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COMPUTATION OF THE COHESIVE ENERGIES OF SOME SELECTED IONIC LIQUID CRYSTALS (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 Ernzerhof (GGA), Perdew Wang and Pardew Zunger 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 4.86eV for LiCl and 4.26eV for NaCl within the reasonable percentage errors of 1.3% and 3.9% respectively. The major source of this deviation comes from the present DFT calculations of the ionic liquid rather than the atom. The result presented have also confirmed a faster and more accurate study of the ionic liquid considered when compared to literature report of other codes reporting higher iterations before convergence.

Keywords: Lattice constant, Ground state energy, Ionic liquid, GGA and LDA

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 Nowadays, ILs has superseded this status and has become an amazing reality.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 (Anderson *et 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 (Dean, 2012). 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 (Kittel, 1996). 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. 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 (Wachowicz and 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.

There are various methods developed to solve Schrodinger equation. Relatively simple system as Hydrogen atom and H_2^+ could be solved analytically. To solve relatively complex system, methods like Nearly free electron method and Tight binding method have been developed. These methods are not accurate as we have to take a lot approximation to simplify the problem (Kohn, 1965). After this grand success many methods have been developed to compute various properties such as Quantum Chemistry (Hartree-Fock), Quantum Monte Carlo, Perturbation theory and Density Functional Theory (DFT). In this research work DFT the most successful of them all were used. By successful we mean it is best combination of accuracy and efficiency.

The first principles of Hohenberg and Kohn (H-K) theorem demonstrates that the ground state properties of a many-electron system are uniquely determined by an electron density that depends on only three spatial co-ordinates which reduces our problem to 3 spatial co-ordinates from 3N spatial co-ordinates for N body problem because of the use of density functional. The N particle system of interacting particles with 3N degrees of freedom is reduced to a significantly more tractable problem, which deals with a function (density) of only three variables. The many-body effects incorporated in the exchange-correlation potential are typically approximated within either the local density approximation or the generalized gradient approximation. 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.

For the purposes of this research work, FHI-aims code were been used. FHI-aims is an accurate all-electron full potential electronic structure code package for computational material science. It is simply means Fritz Haber Institute- *ab initio* molecular simulations. FHI-aims is a computer program package for computational materials science based only on quantum-mechanical first principles. The main production method is density functional theory (DFT) of HK and KS to compute the total energy and derived quantities of molecular or solid condensed matter in its electronic ground state. In addition, FHI-aims allow describing a wave-function based molecular total energy calculation based on Hartree-Fock and perturbation theory (MP2 and MP4) (Blum *et al*, 2009).The basic reason we adopt this code is to avoid further making of approximation and to minimize numerical errors.

THEORETICAL FRAME WORK

The system of interacting electrons is mapped onto a fictitious 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) ψ_i, (Giannozzi, 2005; Martin, 2004).

$$n(r) = 2\sum_i \left|\psi_i(r)\right|^2 \qquad 1$$

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:

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

(m is the electron mass) obeying orthogonality constants;

The existence of a unique potential V_{KS} in equation (2) 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:

$$n(\uparrow)(r) = n(\downarrow)\tfrac{1}{2}(n) \qquad 3$$

(Kittel, 1996)

Again the density can be written as:

$$n(r) = \sum_{i=1}^{N/2} \square\Psi_i(r)\square^2 \qquad 4$$

And the kinetic energy as

$$T_S = -\frac{1}{2}\sum_{i=1}^{N/2} < \Psi_i\square(r)\square\nabla^2\square\Psi_i(r) > \qquad 5$$

The existence of a unique potential *VKS* in equation (2) 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:

$$E = T\,[n(r)] + E_H[n(r)] + E_{xc}[n(r)] + \int n(r)V_{(r)}d_r \qquad 6$$

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;

$$-\frac{1}{2}\nabla^2\Psi_i(r) + \left[V_r + \int d_{r\square}\frac{n(r^{\square})}{\square r - r^{\square}\square} + \left\{E_{xc}(r) + n(r)\frac{\delta_{E_{xc}}[n]}{\delta_n(r)}\right\}\right]\Psi_i(r) = E_{\square}\Psi_i \qquad 7$$

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

$$V_{KS} = V(r) + V_H + V_{xc} \qquad 8$$

where V_H is introduced as the Hatree potential, and the exchange correlation potential V_{xc}

Equation (7) 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).

There are many computational codes of DFT among which are Abinit, Vasp, Castep, Quantum-Espresso,Dacapo, FHI-aims e.t.c. On the other hand, there are many GGA versions among which is the Perdew Burke Ernzerhof (pbe) functional (1997) used in this study. The goal in DFT is to find the value of the functional F, and to do this we need to make approximations. Indeed, one of the reasons why there are so many different DFT methods is that there are multiple ways of approximating the functional (Havu *et al*, 2016).

Procedure

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 (lPlanck-Gessellschaf, and 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 NaCl, and 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 three 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 of NaCl and 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*.

Calculation of the Cohesive Energies

The total energy of a free atom for NaCl and LiCl unit cell for fcc were calculated as follows: for single atom energy, special care were been 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"**. Secondly, we use more converged basis, in particular, we use all basis functions up to "tier 3", the cutting potential was increased to **"cut_pot_8.3.1."** and basis dependent confining potential was turned off with **"basis_dep_cutoff 0".** After calculating total energies of NaCl and LiCl crystal structure, the energies are then converted to the cohesive energies using the equation:

$$E_{coh} = -\frac{E_{bulk-NE_{atom}}}{N} = -\left[\frac{E_{bulk}}{N} - E_{atom}\right] \qquad 9$$

where E_{bulk} is the 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 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 (Pillai, 2010).

Cohesive energy = energy of free atoms – crystal energy 10

RESULTS AND DISCUSSION

The result obtained for the calculations of the total and cohesive energies of LiCl and NaCl are presented and discussed below.

Table 1: Ground state energy of NaCl in eV

Functionals Computations	Pbe Ground State Energy (eV)	Pw_lda Ground State Energy (eV)	Pz_lda Ground State Energy (eV)
Light	-16933.49810232	-16878.42265343	-16878.30480182
Tight	-16933.54110981	-16878.46453510	-16878.34676004

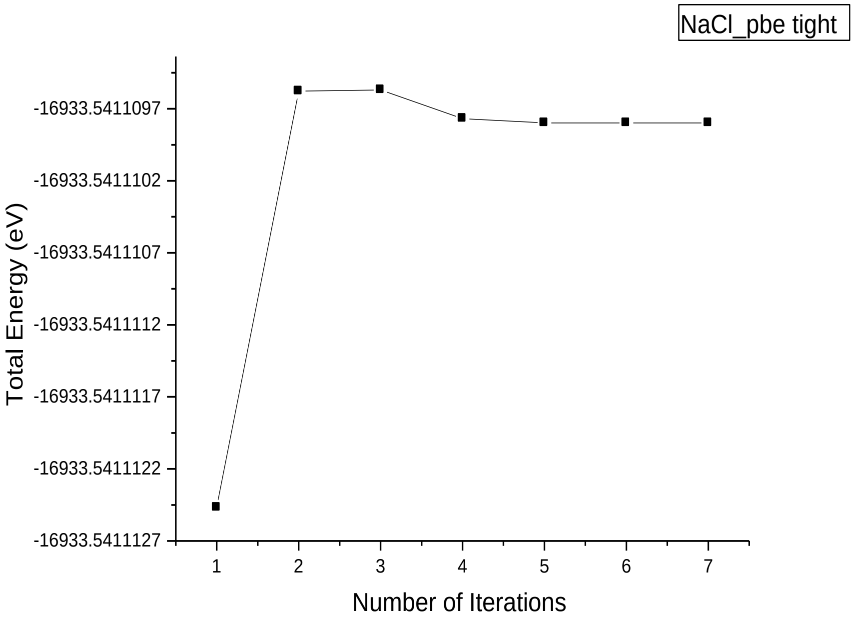

Fig. 1: Binding curve of total energy against number of iterations for pbe NaCl

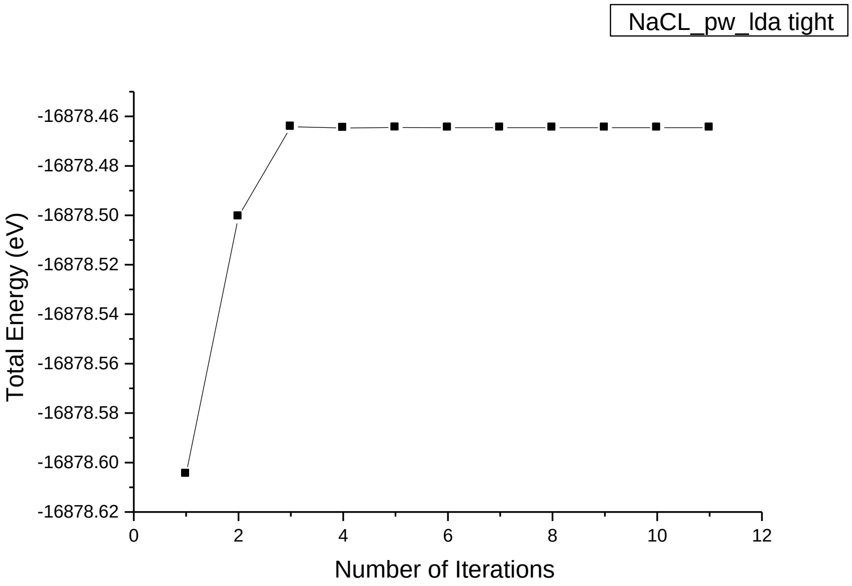

Fig. 2: Binding curve of total energy against number of iterations for pw-lda NaCl

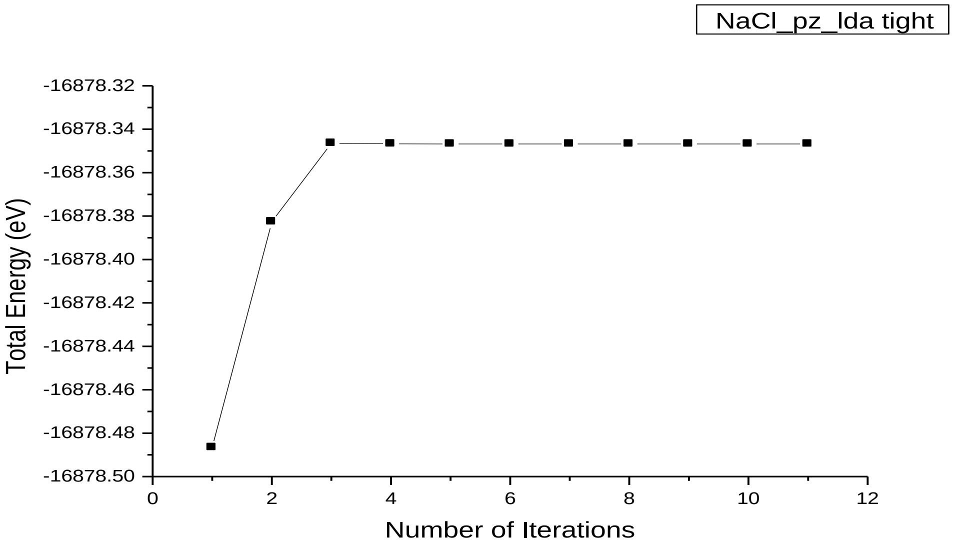

Fig..3: Binding curve of total energy against number of iterations for pz_lda NaCl

The total energy of NaCl (pbe) in the fig. 1 rises from the 1st iteration before attaining stability at the 5th iteration while fig.2 NaCl (pw_lda) and fig. .3 NaCl (pz_lda) rises from 1st iteration 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 to 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, this implies that, 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 respectively which 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 (Philipsen and Baerends, 1996).

Table .2: Ground state energy of LiCl ineV

Functionals Computations	Pbe Ground State Energy (eV)	Pw_lda Ground State Energy (eV)	Pz_lda Ground State Energy (eV)
Light	-12724.26064031	-12685.86077837	-12685.80582459
Tight	-12724.37339432	-12685.97538452	-12685.92012133

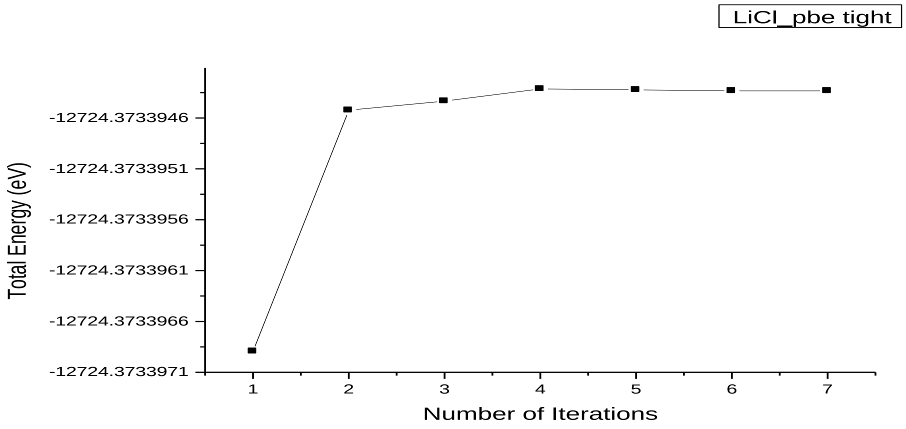

Fig. 4: Binding curve of total energy against number of iterations for pbe LiCl

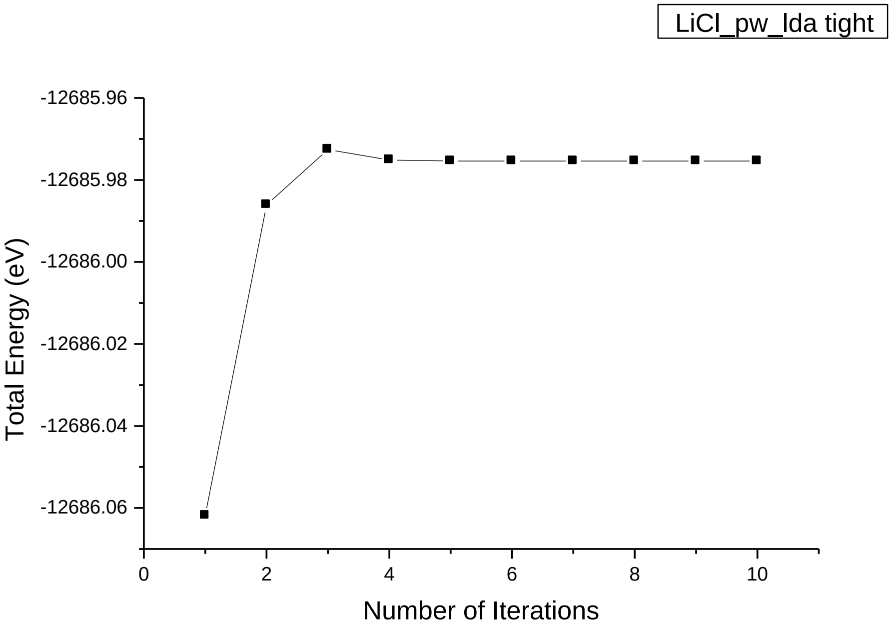

Fig.5: Binding curve of total energy against number of iterations for pw-lda LiCl

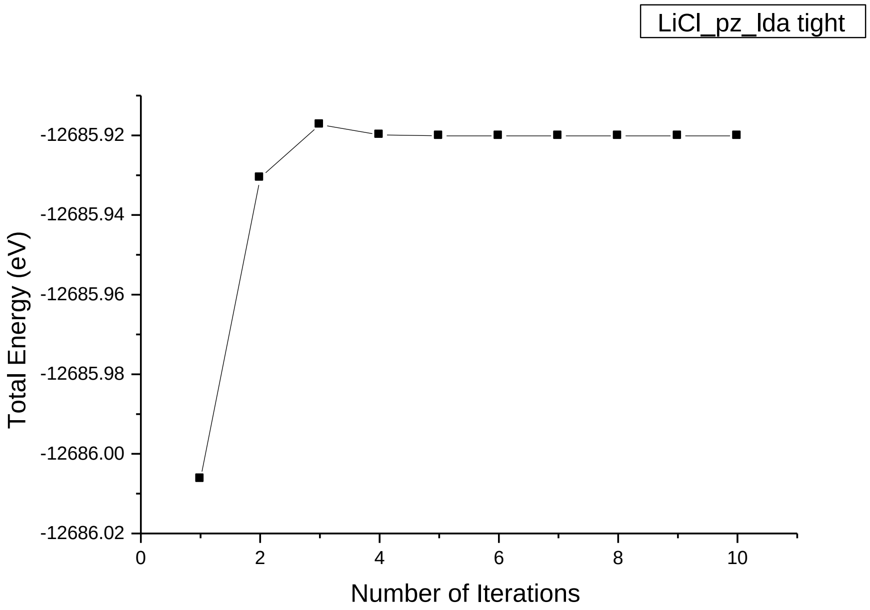

Fig. 6: Binding curve of total energy against number of iterations for pz_lda LiCl

The binding curve in fig.4 for LiCl (pbe) shows that the total energy tends towards stability as the number of iterations increases. While fig. 5 and fig.6 for LiCl pw_lda and pz_lda shows 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 (Griffith and David, 2008; Heald and Mark, 2003).

Table 3:Ground State Energies of Na Atom

Functionals Computations	Pbe Ground State Energy (eV)	Pw_lda Ground State Energy (eV)	Pz_lda Ground State Energy (eV)
Tight	-4412.92282859	-4393.08826463	-4393.0065098

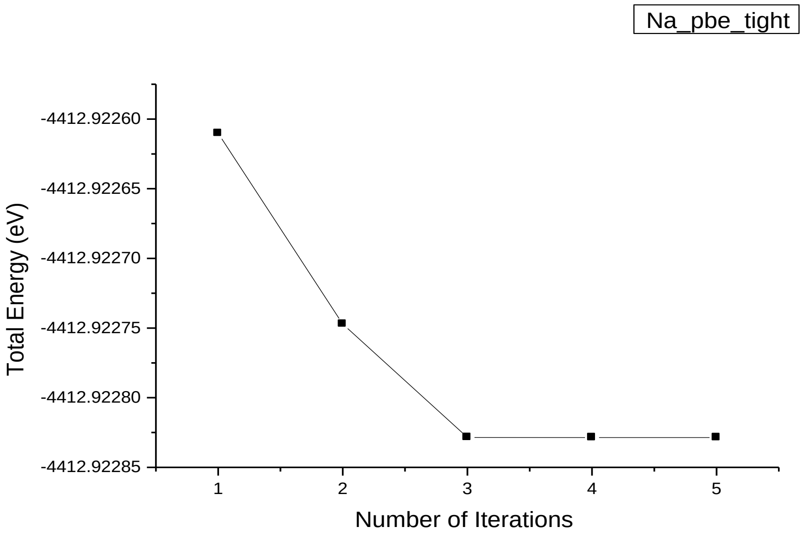

Fig.7: Binding curve of total energy against number of iterations for pbe Na atom

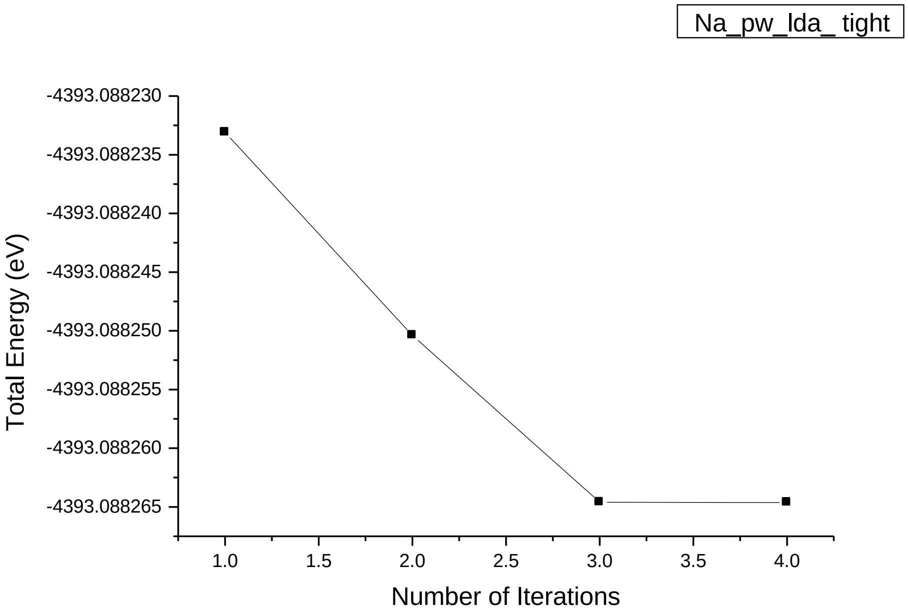

Fig.8: Binding curve of total energy against number of iterations for pw_lda Na atom

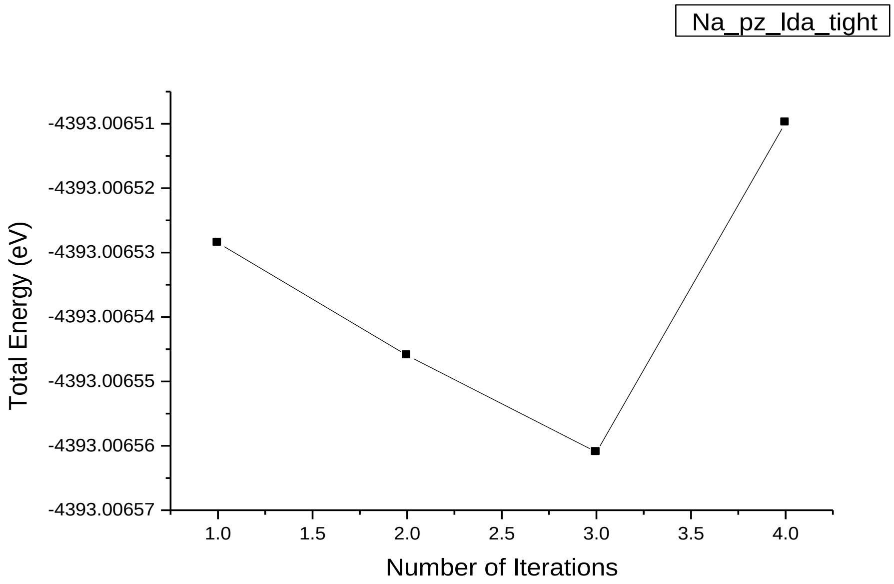

Fig.9: Binding curve of total energy against number of iterations for pz_lda Na atom

The resulting binding curves for Na atom in fig.7 for pbe and fig.8 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. 9 shows clearly the total energy for single Na atom is unstable decreasing after the 1st and 2nd iteration but rises at the 4thconsistent iteration.

Table 4: Ground State Energies of Cl Atom

Functionals / Computations	Pbe Ground State Energy (eV)	Pw_lda Ground State Energy (eV)	Pz_lda Ground State Energy (eV)
Tight	-4412.92282859	-4393.08826463	-4393.0065098

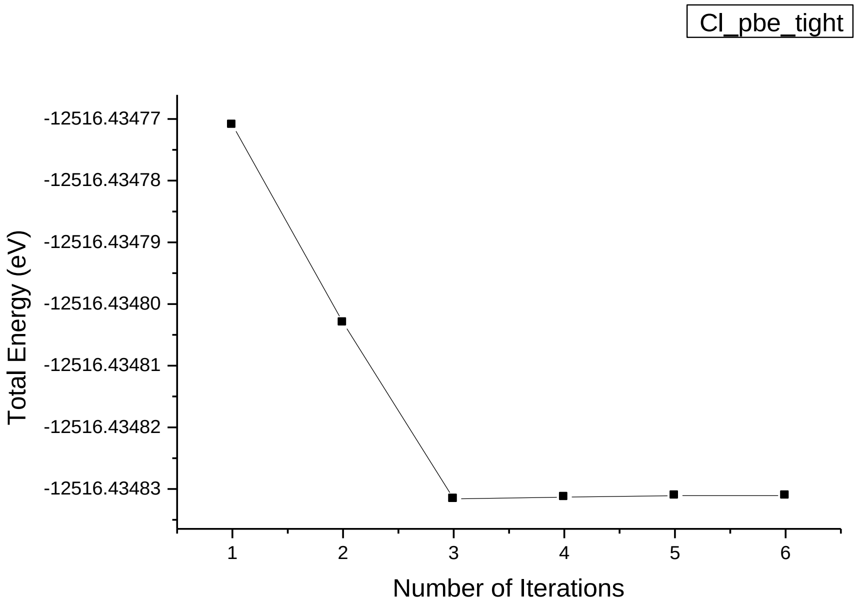

Fig.10: Binding curve of total energy against number of iterations for pbe Cl atom

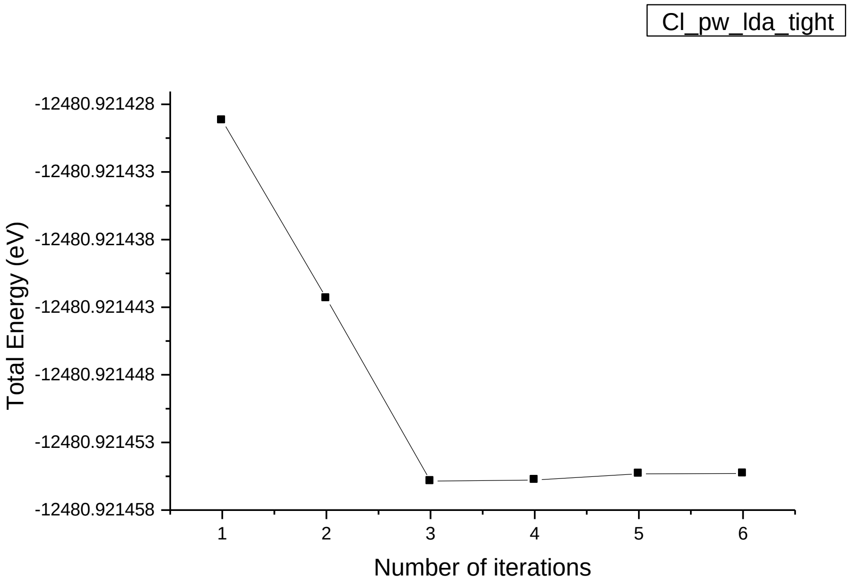

Fig.11: Binding curve of total energy against number of iterations for pw_ldaCl atom

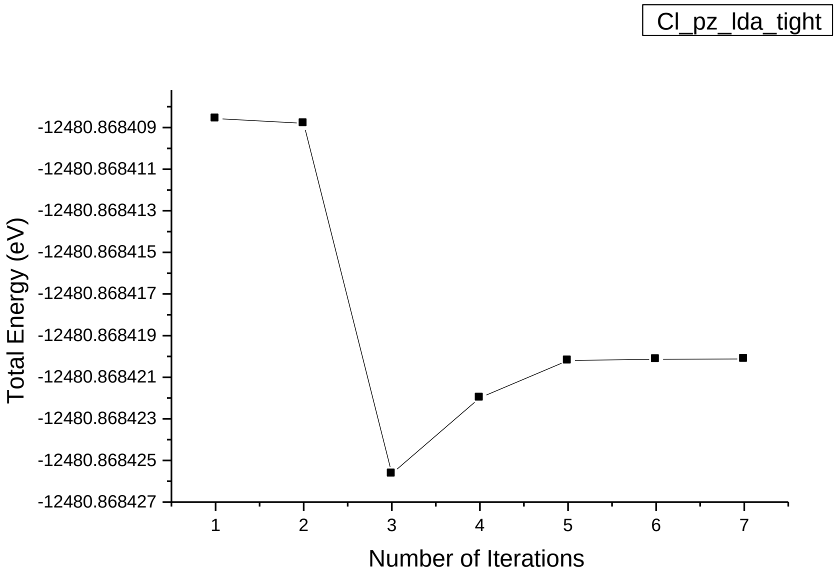

Fig.12: Binding curve of total energy against number of iterations for pz_lda Cl atom

The resulting binding curves for Cl atom in fig.10 for pbe and fig.11 for pw_ ldaalso show 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.12 shows clearly the total energy for single Cl atom is unstable decreasing after the 1stand 2nd iteration but attained its stability at the 5thiteration.

Table 5: Ground State Energies of Li Atom

Functionals / Computations	Pbe Ground State Energy (eV)	Pw_lda Ground State Energy (eV)	Pz_lda Ground State Energy (eV)
Tight	-203.03890836	-199.80536123	-199.78824162

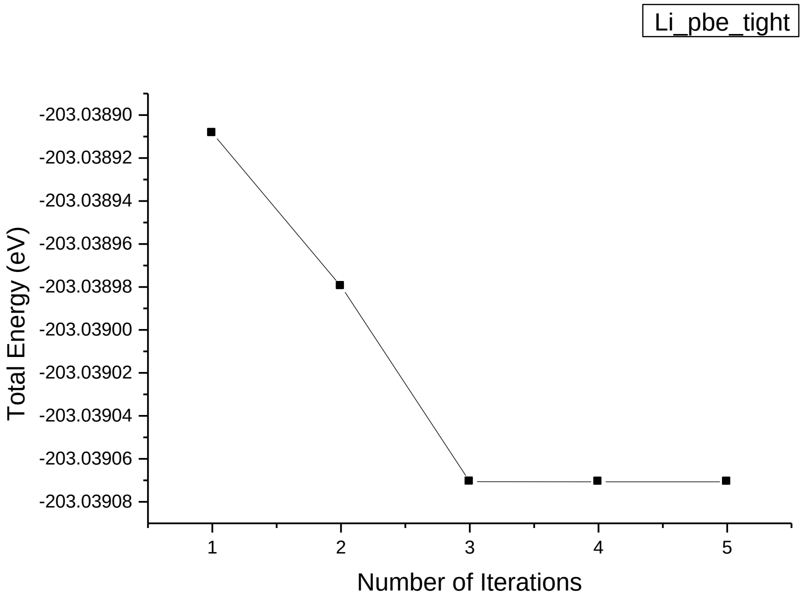

Fig. 13 Binding curve of total energy against number of iterations for pbe Li atom

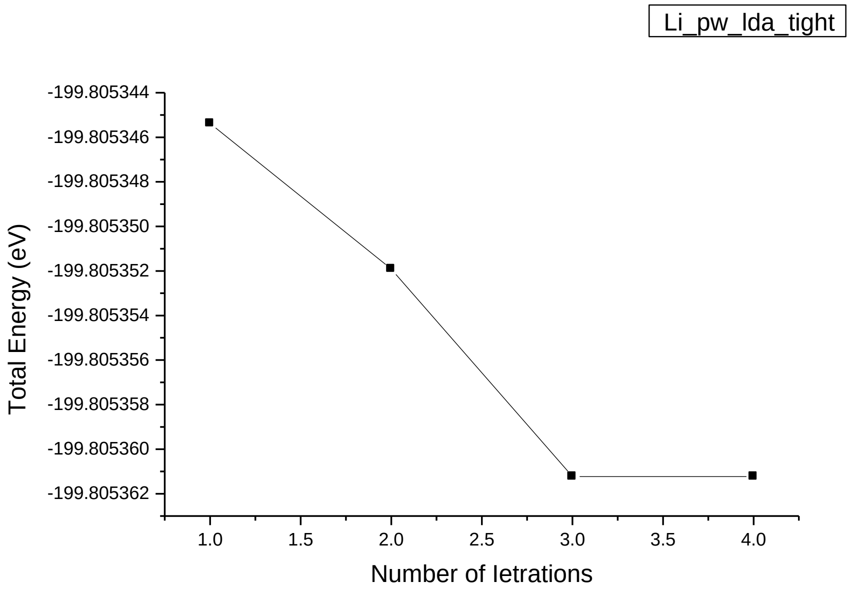

Fig.14: Binding curve of total energy against number of iterations for pw_ldaLi atom

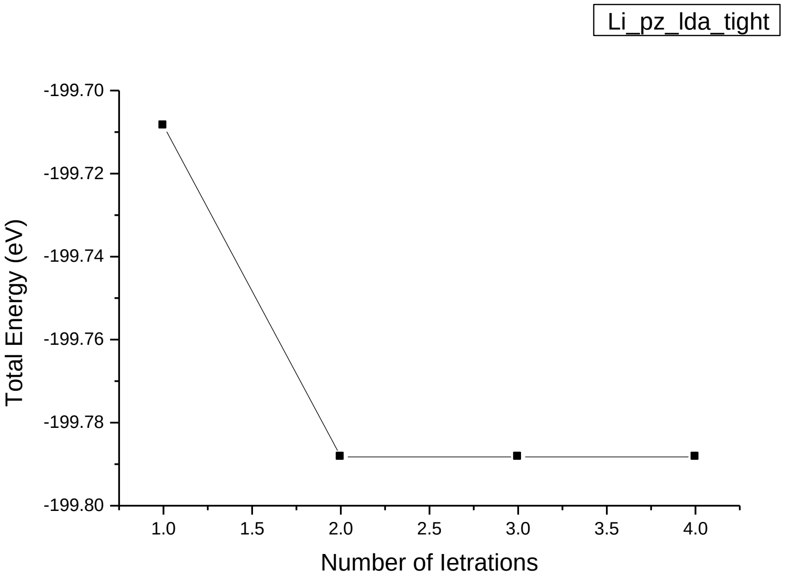

Fig.15: Binding curve of total energy against number of iterations for pz_lda Li atom

The resulting binding curves for Li atom in fig.13 for pbe and fig.14 for pw_ lda and fig.15 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.

CONCLUSION

The result of the total and 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 within the K-grids of 12 X 12 X 12 for all compounds 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 of NaCl and LiCl was computed to be 4.1835eV and 4.8995eV respectively. They were of sufficiently accurate result when compared to experimental data. The values obtained are in agreement with experimental values and literature reports within some reasonable percentage error of 1.3% and 3.9% respectively. The major source of this deviation comes from the present DFT calculations of the ionic liquid rather than the atom. The result presented have also confirmed a faster and more accurate study of the ionic liquid considered when compared to literature report of other codes reporting higher iterations before convergence.

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