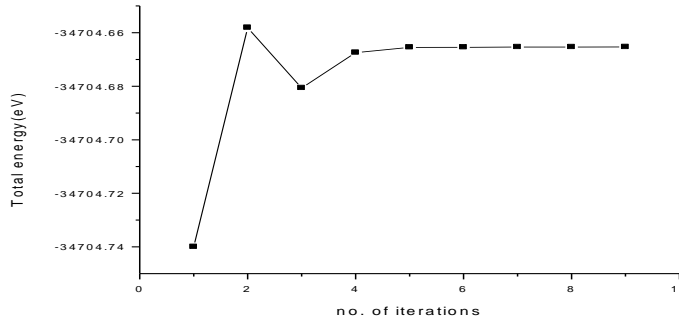| No. of iteration	Total Energy(eV)
1	-34704.74
2	-34704.65815
3	-34704.68068
4	-34704.66745
5	-34704.66548
6	-34704.66546
7	-34704.66535
8	-34704.66535
9	-34704.66535

Fig. 6. Binding curve of total energy against no. of iteration 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 rises to the 4th iteration to become stable and then converges. To attain efficient convergence the linear mixing parameter and broader smearing were chosen carefully since magnetic metals are hard to converge [5]. The cohesive energy was calculated to be approximately 5.35eV which is in reasonable agreement with experimental value of 4.28eV (Jian-Min *et al.,* 2006). Other result shows cohesive energy of Fe to be 6.25eV (Philipsen, and Baerends, 1996).

Table 7 Pw- LDA Mo atom

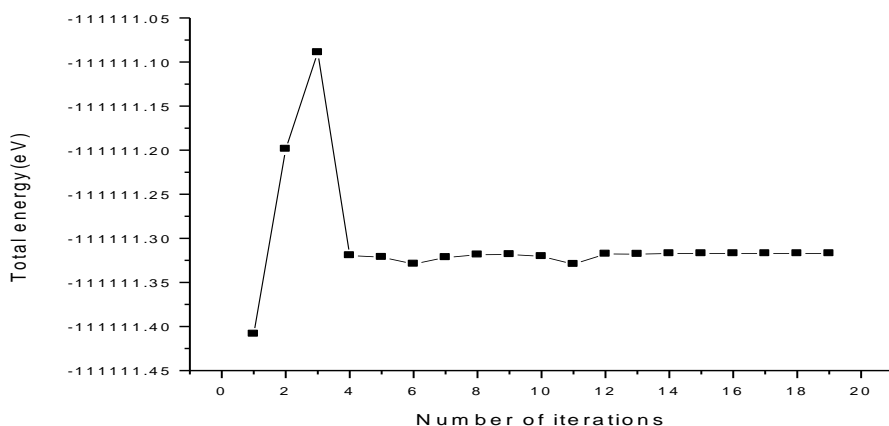| No. of iteration	Total Energy(eV)
1	-111111.4085
2	-111111.1987
3	-111111.0892
4	-111111.3195
5	-111111.3213
6	-111111.3291
7	-111111.3217
8	-111111.3187
9	-111111.3182
10	-111111.3205
11	-111111.3293
12	-111111.3177
13	-111111.3179
14	-111111.3173
15	-111111.3173
16	-111111.3173
17	-111111.3173
18	-111111.3173
19	-111111.3173

Fig. 7. Binding curve of total energy against no. of iteration for Pw- LDA Mo atom

Table 8 Pw- LDA Mo bulk

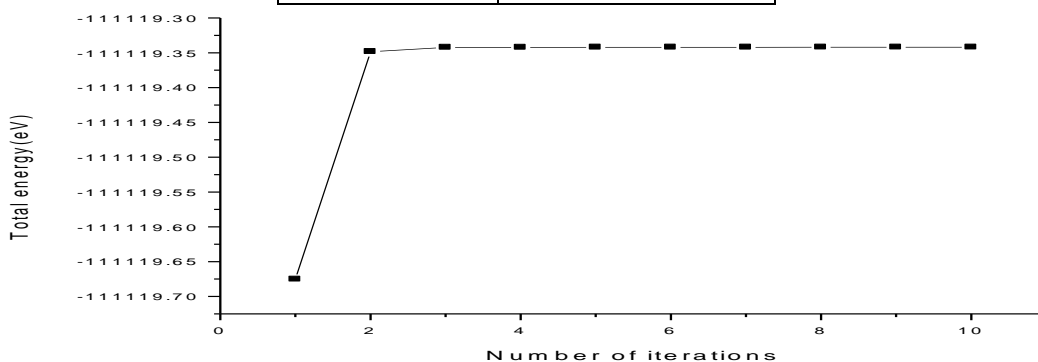| No. of iteration	Total Energy(eV)
1	-111119.67534722
2	-111119.34843093
3	-111119.34229253
4	-111119.34219952
5	-111119.34205003
6	-111119.34205366
7	-111119.34204999
8	-111119.34204708
9	-111119.34204694
10	-111119.34204722

Fig. 8. Binding curve of total energy against no. of iteration 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 agreement with experimental value of 6.82eV (Jian-Min *et al.,* 2006). LAPW calculation of cohesive energy of Mo is 7.782eV (Matheiss, and Hamann, 1986).

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Table 9 Pw- LDA LiCl

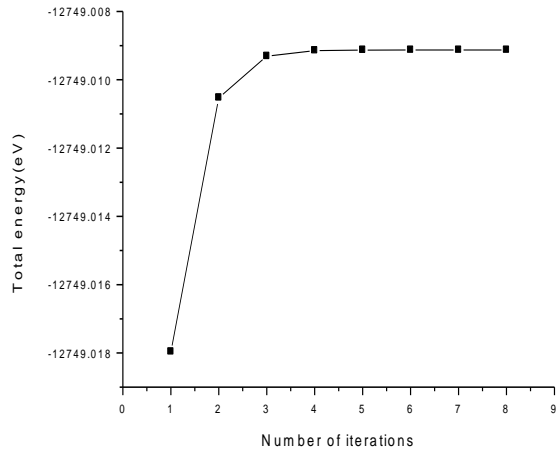| No. of iteration	Total Energy(eV)
1	-12749.01796
2	-12749.01053
3	-12749.00931
4	-12749.00914
5	-12749.00913
6	-12749.00913
7	-12749.00913
8	-12749.00913

Fig.9 Binding curve of total energy against no. of iteration for Pw- LDA LiCl

Table 10 Pw- LDA NaCl

No. of iterations	Total Energy(eV)
1	-16950.80392442
2	-16950.70609620
3	-16950.69561393
4	-16950.69656456
5	-16950.69506612
6	-16950.69503460
7	-16950.69502707
8	-16950.69502716
9	-16950.69502705

Fig.10. Binding curve of total energy against no. of iteration for Pw- LDA NaCl
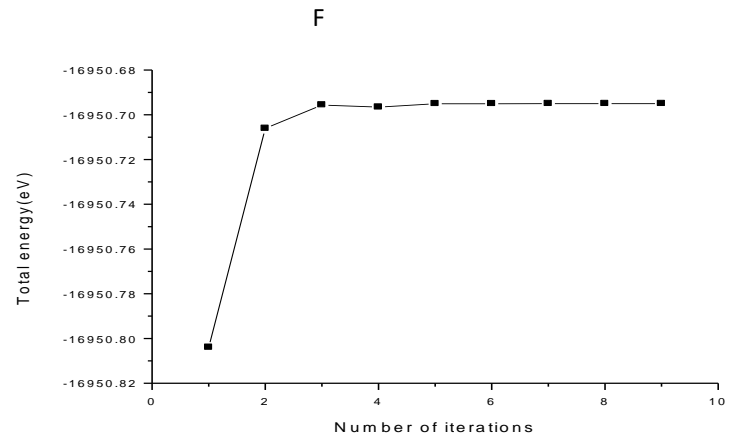
The binding curves in fig.9 and fig.10 show that the total energy is stable and more converged. This implies that crystals of LiCl and NaCl are more stable than a collection of free Li and Cl atoms, and also Na and Cl atoms. This implies that the corresponding atoms attract each other, that is, there 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 (Hans-Eric 2016).

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. Other results are 8.98eV and 8.18eV respectively. (Nagasaka, and Kojima, 1987)

Table 11 Pw- LDA RbBr

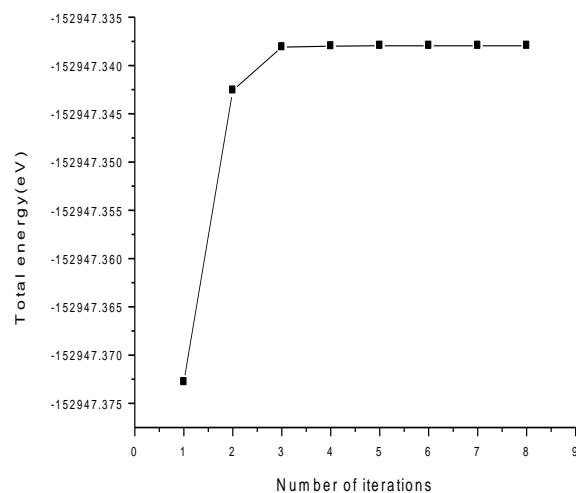| No. of iteration	Total Energy(eV)
1	-152947.3728
2	-152947.3426
3	-152947.3381
4	-152947.338
5	-152947.338
6	-152947.338
7	-152947.338
8	-152947.338

Fig.11. Binding curve of total energy against no. of iteration for Pw- LDA RbBr

Table 12 Pw- LDA KI

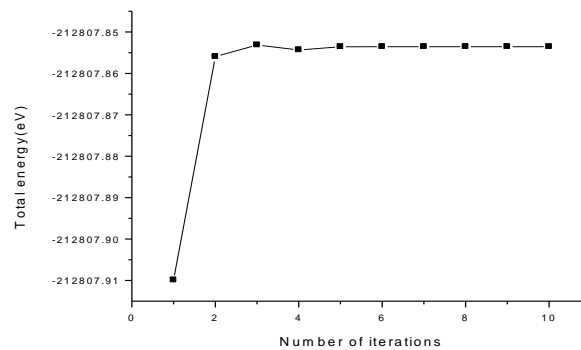| No. of iteration	Total Energy(eV)
1	-212807.9099
2	-212807.856
3	-212807.8531
4	-212807.8543
5	-212807.8536
6	-212807.8535
7	-212807.8536
8	-212807.8536
9	-212807.8536
10	-212807.8536

Fig.12. Binding curve of total energy against no. of iteration for Pw- LDA KI

The resulting binding curves in fig.11 and fig.12 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 (Hans-Eric 2016).

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. Other results are 6.70eV and 6.53eV respectively. (Nagasaka, and Kojima, 1987)

3.2 Discussion

The results from the output files of the FHI-aims code were used to generate tables of the total energies against the number of iterations. Graphs were plotted using "origin" software to obtain the optimized parameters for Li, Cr, Fe, Mo, LiCl, NaCl, RbBr and KI, within LDA. These parameters were then used to obtain the cohesive energies of all the BCC and FCC lattices under study. The results obtained for the computation of the cohesive energies of (Li, Cr, Fe, Mo, LiCl, NaCl, RbBr and KI,) are presented in the tables and plots below.

4. Conclusion

The total energies of BCC (Li, Cr, Fe, Mo) and FCC (LiCl, NaCl, RbBr, KI) lattices were calculated with grids of 12x12x12 for all metals and ionic compounds except iron with 16x16x16. All values obtained are in the neighborhood of experimentally found values and literature reports with some reasonable percentage error. The overestimation observed in Cr and Fe, 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. The cohesive energies of FCC LiCl, NaCl, RbBr and KI were calculated with the values underestimated within LDA. Also the lattice constants of these ionic crystals are inversely proportional to their respective cohesive energies. The cohesive energies calculated for Li, Cr, Fe, Mo, LiCl, NaCl, RbBr and KI, vary from experiment by 11.4%, 30.0%, 25.0%, and 17.6%, 13.3%, 11.6%, 3.6%, and 3.6% respectively. The major source of this deviation comes from the DFT calculations of the solid rather than the atom.

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