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Ionic Liquid Crystal Computation of the Cohesive Energy of (NACL and LICL) Using Density Functional Theory Fhi-Aims Code

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ABSTRACT;The cohesive energies of lithium chloride (LiCl) and sodium chloride (NaCl) 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 and NaCl were calculated within Pardew Burke Ernzerh of (GGA), Perdew Wang and PardewZunger local density approximations (LDA) of DFT; the results obtained from the calculations of cohesive energies of LiCl and NaCl were approximately 4.8eV and 4.1eV respectively. These results obtained are in the neighborhood of experimentally found values of 4.86eVand 4.26eV for LiCl and NaCl, respectively within reasonable percentage errors.

KEYWORDS: DFT, FHI-aims, LDA Density of State, Ionic Liquids, Cohesive energy, Exchange correlation and GGA

I. INTRODUCTION

In the field of modern chemistry, solid state and condensed matter Physics, ionic liquids (ILs) were regarded as the promising solvents and materials for a wealth of possible applications. Nowadays, ILs has superseded this status and has become an amazing reality. Indeed, ILs are currently used in a plethora of industrial processes, as reviewed elsewhere (Andersonet al 2005). There is no doubt about the great utility of ILs in Physics, modern chemistry and technological applications (Reight, 2014). The importance of ILs can be easily evidenced by measuring the number of important reviews published on the subject and their related applications. Many literature surveys are available to different audiences spanning disciplines from asymmetric catalysis, homogeneous catalysis, organic synthesis, green chemistry, biotransformation, analytical chemistry, industrial applications, enzymatic reactions and others (Pentel and Joe, 2013).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 ILs are used as measure of these forces among atoms in them. (Hoketi, 2016).

Cohesive energy of a system is seen as the energy required to break all the bonds associated with one of its constituent molecules into neutral free atoms at rest and at infinite separation with the same electronic configuration. Cohesive energy is one of the parameters that described the nature of chemical bonding and other important properties. Its magnitude tells us about the stability and chemical reactivity of substances. Eventually, it is the quantity which determines the structure of a substance, because different possible structures would have different cohesive energies. The determination of cohesive energy therefore helps us to understand the nature and magnitude of interactions that exist among constituent parts of ILs (Edward, 2012). In ILs, solid compounds and transition metals, the description of cohesive energy involves the study of nature of the different fundamental types of interaction and bulk modules of diatomic liquid or solid. For any given element its surface energy is a fraction of its cohesion.

Cohesive energy calculations via the first principle total energy calculations using DFT is considered satisfactory in the physics of condensed matter systems, material science and physical chemistry (Francis, et al, 2016). The 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. (Wachowiczand Kiejna, 2011). Bulk calculations help us to understand, characterize, and predict mechanical properties of materials in surroundings. Under extreme conditions, DFT based FHI-aims code as a tool to calculate the cohesive energies of many body systems. 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-centered cubic (FCC) lattice with a two-atom basis or as two interpenetrating face centered cubic lattices (Blum, et al, 2009). DFT is useful for studying binding strength in crystal structures and can help to gain information about structural preferences of solids (Sholl and Steckel, 2009). 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.

In this paper, the cohesive energy of ionic crystals LiCl and NaCl were calculated and the results obtained were 4.8eV and 4.1eV respectively. These results are in the neighborhood of experimentally found values of 4.86eV and 4.26eV for LiCl and NaCl, respectively within reasonable percentage errors.

II. THEORETICAL WORK

Density functional theory (DFT) as 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 (Galadanci and Garba, 2013). 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 (Galadanci and Garba, 2013).

2.1 The Hohenberg-Kohn (H-K) Theorem

Hohenberg-Kohn (H-K) first 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 (spin less) 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 charges 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

$$n(r) = N\int \left|\psi\left(r_1, r_2, r_3, \ldots, r_N\right)\right|^2 dr_{2\ldots} dr_N \qquad (2.1)$$

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

Assuming that the ground state charge densities are the same: $n[V] = n'[V']$. The following inequality holds [(Giannozzi, 2005), (Galadanci and Garba 2013)]:

$$E < \left\langle \psi' \middle| H \middle| \psi' \right\rangle = \left\langle \psi' \middle| H' \middle| \psi' \right\rangle + \left\langle \psi' \middle| H - H' \middle| \psi' \right\rangle \qquad (2.2)$$

$$E < E' + \left\langle \psi' \middle| T + U + V - T - U - V' \middle| \psi' \right\rangle \qquad (2.3)$$

That is

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

Conversely,

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

(2.5)

Adding (4) and (5) gives

$$E + E^{'} < E^{'} + E$$

(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 that has a straight forward consequence is that of 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 (Sholl and Steckel, 2009).

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 (Tuckerman, 2004). 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)] is not known (Giannozzi, 2005, Galadanci and Garba, 2013).

2.2 The Kohn-Sham (K-S) 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 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 orbital's (the KS orbital's) $\psi_{i,}$ (Giannozzi, 2005, Martin, 2004).

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

(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:

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

(2.9)

(m is the electron mass) obeying orthogonality constants;

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.

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:

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

Again the density can be written as:

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

And the kinetic energy as

$$T_S = -\frac{1}{2}\sum_{i=1}^{N/2} < \Psi_i|(r)|\nabla^2|\Psi_i(r) >$$

(2.12)

The existence of a unique potential VKS 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 VKS(r) for a given n(r). To solve this problem it is convenient to rewrite the energy functionals as:

$$E = T[n(r)] + E_H[n(r)] + E_{xc}[n(r)] + \int n(r)V_{(r)}d_r$$

(2.13)

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 only term for which no explicit form can be given is Exc [Giannozzi,(2005),Galadanci and Garba (2013)]

Therefore;

$$-\ \frac{1}{2}\nabla^2\Psi_i(r) + \Big[V_r + \int d_{r`}\,\frac{n(r`)}{|r-r`|} + \Big\{E_{xc}(r) +$$

nrδExcnδnrΨir= EὶΨi (2.14)

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

$$V_{KS} = V(r) + V_H + V_{xc} \qquad (2.15)$$

whereV_H is introduced as the Hatree potential, and the exchange correlation potential V_{xc}
Equation (2.14) is a system of equations, which when solved simultaneously represents the many system in terms of single-particle orbital. 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 (Sholl and Steckel, 2009).

III. MATERIALS AND METHOD

In computing the total and cohesive energies of LiCland NaCl for single free atom and their bulk, FHI-aims code is used in the analysis of this research work. FHI-aims (Fritz Haber Institute ab-initio molecular simulations) is an efficient, accurate all-electron, full-potential electronic structure code package for computational molecular and materials science (non-periodic and periodic systems) based on quantum-mechanical first principles. The main production method is the use of DFT to compute the total energy and derived quantities of molecules and solids of condensed matter in its electronic ground state.

3.1Procedure

The first task is to have a Linux based operating system (0S) (Ubuntu 16.04 version installed for this research work) on a computer. FHI-aims is not supported on windows. Since FHI-aims is distributed in source code form, the next task is to compile a powerful executable program. For this, the following mandatory prerequisites are needed.

- A working FORTRAN compiler. A good example is Intel's ifort compiler.
- A compiled version of the lapack library, and a library providing optimized basic linear algebra subroutines (BLAS). Standard commercial libraries such as Intel's mkl provide both lapack and BLAS support. Having an optimized BLAS library for a specific computer system is critical for the performance of FHI-aims.

FHI-aims require two input files — Control.in and Geometry.in— located in the same directory from where the FHI-aims binary is invoked. An output file contains the basic information and result of the calculation such as the total energy, atomic forces, etc. The Geometry.in file contains all information concerning the atomic structure of the system. This includes the nuclear coordinates, which are specified by the keyword atom, followed by Cartesian coordinates (in units of Å) and the descriptor of the species. The Control.in file contains all other physical and technical settings for accurate and efficient convergence of the computations. In particular, it specifies the physical and technical settings for the equations to be solved.

The full algorithmic framework embodied in the FHI-aims computer program package is described in (l-Planck-Gessellschaf, Berlin 2011). The algorithms are based on numerically tabulated atom-centered orbitals (NAOs) to capture a wide range of molecular and materials properties from quantum-mechanical first principles and 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.

The programme runs interactively. You make a menu choice and change physical parameters to the system of interest. First step towards studying periodic systems with FHI-aims is to construct the periodic geometries in the FHI-aims geometry input format (Geometry.in), Next, followed by setting of basic parameters in Control.in for periodic calculations and finally compute total and cohesive energies of these ionic liquids; NaCl and LiCl in geometries.

Geometry.in files for the NaCl and LiCl structures were constructed varying the lattice constants around the experimental lattice constants a of 5.6402Å for NaCland 2.56 Å for LiCl. At each lattice constant, if the symmetry of the system allows the ions to move, a separate geometric optimization must be performed (Aungwa Francis, et al 2017).

In setting up the Geometry.in file of a periodic structure in FHI-aims, the lattice vectors of the two ionic liquids as well as their atomic positions in the unit cell are specified.

Then the output was displayed on the screen and also saved in a file with a file name. The code was then run which displays output on the screen and also saved the result of the run in a file. The total and cohesive energies ofNaCland LiCl were calculated in the Generalized Gradient

Approximation (GGA) and Local Density Approximation (LDA) using the exchange-correlation energy functional respectively. The calculation was performed by using Brillouin-zone of 12×12×12 k the SCF convergence.The total energy for each iteration step is then recorded in a table. The results are then analyzed using the plotting software Origin 5.0.

3.2 Calculation of the Cohesive Energies

The total energy of a free atom for NaCl and LiCl will be calculated as follows: for 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_momenthund"**. Second, we use more converged basis. In particular, we use all basis functions up to "tier 3", the cutting potential will be increased to cut **"cut_pot_8.3.1."** and basis dependent confining potential was turned off with **"basis_dep_cutoff 0".** After calculation total energies of NaCland LiCl crystal structure, the energies are then converted to the cohesive energies using the equation:

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

where E_{bulk} is the total energy per unit cell and N the number of atoms I the unit cell. E_{atom} is the energy of the isolated atom calculated above. Also the amount of energy which is required to pull the crystal apart into a set of free atoms is referred to as the cohesive energy of the crystal.

Cohesive energy = energy of free atoms – crystal energy.

IV. RESULTS AND DISCUSSION

The results obtained are based on the output files from the FHI-aims code used for computation. This is used to deduce the tables of the total energies against the number of iterations. Graphs were plotted to obtain the optimized parameters for the ionic molecules (NaCl and LiCl) respectively, within Local Density Approximation (LDA) and Generalized Gradient Approximation (GGA). These ionic liquids were optimized and its parameters were then used to calculate the cohesive energies of NaCl and LiCl.

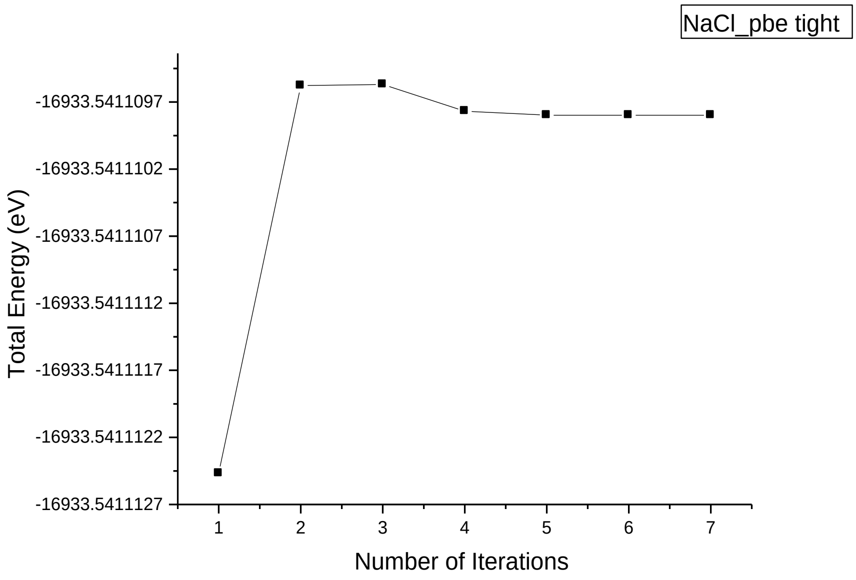

Figure 4.1:Binding curve of total energy against number of iterations for pbeNaCl

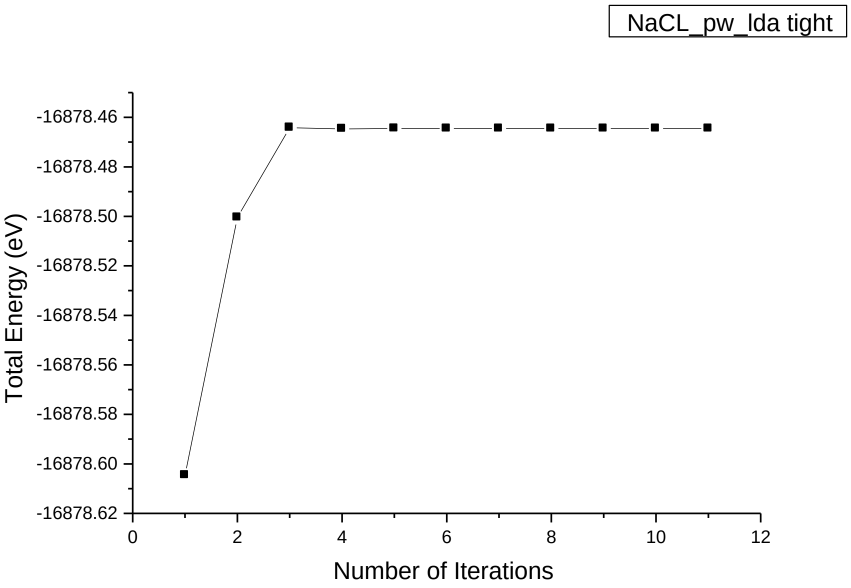

Figure 4.1.2:Binding curve of total energy against number of iterations for pw-ldaNaCl

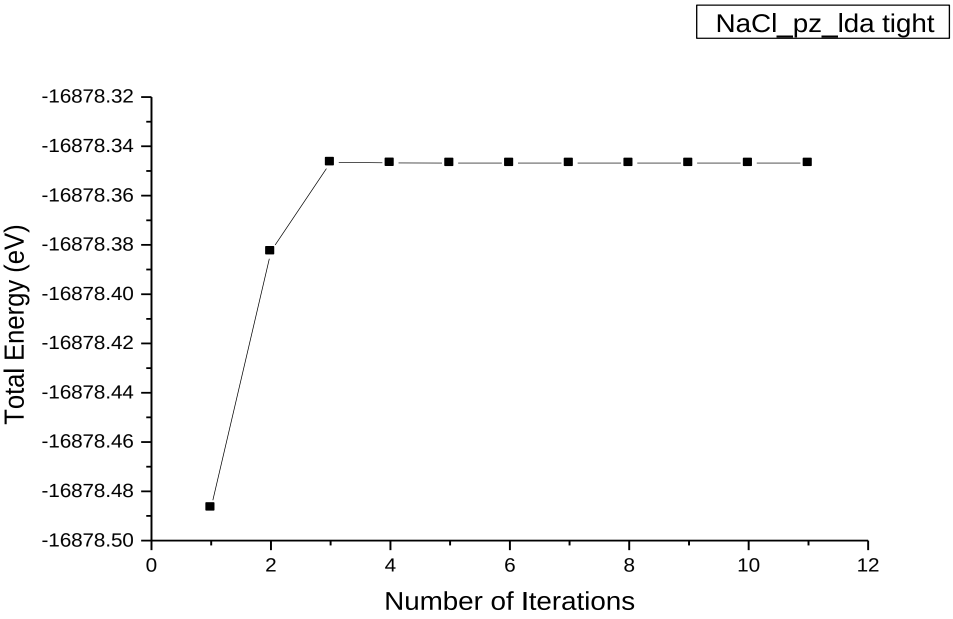

Figure 4.1.3:Binding curve of total energy against number of iterations for pz_ldaNaCl

The total energy of NaCl (pbe) in the fig.4.1rises from the 1st iteration before attaining stability at the 5thiteration while fig.4.1.2 NaCl (pw_lda) and fig 4.1.3 NaCl (pz_lda) rises from 1stiteration to the 2nd,and thenstability is reached at the 3rd iteration as seen in both binding curves. Again, NaCl (pbe) converges to the 7thiteration which is more stable while NaCl (pw_lda) and NaCl (pz_lda) converges through the 11thiteration with even more computational time.

This implies that crystals of NaCl are more stable than a collection of free Na and Cl atoms. Therefore, 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 NaCl for pbe, pw_lda and pz_lda was then calculated and the result obtained for the cohesive energy approximately 4.1835eV, 4.4556eV and 4.4718eV respectivelywhich is in reasonable agreement when compared with experimental value of 4.3eV (Dean L.2016) and 4.26eV (Griffiths and David, 2008); and also an improvement on other LDA result (PhilipsenandBaerends, 1996).

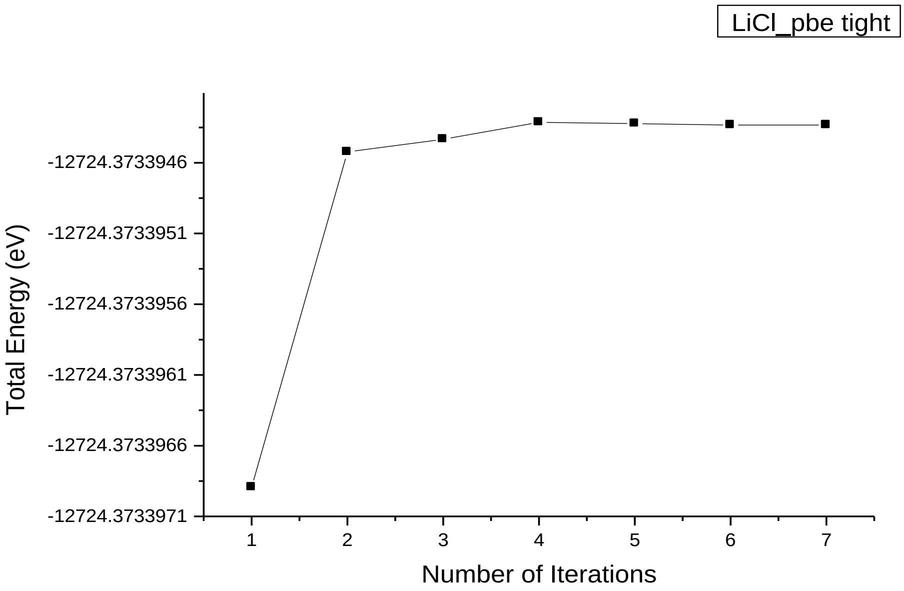

Figure 4.2:Binding curve of total energy against number of iterations for pbeLiCl

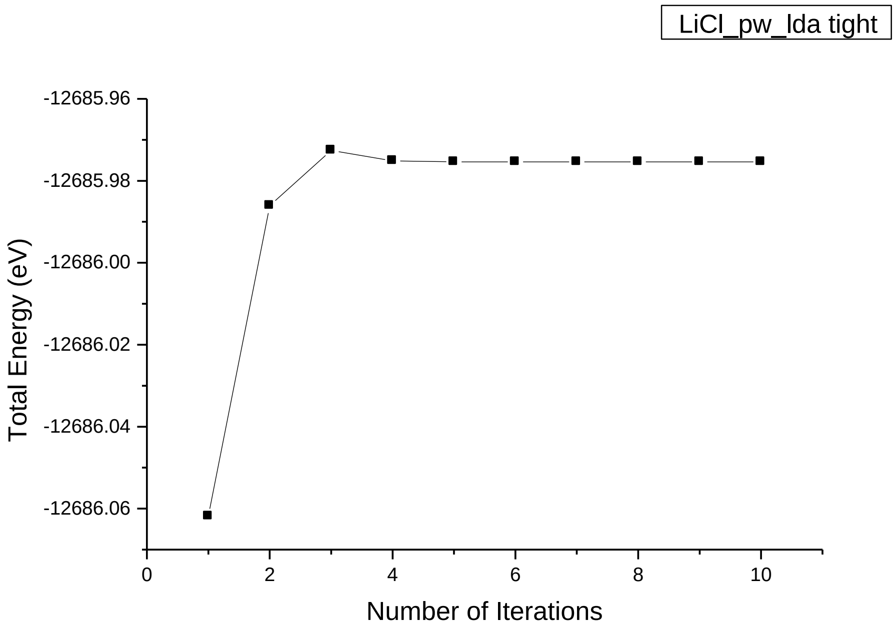

Figure 4.2.2:Binding curve of total energy against number of iterations for pw-ldaLiCl

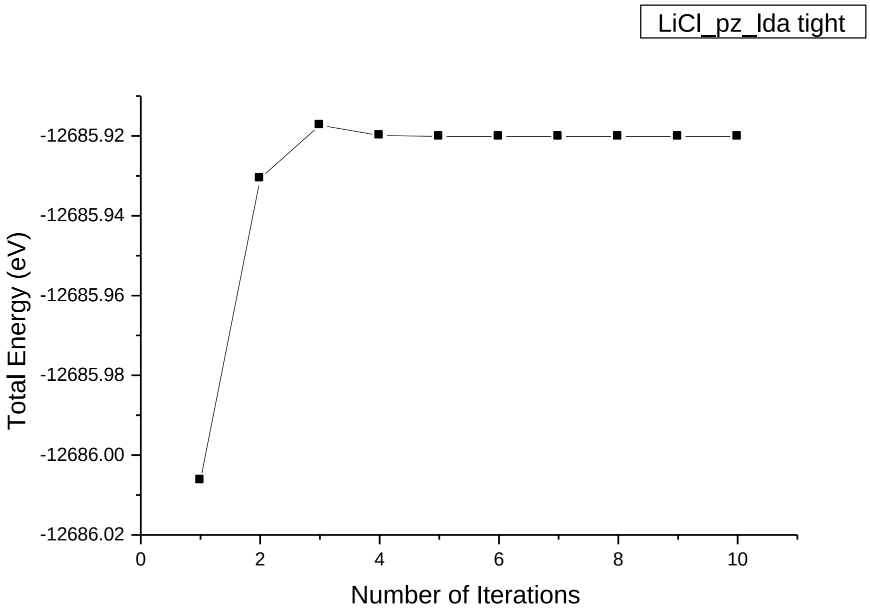

Figure 4.2.3:Binding curve of total energy against number of iterations for pz_ldaLiCl

The binding curve in fig.4.2 for LiCl (pbe) shows that the total energy tends towards stability as thenumber of iterations increases. While fig. 4.2.3 and fig. 4.2.4 for LiClpw_lda and pz_ldashows that the total energy is stable and converged with more number of iterations. This implies that crystals of LiCl are more stable than a collection of free Li and Cl atoms, so that the corresponding atoms attract each other, that is, there exist a stronger attractive intermolecular force that hold the atoms together. (Hans- Eric, 2016). The cohesive energy of LiCl was calculated to be approximately 4.89eV, 5.25eV and 5.26eV for Pbe, pw_lda and pz_lda respectively which is in reasonable agreement when compared with experimental values of 4.86 [(Heald and Mark, 2003) (Griffith and David, 2008)].

Table 4.3:Ground State Energies of Na Atom

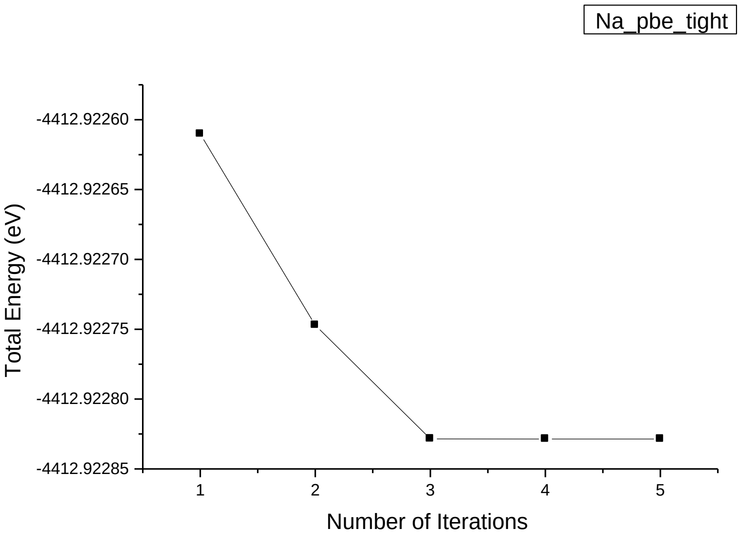

Figure 4.4 Bindingcurve of total energy against number of iterations for pbe Na atom

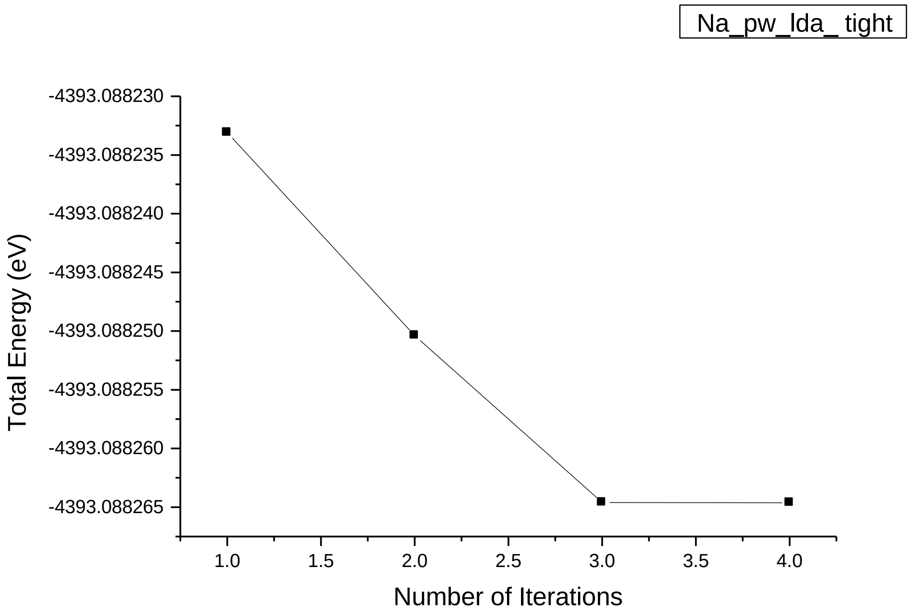

Figure 4.4.1 Binding curve of total energy against number of iterations for pw_lda Na atom

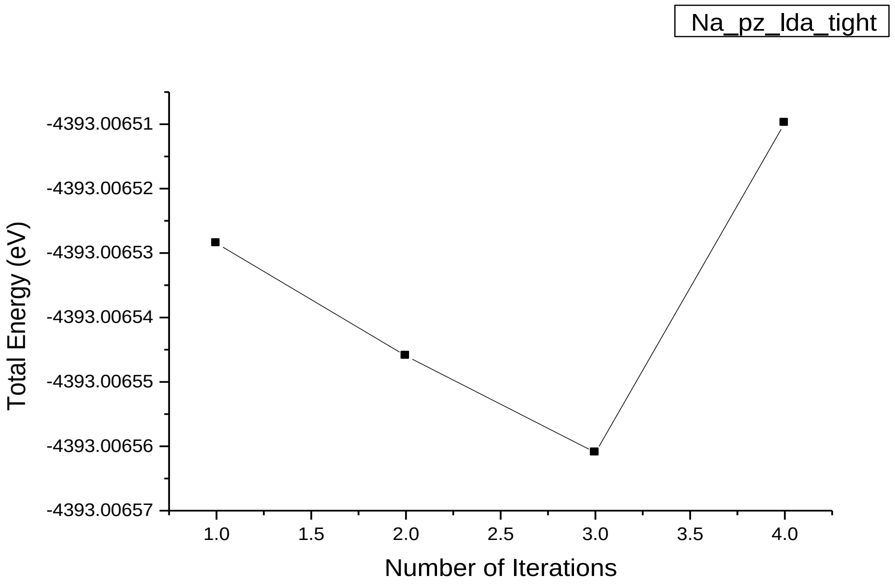

Figure 4.4.3 Binding curve of total energy against number of iterations for pz_lda Na atom

The resulting binding curves for Na atom in fig.4.4 for pbeand fig.4.4.2 for pw_lda show how the total energy lowered significantly after the 1st and 2nd iterations implying instability as a result of low ionization energy of cation (Na ion) before converging through stability for the rest of the iterations. While the binding curve for Na atom (pz_lda) in fig. 4.4.3 shows clearly the total energy for single Na atom is unstable decreasing after the 1st and 2nd iteration but rises at the 4thconsistent iteration.

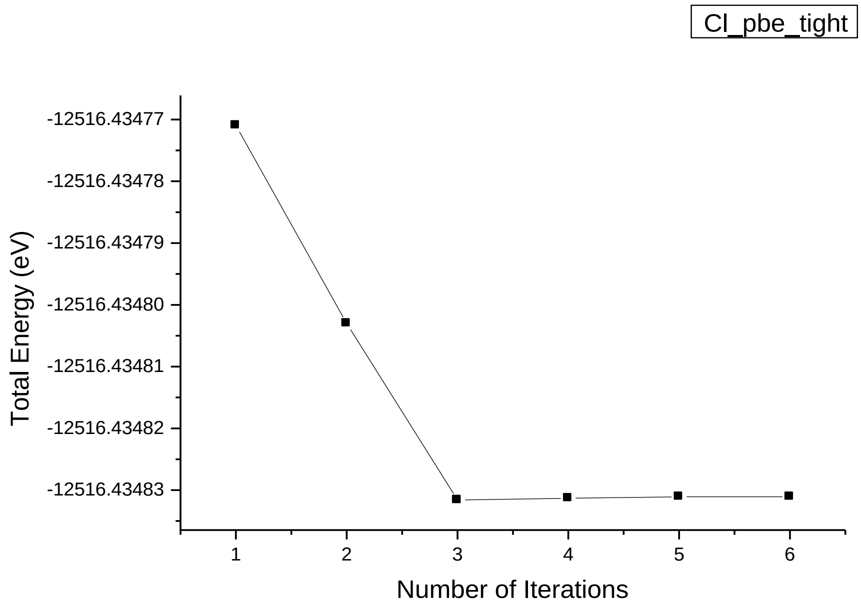

Figure 4.5 Bindingcurve of total energy against number of iterations for pbeCl atom

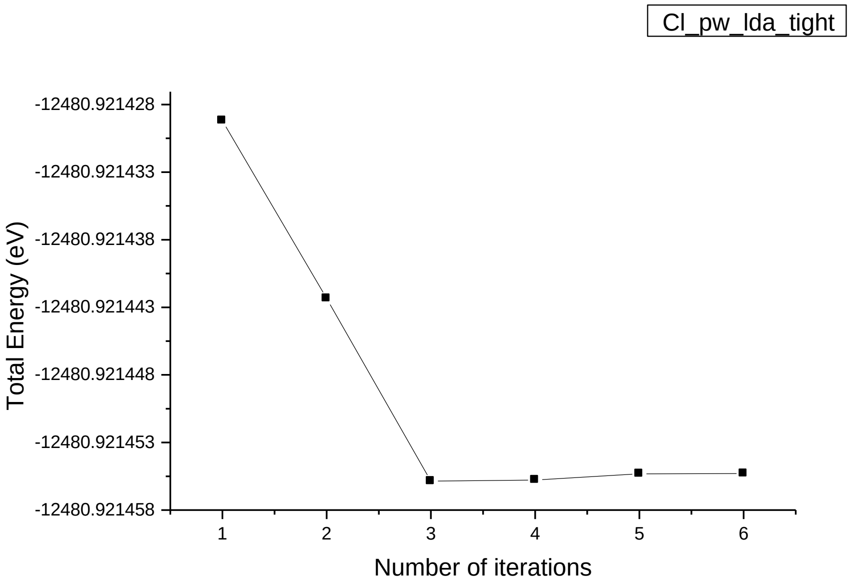

Figure 4.5.2Binding curve of total energy against number of iterations for pw_ldaCl atom

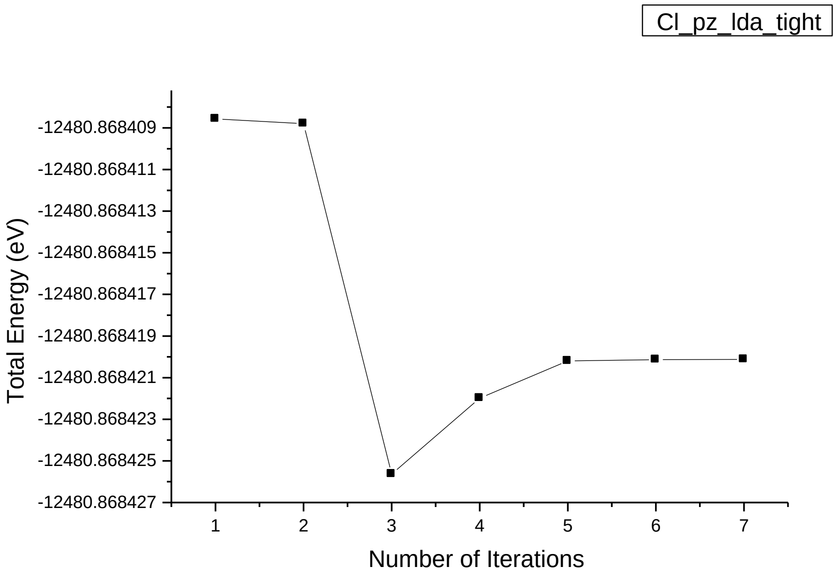

Figure 4.5.3 Binding curve of total energy against number of iterations for pz_ldaCl atom

The resulting binding curves for Clatom in fig.4.5 for pbeand fig.4.5.2 for pw_ldaalsoshow how the total energy lowered significantly after the 1stand2nditerations implying instability as a result of low ionization energy of cation (Cl ion) before converging through stability for the rest of the iterations. While the binding curve for Cl atom (pz_lda) in fig. 4.5.3 shows clearly the total energy for single Cl atom is unstable decreasing after the 1stand 2nd iteration but attained its stability at the 5thiteration.

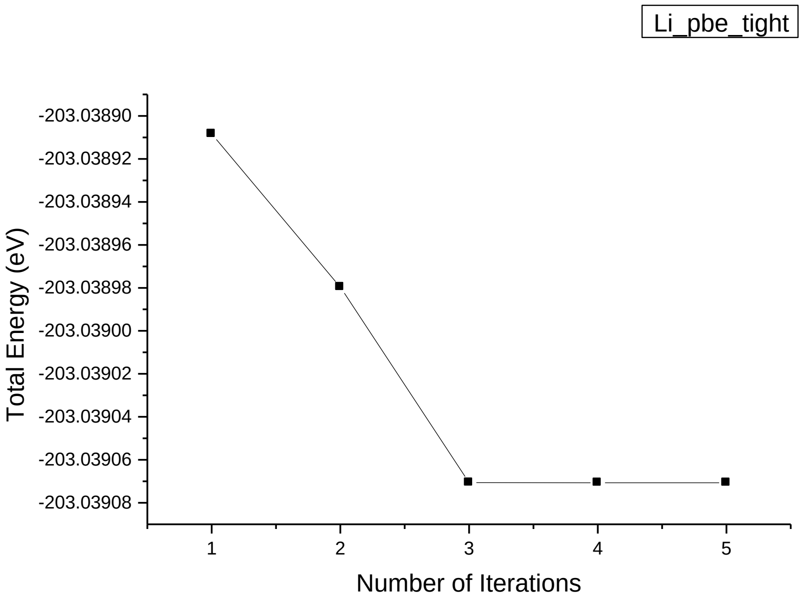

Figure 4.6 Binding curve of total energy against number of iterations for pbe Li atom

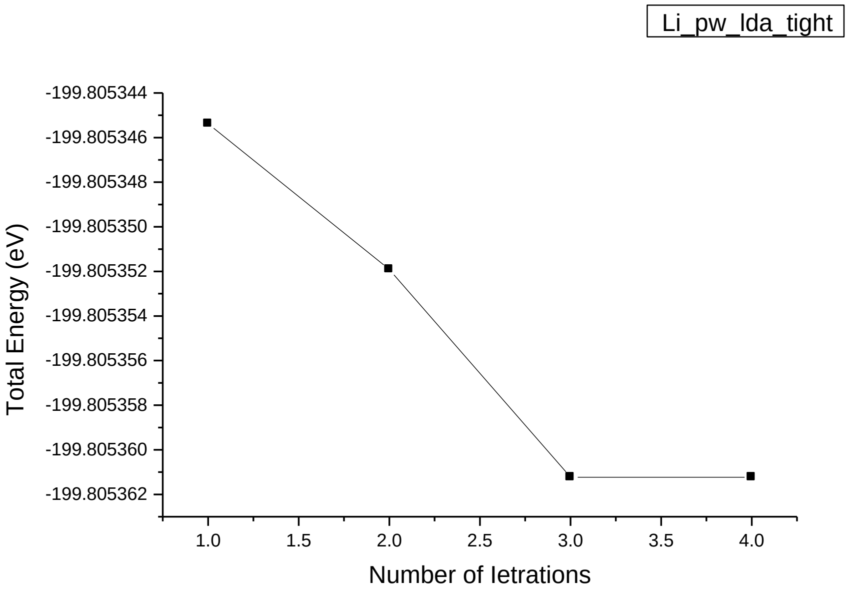

Figure 4.6.2 Binding curve of total energy against number of iterations for pw_ldaLi atom

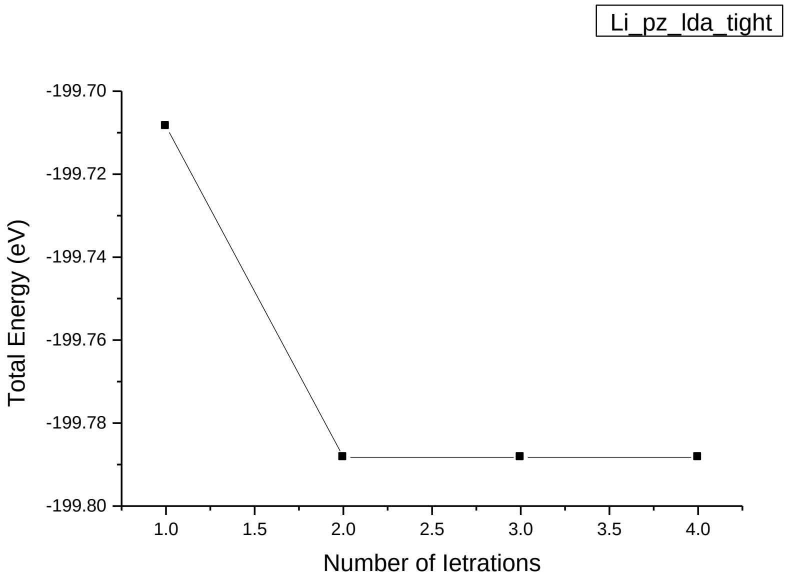

Figure 4.6.3Binding curve of total energy against number of iterations for pw_ldaLi atom

The resulting binding curves for Li atom in fig.4.6 for pbe and fig.4.6.2 for pw_ lda and fig.4.6.23 respectively 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

Table 4.6: Ground State Energies of I Atom

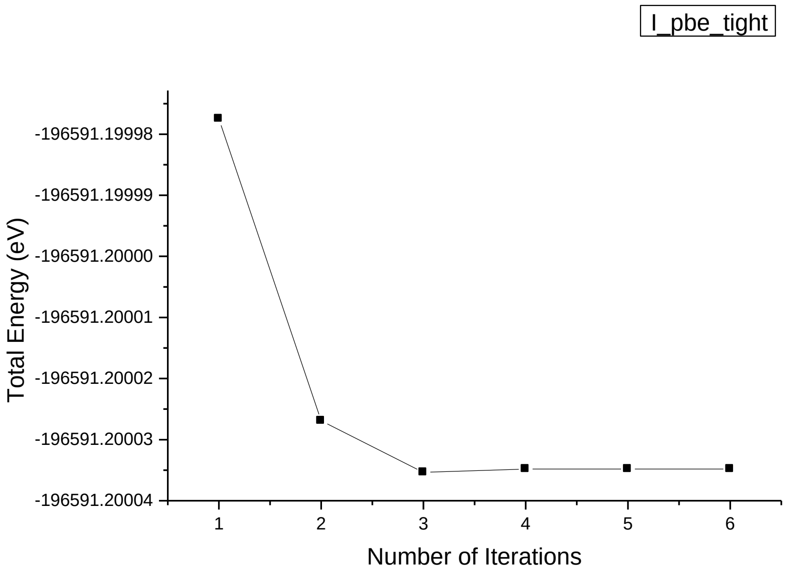

Figure 4.8 Binding curve of total energy against number of iterations for pbe I atom

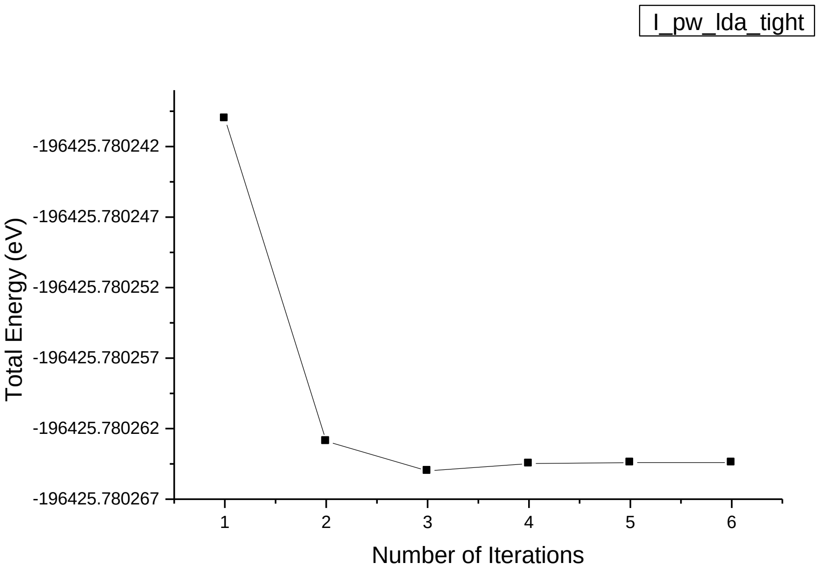

Figure 4.8.2Binding curve of total energy against number of iterations for pw_lda I atom

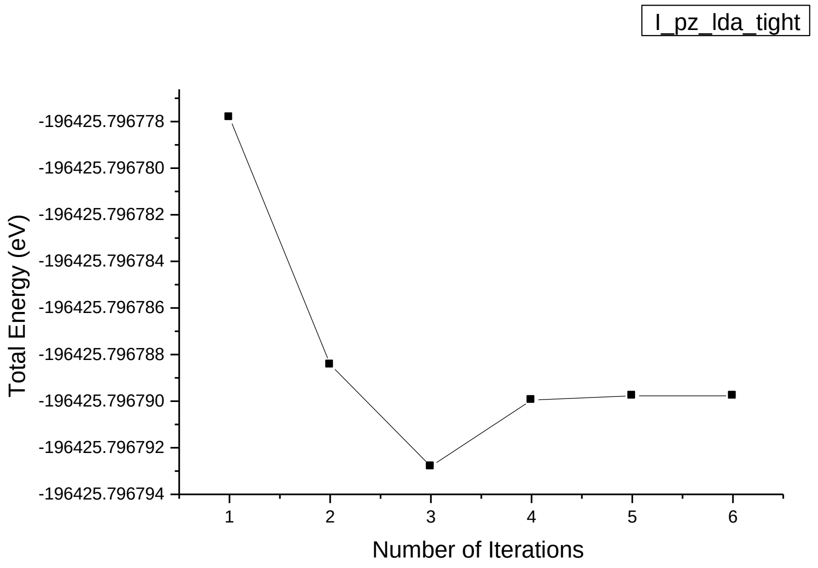

Figure 4.8.3 Binding curve of total energy against number of iterations for pz_lda I atom

The resulting binding curves for I atom in fig.4.8 for pbe and fig.4.8.2 for pw_ lda and fig.4.8.3 respectively also show how the total energy lowered significantly after the 1st iterations implying instability. It also describes that the total energy decreases while number of iterations increases and converges faster with stability from 4th iteration.

Ionic Liquids	Calculated Cohesive Energy, E_{coh} (eV)	Experimental E_{coh} (eV)
Sodium Chloride (NaCl)	4.1835	4.2
Lithium Chloride (LiCl)	4.8995	4.8

V. CONCLUSION

The result of the total cohesive energies of some of the properties of two ILs: NaCl and LiCl based on the computer code Fritz Haber Institute ab-initio Molecular Simulations (FHI-aims) code were computed using Density Functional Theory (DFT) as a tool. which enable one to obtain the optimized parameters that exist between the molecules of each compound, their constituents and the nature and magnitude of interaction that exist among constituents parts of these ionic liquid. The cohesive energy that exists between the molecules of these ionic liquids was optimized and the nature of performance of Generalized Gradient Approximation (GGA) in the study of ionic liquids was understood to be more efficient and the cohesive energy was computed to be 4.1835eV and 4.8995eV. They were of sufficiently accurate result when compared to experimental data.

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