Computational study of electronic structure and bonding properties of Lithium pnictides

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requirements for the award of the degree of

Master of Technology
in
Computational Techniques

by

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To

My Family & Friends

DECLARATION

I hereby declare that the work reported in this thesis has been carried out by me independently in the school of physics, University of Hyderabad, under the supervision of **Dr. G.S.Vaitheeswaran**, Advanced Centre of Research in High Energy Materials (ACRHEM), University of Hyderabad. I also declare that this is my own work and effort, and it has not been submitted at any other University or Institution for any degree. Wherever contributions of others are involved, every effort is made to indicate that clearly with due reference to literature, and acknowledgement of collaborative research and discussions.

Place:

Date: **RAJENDRA PRASAD J**

CERTIFICATE

This is to certify that the project work entitled "**Computational study of electronic structure and bonding properties of Lithium pnictides**" being submitted to University of Hyderabad by **RAJENDRA PRASAD J** with Reg. No. **09PCMT14**, in partial fulfillment for the award of the degree of Master of Technology in Computational Techniques, is a bonafide work carried out by him under my supervision.

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ABSTRACT

In this present work, we report the electronic band structure, density of states and nature of bonding of Lithium pnictide compounds Li_3P and Li_3As using first-principles density functional theory(DFT) calculations. We have used ultrasoft pseudopotentials for describing the electron-ion interactions. All the calculations are performed within the local density approximation (LDA). The calculated band structure of the two compounds clearly shows that both pnictides are indirect gap semiconductors. The study of density of states reveals that these compounds are mainly ionic and the ionicity increases from Li_3P to Li_3As. This fact also confirmed by the Mulliken bond population analysis and charge density distribution study.

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Chapter 1

Introduction

1.1 Introduction to the problem

An interesting branch of solid state physics is to deal with the bulk properties of materials. Matter consists of atoms and molecules. The fundamental behavior of atoms, molecules and solids is governed by the laws of quantum mechanics. By using first-principles methods, we can calculate the physical and chemical properties of materials by using the fundamental equations of quantum mechanics. Calculations of this type are also called ab initio calculations.

The central task in first principles simulations is to solve the many-body Schrödinger equation and obtain the wave function and the total energy of the system which are the starting points for the most physical properties of the materials.

Many powerful methods have been developed for solving many-body Schrödinger equation. Solutions of some models generally requires the use of approximation schemes, of which the most basic the independent electron approximation, the Hartree theory and Hartree Fock theory. However, there is another approach called Density Functional Theory (DFT) which over the last thirty years or so has become increasingly the method of choice for the solution of such problems. Density-functional theory (DFT) is one of the most popular and successful quantum mechanical approaches to matter. This method has the double advantage of being able to treat many problems to a sufficiently high accuracy, as well as being computationally simple.

Density Functional Theory as the name implies, treats the particle density as the fundamental variable. The idea of using the density as the basic variable for the description of the energies of electronic systems goes back almost to the arrival of quantum mechanics and the realization that the solution of the full equation of Schrödinger was beyond reach in most cases. As always in physics, the goal is to derive the total energy of the system, so our task primarily becomes expressing all contributions to the energy in terms of the density. By definition, density-functional theory is only able to predict the ground-state energy and properties, even though there are certain theories about how to treat excitation energies. Furthermore, since the ground-state energy is a function of a number of parameters of the system, we may also use DFT to find other ground-state properties such as equilibrium bond-lengths by minimizing the ground-state energy with respect to these parameters. DFT is one of the most widely used methods for ab initio calculations of the structure of atoms, molecules, crystals, surfaces, and their interactions. It is nowadays routinely applied for calculating, e.g., the binding energy of molecules in chemistry and the band structure of solids in physics. It is an exact theory of the ground state of an interacting many-particle system.

Cambridge Serial Total Energy Package(CASTEP) is a software package which uses density functional theory with a plane wave basis set to calculate the electronic properties of crystalline solids, surfaces, molecules, liquids and amorphous materials from first principles. CASTEP uses a total energy plane-wave pseudopotential method. It can give information about total energies, forces and stresses on an atomic system, as well as calculating optimum geometries, band structures, optical spectra and much more. It can also perform molecular dynamics simulations. The primary reason that CASTEP has become so powerful is that the numerical methods used to solve the underlying quantum mechanical calculations are both computationally efficient and extremely accurate.

1.2 Lithium pnictides

The compounds with the general formula A_3B (A=alkali metals (Li-Cs), B=group-V elements (N-Bi) in the periodic table) are called alkali pnictides. Similarly, the compounds with the formula Li_3X (X= N, P, As, or Sb) are called Lithium pnictides. Because of the large eletronegativity difference, the alkali metal(Li) transfers its single valence electron to the pnictide element, and the most stable compound is expected for the stoichiometric composition Li_3X. The intermetallic compounds of the alkali metals with elements of the fifth column of the periodic table show a wide variety of chemical bonding properties. Lithium pnictides are also called super ionic conductors.

As we know, the superionic conductors are the materials that act as solid state ion conductors and they conduct electricity due to the movement of ions through voids, or empty crystallographic positions in their crystal lattice structure. And, the crystal remains rigid, but conducts electricity well, as though only one ionic species has melted while the others stayed fixed in the crystal lattice. So, the Superionic conductivity (SIC) is a property of some materials in which one of the atom species is able to move through the crystal while the crystal itself remains in the solid phase. The magnitude of conductivity depends on a number of factors such as presence of interstitial sites, ion size, temperature, crystal structure etc. In the case of lithium pnictides, the conductivity is driven by Li vacancy defects within the hexagonal planes and is orders of magnitude higher perpendicular to the c axis. However, the Li^+ ions are not allowed to migrate freely through the interstitial but they move through the lattice by jumping from one vacant lattice site to another, spending a much higher percentage of the time occupying a particular lattice site.

Lithium-ion conductors are used in solid-state lithium batteries since the lithium atom has a low equivalent weight and a high electropositive character. Solid-state ionic conductors

$Atom$	x	y	z
$Li1$	0	0	1/4
$Li2$	1/3	2/3	0.583
$X(P, As)$	1/3	2/3	1/4

Table 1.1: Li_3X (X=P, As) crystal atomic positions

with a high ionic conductivity are needed for various electrochemical devices such as solid-state batteries and fuel cells, sensors, electrochromic devices, capacitors, etc. Li-ion batteries are widely used in portable electronic industry, and have been considered for large scale applications in electric vehicles. In this present work,we are interested to study the ground state properties of compounds like Li_3P, Li_3As.

1.3 Crystal structure of Li_3P, Li_3As compounds

The compounds Li_3P, Li_3As crystallizes in the hexagonal structure and the space group is $P6_3/mmc$(194)[1,2]. Lithium phosphide, Li_3P, is a good lithium-ion conductor and lithium arsenide Li_3As is a semimetallic compound[3,4]. These compounds are having the layered structure configuration. As the compounds Li_3P, Li_3As crystallizes in a hexagonal structure, each P or As atom is surrounded by eight Li atoms in a layered configuration along the hexagonal axis. The Li atoms in the pure Li and Li_2X (X= P,As) layers can be referred as Li(1) and Li(2) atoms respectively. So, the structural arrangement of these compounds consists of a stacking of two alternating layers perpendicular to the c-direction. The first

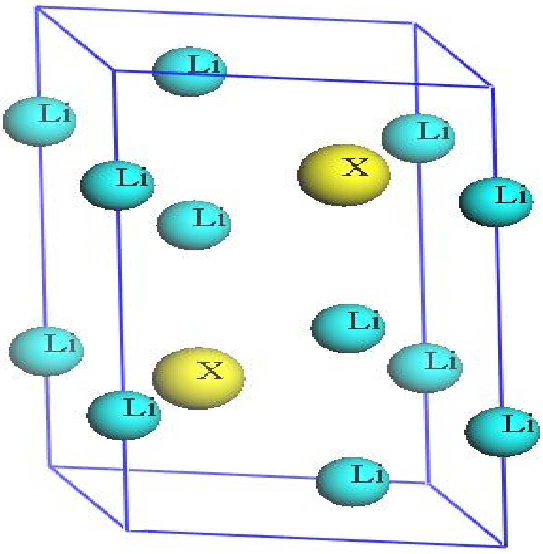

Figure 1.1: Crystal structure of Li$_3$X (X=P, As) compounds

layer is made up of Li(2) and P or As layer, and the second layer is composed of a Li(1) layer. The atomic positions of these compounds are tabulated in Table 1.1.

In this present work, we are interested to study the electronic band structure, density of states and charge density distributions in various planes of these compounds using density functional theory within the frame work of Local Density Approximation(LDA). All the calculations are performed using the Cambridge Serial Total Energy Package (CASTEP) program.

Chapter 2

Theoretical methods

The study of atomistic and electronic structure calculations have become very important in the fields of physics and chemistry. If we need to know the atomic structure of the material and their electronic properties and how can we modify the bonding between atoms or the material chemical content to create new materials with properties different from original properties of the component, we need to have an accurate theoretical methods.

A number of methods can be used to study the properties of materials. It can be divided into two classes: those that do not use any empirically or experimentally derived quantities called first principles methods, like density functional theory (DFT), while the latter methods are called empirical or semi-empirical, like empirical tight binding (ETB). The first principle methods are useful in predicting the properties of new materials such as the calculation of the energy levels of electrons in solids, knowledge of these energies, and electron wave function is required for any calculation of more directly observable properties including electrical and thermal conductivities, optical dielectric function, vibration spectra and so on.

2.1 DFT as a way to solve quantum many body problem

The central result of quantum mechanics is that the behaviour of all physical systems is the result of the properties of the wavefunction of the particles involved, which is governed by the Schrödinger equation. The defining element of the Schrödinger equation is the Hamiltonian H of the system, which incorporates all of the interactions between elements of the system and all the contributions to its energy.

The non-relativistic time-independent Schrodinger equation for a system consisting of N_e electrons and N_n nuclei is,

$$H\Psi = \epsilon\Psi \tag{2.1}$$

here,Ψ and ϵ are the many-particle wavefunction and the total energy of the system respectively, 'H' is the Hamiltonian operator which can be written as,

$$H = -\sum_{i=1}^{N_e} \frac{1}{2}\nabla_i^2 - \sum_{\alpha=1}^{N_n} \frac{1}{2M_\alpha}\nabla_\alpha^2 - \sum_{i=1}^{N_e}\sum_{\alpha=1}^{N_n} \frac{z_\alpha}{|r_i - R_\alpha|} + \sum_{i=1}^{N_e}\sum_{j>i}^{N_e} \frac{1}{|r_i - r_j|} + \sum_{\alpha=1}^{N_n}\sum_{\beta>\alpha}^{N_n} \frac{z_\alpha z_\beta}{|R_\alpha - R_\beta|} \tag{2.2}$$

where M_α, Z_α and R_α are the mass, atomic number and position of nucleus α, respectively. In equation (2.2), the first and second terms are the kinetic energies of the electrons and nuclei, respectively. The third term represents the Coulomb attraction interaction between nuclei and electrons. The fourth and fifth terms describe the Coulomb repulsion interaction between electrons and between nuclei, respectively. The above equation is expressed in atomic units, such that Planck's constant ($\hbar$), the mass of electron (m_e) and electronic charge (e) are equal to one.

In order to find acceptable approximate eigenstates (acceptable solution to Schrodinger equation (2.1)),some assumptions or approximations are made.The first one is called the Born-Oppenheimer approximation [5].

2.2 The Born-Oppenheimer approximation (BO)

One of the most important approximations in material science. In this approximation, for the purpose of constructing the Hamiltonian, the nuclei are held in fixed position in order to separate out the electronic and nuclear degrees of freedom. Because electrons are very much lighter than nuclei ($\frac{M}{m_e}$ =1836.1), it can be considered that the electrons move in the field of fixed nuclei. Hence, within this approximation, the kinetic energy of the nuclei (the second term of equation (2.2)) can be neglected and the Coulomb repulsion interaction between the nuclei (the last term of equation (2.2)) is considered as constant. The remaining terms in equation (2.2) are called the electronic Hamiltonian, i.e., Hamiltonian describing the motion of N_e electrons in the field of N_n nuclei,

$$H_e = -\sum_{i=1}^{N_e} \frac{1}{2}\nabla_i^2 - \sum_{i=1}^{N_e}\sum_{\alpha=1}^{N_n} \frac{Z_\alpha}{|r_i - R\alpha|} + \sum_{i=1}^{N_e}\sum_{j>i}^{N_e} \frac{1}{|r_i - r_j|} \tag{2.3}$$

The following equations (2.4) and (2.5) show both the motion and the energy of the electrons, respectively. They are dependent on the nuclear coordinates.

$$\Psi_e = \Psi_e(r, R), \tag{2.4}$$

$$\epsilon_e = \epsilon_e(R) \tag{2.5}$$

The total energy for fixed nuclei includes the constant nuclear repulsion,

$$\epsilon_{tot}(R) = \epsilon_e(R) + \sum_{\alpha=1}^{N_n}\sum_{\beta>\alpha}^{N_n} \frac{z_\alpha z_\beta}{|R_\alpha - R_\beta|} \tag{2.6}$$

Despite the Born-Oppenheimer approximation, the electron-electron interaction term remains unsimplified. In practice, the motion of electrons are correlated. Electrons with parallel spin keep apart from each other, following Pauli's exclusion principle. Thus, lowering their energy by an amount called the exchange energy. Also, antiparallel electrons keep apart to lower their mutual Coulomb repulsion energy by an amount called the correlation energy.[6]

To deal with a large system of atoms, as in solid state, one of the earliest used approximations for the wavefunction is the Hartree approximation.

2.3 The Hartree Approximation

A common approach for an ab initio treatment of the many-body problem is to break down the many-electron Schrödinger equation into many simpler one-electron equation[7][8][9].

In the Hartree equation, the Hamiltonian (H) of system containing N particles is a sum of one-particle Hamiltonians and the wavefunction Ψ is the product of wavefunctions of each particle,

$$H = \sum_{i}^{N} h(i) \tag{2.7}$$

$$\Psi(r_1 s_1, r_2 s_2, ...r_N s_N) = \psi(r_1 s_1)\psi(r_2 s_2).....\psi(r_N s_N) \tag{2.8}$$

where h_i is the one-particle Hamiltonian (contains the kinetic and potential energy) and s_1,s_2,...s_N are the spins of the N-electrons. Therefore, the Schrödinger equation for one particle can be written as,

$$(-\frac{1}{2}\nabla^2 + V_r)\Psi(rs) = E\Psi(rs) \tag{2.9}$$

Assuming independent electrons and a Hamiltonian of the form of equation (2.7), there is a deficiency in the Hartree product. The Hartree product takes no account of the indistinguishability of electrons, i.e., the Hartree product does not satisfy the antisymmetry principle (Pauli's exclusion principle). Hence the exchange energy is not included in the Hartree equation.

2.4 Slater Determinants

The exchange energy can be added to the Hartree equation using a linear combination of the wavefunctions for each electron instead of the product of them. This is called a Slater determinant. For an N-electron system the generalisation of the Slater determinant is,

$$\Psi(\mathbf{r}_1 s_1, \mathbf{r}_2 s_2, \mathbf{r}_3 s_3 \ldots, \mathbf{r}_N s_N) = \frac{1}{\sqrt{N!}} \begin{vmatrix} \psi_1(\mathbf{r}_1 s_1) & \psi_1(\mathbf{r}_2 s_2) & \cdots & \cdots & \psi_1(\mathbf{r}_N s_N) \\ \psi_2(\mathbf{r}_1 s_1) & \psi_2(\mathbf{r}_2 s_2) & \cdots & \cdots & \psi_2(\mathbf{r}_N s_N) \\ \vdots & \vdots & \vdots & \vdots & \vdots \\ \psi_N(\mathbf{r}_1 s_1) & \psi_N(\mathbf{r}_2 s_2) & \cdots & \cdots & \psi_N(\mathbf{r}_N s_N) \end{vmatrix} \tag{2.10}$$

where $\frac{1}{\sqrt{N!}}$ is the normalisation factor.

2.5 Hartree-Fock (HF) Approximation

Hartree-Fock[7][8][9] theory tries to take the wavefunction's antisymmetry into account in a more coherent way. The Hartree equations are a good first attempt at solving the many-body Schrödinger equation, but inadequately describe a few very important properties of electrons: quantum mechanical indistinguishability of particles and exchange, and explicit, unaveraged Coulomb correlation. Quantum mechanics demands that the wave-function be noncommittal as to which electron is in which state because all electrons are identical. This gives rise to two types of quantum particles: bosons and fermions. Electrons are fermions whose wavefunction must be antisymmetric under the interchange of two particles, obeying the Pauli exclusion principle. The Pauli exclusion principle leads to the exchange energy of electrons, which can be thought of as another means of minimizing the Coulomb energy. The term correlation energy refers to the explicit electron-electron Coulomb interaction, which mean field approaches only compute as the average effect of Coulomb repulsion.

The Slater determinant can be written as,

$$\Psi(\mathbf{r}s) = \frac{1}{\sqrt{N!}} det|\psi(\mathbf{r}s)| \tag{2.11}$$

The variational method is the most common method used to minimise the energy. The variational principle states simply that the Rayleigh quotient (Rc, a provided energy of a system) is always larger than the exact energy of the ground state, i.e., $R_c \geq E_{exact}$. According to the variational principle, the best spin orbitals are those which minimise the energy. Hence, the ground state energy can be obtained by minimising the energy with respect to the spin orbitals, which have to remain orthonormal.

Using the variational method, the single-particle Hartree-Fock equations for a given orbital λ, can be defined as,

$$\{-\frac{1}{2}\nabla^2 + V_{e-ion}(\mathbf{r}) + V_H(\mathbf{r}) + V^x_\lambda(\mathbf{r}) - E_\lambda\}\psi_\lambda(\mathbf{r}) = \sum_{\mu\neq\lambda} E_{\lambda\mu}\psi_\mu(\mathbf{r}) \tag{2.12}$$

$$V_H(\boldsymbol{r})\psi_\lambda(\boldsymbol{r}) = \int \frac{n(\boldsymbol{r}_1)\psi_\lambda(\boldsymbol{r})}{|\boldsymbol{r}\text{-}\boldsymbol{r}_1|} d\boldsymbol{r}_1,$$

$$V^x_\lambda(\mathbf{r})\psi_\lambda(\mathbf{r}) = \int \psi^*_\mu(\mathbf{r}_1)\psi_\lambda(\mathbf{r}_1)\frac{1}{|\mathbf{r}\text{-}\mathbf{r}_1|}\psi_\mu(\mathbf{r})d\mathbf{r}_1$$

In equation (2.12), the first and second terms are the kinetic and potential energies, i.e., the one-electron energy. The third term is the Coulomb energy: the Coulomb interaction of an electron in spin orbital $\psi_\lambda(\mathbf{r})$ with the average charge distribution of the other electrons. Hence, the Hartree-Fock theory is considered as a mean field theory. The fourth term is the exchange energy, which arises because of the antisymmetric nature of the determinant wavefunction. The solution of the Hartree-Fock equation depends on the chosen spin orbitals. An initial guess of spin orbitals is made, then they are refined through the variational method iteratively. Therefore, the Hartree-Fock approximation is also known as a self-consistent-field. The exact solution to the Hartree-Fock equation is obtained only if we have the exact spin orbital.

2.6 Density-Functional Theory (DFT)

Density Functional theory (DFT) was introduced in 1960's by Hohenberg and Kohn[10] (1964), then modified by Kohn and Sham[11] (1965). Over the past few decades, density functional theory (DFT) has been the most successful, widely used method in condensed-matter physics, computational physics and quantum chemistry to describe properties of condensed matter systems, which include not only standard bulk materials but also complex materials such as molecules, proteins, interfaces and nanoparticles. The main idea of DFT is to describe a many-body interacting system via its particle density and not via its many-body wavefunction. Its significance is to reduce the 3N degrees of freedom of the N-body system to only three spatial coordinates through its particle density.

The particle density which is the key variable in DFT is given by,

$$n(\vec{r}) = N \int d^3r_2 \int d^3r_3 ...... \int d^3r_n \psi^*(\vec{r_1}, \vec{r_2}, ...\vec{r_N}) \psi(\vec{r_1}, \vec{r_2} ....\vec{r_N}) \tag{2.13}$$

The electron density only depends on three coordinates instead of 3N spatial coordinates, but still contains all the information needed to determine the Hamiltonian, for example number of electron N, the coordinate of nuclei R_A and the charge of nuclei Z_A. This is the advantage of electron density compared to wavefunction. N is simply given by the integral over $n(\vec{\mathbf{r}})$:

$$\int n(\vec{\mathbf{r}}) d^3\mathbf{r} = N \tag{2.14}$$

2.6.1 Thomas-Fermi model

The predecessor to DFT was the Thomas-Fermi (TF) model proposed by Thomas[12] and Fermi[13] in 1927. In this method, they used the electron density n(r) as the basic variable instead of the wavefunction. The total energy of a system in an external potential $V_{ext}(\mathbf{r})$ is written as a functional of the electron density n(r) as:

$$E_{TF}[n(\mathbf{r})] = A_1 \int n(\mathbf{r})^{5/3} d\mathbf{r} + \int n(\mathbf{r}) V_{ext}(\mathbf{r}) d\mathbf{r} + \frac{1}{2} \int \int \frac{n(\mathbf{r}) n(\mathbf{r}')}{|\mathbf{r}\text{-}\mathbf{r}'|} d\mathbf{r} d\mathbf{r}' \tag{2.15}$$

where the first term is the kinetic energy of the non-interacting electrons in a homogeneous electron gas (HEG) with $A_1 = \frac{3}{10}(3\pi^2)^{\frac{2}{3}}$ in atomic units ($\hbar = m_e = e = 4\pi/\varepsilon_0 = 1$). The second term is the classical electrostatic energy of the nucleus-electron Coulomb interaction. The third term is the classical electrostatic Hartree energy approximated by the classical Coulomb repulsion between electrons. In the original TF method, the exchange and correlation among electrons was neglected. In 1930, Dirac[14] extended the Thomas-Fermi method by adding a local exchange term $A_2 \int n(r)^{4/3} dr$ to Eq.(2.15) with $A_2 = -\frac{3}{4}(3/\pi)^{1/3}$,which leads Eq.(2.15) to

$$E_{TFD}[n(\mathbf{r})] = A_1 \int n(\mathbf{r})^{5/3} d\mathbf{r} + \int n(\mathbf{r}) V_{ext}(\mathbf{r}) d\mathbf{r} + \frac{1}{2} \int \int \frac{n(\mathbf{r}) n(\mathbf{r}')}{|\mathbf{r}\text{-}\mathbf{r}'|} d\mathbf{r} d\mathbf{r}' + A_2 \int n(\mathbf{r})^{4/3} d\mathbf{r} \tag{2.16}$$

The ground state density and energy can be obtained by minimizing the Thomas-Fermi-Dirac equation(2.16) subject to conservation of the total number (N) of electrons.

The approximations used in Thomas-Fermi-type approach are so crude that the theory suffers from many problems. The most serious one is that the theory fails to describe bonding between atoms, thus molecules and solids cannot form in this theory[15]. Although it is not good enough to describe electrons in matter, its concept to use electron density as the basic variable illustrates the way DFT works.

2.6.2 The Hohenberg-Kohn (HK)Theorems

DFT was proven to be an exact theory of many-body systems by Hohenberg and Kohn[16] in 1964. It applies not only to condensed-matter systems of electrons with fixed nuclei, but also more generally to any system of interacting particles in an external potential $V_{ext}(\mathbf{r})$.The theory is based upon two theorems.

The first Hohenberg - Kohn theorem: *The ground state particle density n(**r**) of a system of interacting particles in an external potential* $V_{ext}(\boldsymbol{r})$ *uniquely determines the external potential* $V_{ext}(\boldsymbol{r})$*,except for a constant.*

Thus the ground state particle density determines the full Hamiltonian, except for a constant shift of the energy. In principle, all the states including ground and excited states of the many-body wavefunctions can be calculated. This means that the ground state particle density uniquely determines all properties of the system completely.

The second Hohenberg - Kohn theorem: *There exists a universal functional F[n(**r**)] of the density, independent of the external potential* $V_{ext}(\boldsymbol{r})$*,such that the global minimum value of the energy functional E[n(**r**)]* $= \int n(\boldsymbol{r}) V_{ext}(\boldsymbol{r}) d\boldsymbol{r} + F[n(\boldsymbol{r})]$ *is the exact ground state energy* *of the system and the exact ground state density* $n_0(\boldsymbol{r})$ *minimizes this functional.Thus the exact ground state energy and density are fully determined by the functional E[n(***r***)].*

According to variational principle,the energy functional E[n($\mathbf{r}$)] evaluated for the correct ground state density $n_0(\mathbf{r})$ is indeed lower than the value of this functional for any other density n($\mathbf{r}$). Therefore by minimizing the total energy functional of the system with respect to variations in the density n($\mathbf{r}$), one would find the exact ground state density and energy. Although HK theorems put particle density n($\mathbf{r}$) as the basic variable, it is still impossible to calculate any property of a system because the universal functional F[n($\mathbf{r}$)] is unknown. This difficulty was overcome by Kohn and Sham[7] in 1965.

2.6.3 Kohn-Sham equations

Kohn-Sham equations puts Hohenberg-Kohn theorems into practical use and make DFT calculations possible with even a single personal computer. This is part of the reason that DFT became the most popular tool for electronic structure calculations. These Kohn-Sham equations was so successful that Kohn was honored the Nobel prize in chemistry in 1998.

Here we will replace the original many-body system by an auxiliary independent-particle system and assume that the two systems have exactly the same ground state density. It maps the original interacting system with real potential onto a fictitious non-interacting system whereby the electrons move within an effective Kohn-Sham single-particle potential $V_{KS}(\mathbf{r})$. For the auxiliary independent-particle system, the auxiliary Hamiltonian is

$$\hat{H}_{KS} = -\frac{1}{2}\nabla^2 + V_{KS}(\mathbf{r}) \tag{2.17}$$

in atomic units $\hbar = m_e = e = 4\pi/\varepsilon_0 = 1$. For a system with N independent electrons, the ground state is obtained by solving the N one-electron Schrodinger equations,

$$(\frac{1}{2}\nabla^2 + V_{KS}(\mathbf{r}))\psi_i(\mathbf{r}) = \varepsilon_i\psi_i(\mathbf{r}) \tag{2.18}$$

where there is one electron in each of the N orbitals $\psi_i(\mathbf{r})$ with the lowest eigenvalues ε_i.

The density of the auxiliary system is constructed from:

$$n(\mathbf{r}) = \sum_{i=1}^{N} |\psi_i(\mathbf{r})|^2 \tag{2.19}$$

which is subject to the conservation condition:

$$\int n(\mathbf{r}) d\mathbf{r} = N \tag{2.20}$$

The non-interacting independent-particle kinetic energy $T_s[n(\mathbf{r})]$ is given by,

$$T_s[n(\mathbf{r})] = -\frac{1}{2}\sum_{i=1}^{N} \int \psi_i^*(\mathbf{r}) \nabla^2 \psi_i(\mathbf{r}) d\mathbf{r} \tag{2.21}$$

Then the universal functional F[n($\mathbf{r}$)] can be written as,

$$F[n(\mathbf{r})] = T_s[n(\mathbf{r})] + E_H[n(\mathbf{r})] + E_{XC}[n(\mathbf{r})] \tag{2.22}$$

where $E_H[n(\mathbf{r})]$ is the classic electrostatic (Hartree) energy of the electrons,

$$E_H[n(\mathbf{r})] = \frac{1}{2}\int\int \frac{n(\mathbf{r})n(\mathbf{r}')}{|\mathbf{r}\text{-}\mathbf{r}'|} d\mathbf{r} d\mathbf{r}' \tag{2.23}$$

and $E_{XC}[n(r)]$ is the XC energy, which contains the difference between the exact and non-interacting kinetic energies and also the non-classical contribution to the electron-electron interactions, of which the exchange energy is a part. Since the ground state energy of a many-electron system can be obtained by minimizing the energy functional $E[n(\mathbf{r})] = F[n(\mathbf{r})] + \int n(\mathbf{r}) V_{ext}(\mathbf{r}) d\mathbf{r}$, subject to the constraint that the number of electrons N is conserved,

$$\delta\{F[n(\mathbf{r})] + \int n(\mathbf{r}) V_{ext}(\mathbf{r}) d\mathbf{r} - \mu(\int n(r) dr - N)\} = 0 \tag{2.24}$$

and the resulting equation is

$$\begin{aligned} \mu &= \frac{\delta F[n(\mathbf{r})]}{\delta n(\mathbf{r})} + V_{ext}(\mathbf{r}) \qquad (2.25) \\ &= \tfrac{\delta T_s[n(\mathbf{r})]}{\delta n(\mathbf{r})} + V_{KS}(\mathbf{r}) \end{aligned}$$

where μ is the chemical potential,

$$V_{KS}(\mathbf{r}) = V_{ext}(\mathbf{r}) + V_H(\mathbf{r}) + V_{XC}(\mathbf{r}) \tag{2.26}$$

$$= V_{ext}(\mathbf{r}) + \tfrac{\delta E_H[n(\mathbf{r})]}{\delta n(\mathbf{r})} + \tfrac{\delta E_{XC}[n(\mathbf{r})]}{\delta n(\mathbf{r})}$$

is the KS one-particle potential with the Hartree potential $V_H(\mathbf{r})$

$$V_H(\mathbf{r}) = \frac{\delta E_H[n(\mathbf{r})]}{\delta n(\mathbf{r})} \tag{2.27}$$

$$= \int \tfrac{n(\mathbf{r}')}{|\mathbf{r}\text{-}\mathbf{r}'|} d\mathbf{r}'$$

and the XC potential $V_{XC}(\mathbf{r})$

$$V_{XC}(\mathbf{r}) = \frac{\delta E_{XC}[n(\mathbf{r})]}{\delta n(\mathbf{r})} \tag{2.28}$$

Equations (2.18) , (2.19), (2.26) together are the well-known KS equations,which must be solved self-consistently because $V_{KS}(r)$depends on the density through the XC potential. In order to calculate the density, the N equations in Eq.(2.18) have to be solved in KS theory as opposed to one equation in the TF approach. However an advantage of the KS method is that as the complexity of a system increases, due to N increasing, the problem becomes no more difficult, only the number of single-particle equations to be solved increases.

It is crucial to have an accurate XC energy functional $E_{XC}[n(r)]$ or potential $V_{XC}(r)$ in order to give a satisfactory description of a realistic condensed-matter system. The most widely used approximations for the XC potential are the local density approximation (LDA) and the generalized-gradient approximation (GGA).

2.6.4 Exchange-correlational functionals

The Kohn-Sham equations successfully map the original interacting many-body system onto a set of independent single-particle equations and makes the problem much easier. In the meantime, without knowing the exact form of the XC energy functional $E_{XC}[n(r)]$,the KS equations are unsolvable. Although the exact XC energy functional $E_{XC}[n(r)]$ should

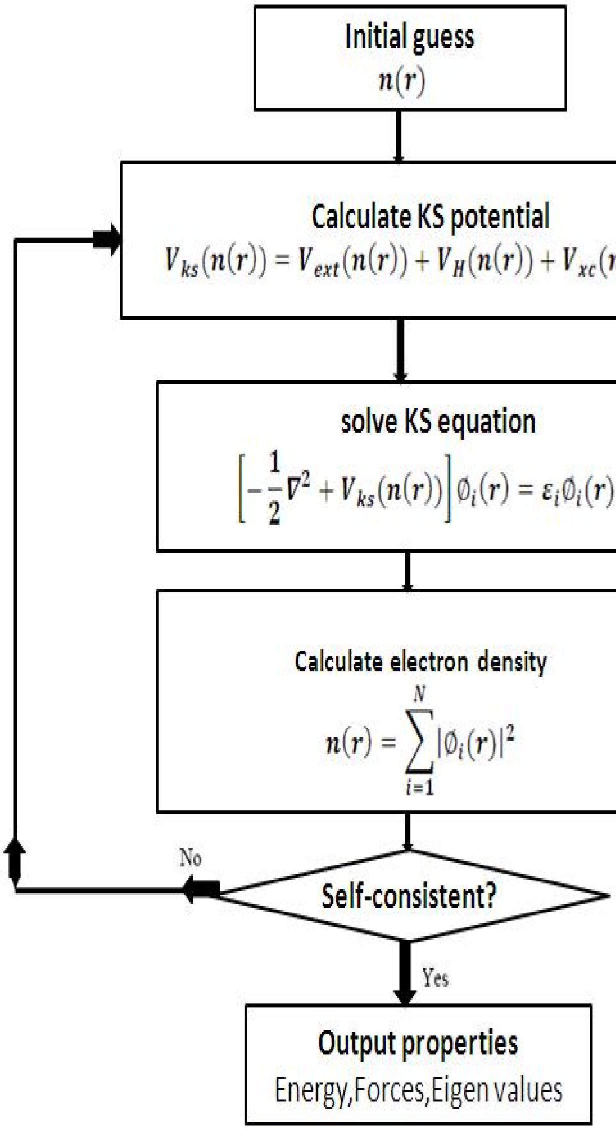

Figure 2.1: DFT algorithm

be very complicated, simple but successful approximations to it have been made, which not only predict various properties of many systems reasonably well but also greatly reduce computational costs, leading to the wide use of DFT for electronic structure calculations. Of these approximations, the local density approximation (LDA) is the most widely used one.

In general,the exchange-correlation energy consists of two terms,

$$E_{XC}[n] = E_X[n] + E_C[n] \tag{2.29}$$

where $E_X[n]$ and $E_C[n]$ are the exchange and correlation energies, respectively. In DFT within LDA, ϵ_{xc} at a point r in inhomogeneous electron density is replaced by ϵ_{xc} for a homogenous electron gas of the same density, $\epsilon_{xc}^{hom}[n(\mathbf{r})]$

$$E_{XC}^{LDA}[n(\mathbf{r})] = \int n(\mathbf{r})\epsilon_{xc}^{hom}[n(\mathbf{r})]dr \tag{2.30}$$

$\epsilon_{xc}^{hom}[n(\mathbf{r})]$ is divided into two terms (exchange and correlation),

$$\epsilon_{XC}^{hom}[n(\mathbf{r})] = \epsilon_{x}^{hom}[n(\mathbf{r})] + \epsilon_{c}^{hom}[n(\mathbf{r})] \tag{2.31}$$

The exchange energy at a point **r** can be calculated via an analytic Hartree-Fock treatment of the uniform electron gas,

$$\epsilon_x[n(\mathbf{r})] = -\frac{3}{4}\left(\frac{3}{\pi}\right)^{1/3}[n(\mathbf{r})]^{1/3} \tag{2.32}$$

and the correlation energy is determined by a mixture of analytic treatments and Monte Carlo simulation. Then these numerical results are fitted to the Perdew- Wang (PW)[17] parameterised form. Other commonly available parameterisation forms are Perdew-Zunger (PZ)[18] and Vosko-Wilk-Nusair (VWN)[19].

An approach to improve LDA is to consider the first-order approximation to the exchange-correlation (XC) potential, the gradient correction of the charge density, $|\nabla_n|$ which takes into account the inhomogeneity of the electron gas. This method, where the XC potential is a function of both the charge density at a certain point and the first-order gradient of the charge density at the same point, $\epsilon_{XC}(n, |\nabla_n|)$,is known as the generalised gradient approximation (GGA). LDA tends to underestimate atomic ground state energies and overestimate the binding energies. The GGA method generally gives better total energies, especially for small molecules, but computationally it is more time consuming than LDA.

Chapter 3

Computational details

3.1 CASTEP

In this work we have used Cambridge Series of Total Energy Package (CASTEP), which is originally developed by Payne and co-workers in the early 1990s [20,21,22]. In this thesis plane-wave pseudo-potential calculations have been performed using the CASTEP program. CASTEP is a commercially available code for ab-initio quantum mechanical calculations based on density-functional theory to simulate the properties of solids, interfaces, and surfaces for a wide range of materials classes such as ceramics, semiconductors, and metals. CASTEP uses density functional theory (DFT) (specifically, using planewaves and pseudopotentials) to solve approximately the Schrodinger equation for periodic systems of atoms, yielding the total energy, atomic forces and internal stresses in the system, as well as interesting electronic properties (the electron wavefunction, charge density distribution,density of electronic states, etc). Based on the total energy pseudopotential methods, CASTEP takes the number and type of atoms in a system and predicts its properties such as lattice constants, molecular geometry, elastic constants, band structures,density-of-states, charge densities and optical properties.

3.2 The Plane-wave basis set

The plane-wave method is applied to 3D periodic systems and is based on Blochs theorem[23,24]. According to this theorem, due to the translational symmetry, each electronic wave function can be expressed as a product of a cell periodic part $u_i(\mathbf{r})$ and a plane wave part $e^{ik.r}$ with the wave vector k,

$$\psi_i(\mathbf{r}) = u_i(\mathbf{r})e^{ik.r} \tag{3.1}$$

The cell periodic part $u_i(\mathbf{r})$ is expanded using a basis set of plane waves with reciprocal lattice vectors G:

$$u_i(\mathbf{r}) = \sum_G c_{i,G}e^{iG.r} \tag{3.2}$$

where $c_{i,G}$ represent the expansion coefficients. The electronic wave function becomes a sum of plane waves:

$$\psi_i(\mathbf{r}) = \sum_G c_{i,k+G}e^{i(k+G)r} \tag{3.3}$$

Here, the exponential term is a plane wave of wave vector k.

Bloch's theorem simplifies the problem of calculating a large number of plane waves for an infinite number of k-points to a reduced number of plane waves for an infinite number of k-points over the reciprocal lattice vectors. This simplification known as k-point mesh (or k-point sampling) and can be achieved by considering that the change in the wave function with k becomes negligible for k-points that are close to each other, and therefore a finite set of plane waves is calculated.

The electronic wave function at each k-point is expressed in terms of a discrete plane wave basis set. The plane wave basis set is truncated such as to include plane waves with coefficients that have kinetic energy smaller than a particular cut-off energy,

$$E_{cut-off} = \frac{\hbar^2(G+k)^2}{2m} \tag{3.4}$$

However, the plane waves coefficients with a smaller kinetic energy have a more important role than those with a very high kinetic energy.

3.3 Pseudopotentials

The electrons in a solid are divided into core electrons and valence electrons. The core electrons are localized around the nucleus in closed shells while the valence electrons take part in the bonding between atoms. The valence electrons determine the chemical and transport properties of the material and they are consequently the most interesting electrons to study. The core electrons screen the charge of the nuclei such that the valence electrons experience a smoother potential in the core region than the bare Coulomb potential. The pseudopotential approximation exploits this fact by considering that the valence electrons are moving in a pseudo potential, formed by bare the nuclei potential screened by the core electrons.

The core electrons in an atom are highly localised and do not take part in chemical reactions, and it is therefore only the valence electrons that determine the atom's chemical properties. The modelling of core electrons in a calculation is dificult to perform accurately, since in order to satisfy orthogonality, their wavefunctions must oscillate strongly near to the core, and the number of basis functions required to fit all states accurately becomes prohibitively large. In addition, full-electron calculations give large total energies, with correspondingly large errors introduced when comparing the energies of similar systems.

For these reasons, it is desirable to remove the core electrons from electronic structure calculations. This can be done by considering that, due to the presence of the core electrons nearer to the nucleus, the valence electrons in an atom experience an effective, screened nuclear potential - `a pseudo potential`. The core electrons are therefore removed, and their influence and that of the nucleus is replaced with a pseudopotential[25−28].

Several approximations/assumptions must be made when making use of pseudopotentials, namely that:

- The all-electron Coulomb operator can be decomposed into two separate parts: one that deals with the core states, and the other that takes care of the valence states.
- The core states are unaffected by changes in the local environment of the atom. This

is called the frozen-core approximation.

- There is negligible overlap between the core and valence states, hence the approximation $E_{XC}(n_{core} + n_{valence}) = E_{XC}(n_{core}) + E_{XC}(n_{valence})$ is valid.

A practical pseudopotential must also give rise to pseudo-wavefunctions that, outside of a certain 'cut-off' radius from the core, are identical to those derived from an all-electron calculation. This is known as *norm conservation*, and one example of a set of normconserving pseudopotentials is that of Bachelet, Hamann, and Schluter (BHS)[29,30].

There is no unique recipe to construct a pseudopotential for a particular element. An infinite amount of choices are possible. Two criteria to judge whether a particular pseudopotential is good, are *softness* and *transferability*. A pseudopotential is called *soft* when few plane waves are needed. A specific class of pseudopotentials is even called *ultrasoft*, because of the very small amount of plane waves it calls for. Generally, making a pseudopotential soft means that it gets tailored for an element in a specific environment. What one really wants is a potential that can be used in whatever environment (molecule, cluster, solid, surface, insulator, metal,...) the corresponding element can be. Such a pseudopotential is called *transferable*. The art of creating good pseudopotentials is to find potentials that are both (ultra)soft and transferable.

The quality of a given pseudopotential can be assessed by investigating its *transferability*. That is, a transferable pseudopotential is one that will reproduce the properties of an atom's valence electrons sufficiently well in a wide range of different local environments. For example, a high-quality pseudopotential for the carbon atom would give accurate results when used in diamond, graphite, or in fullerenes.

A schematic illustration of the pseudopotential concept is shown in Fig. 3.1. The choice of the cutoff radius r_c is very important. In general, the larger r_c will result in a softer pseudopotential,but also the less transferable. There is no well-defined answer for how to choose a r_c. In practice, r_c should be larger than the outermost node(if any) of the wavefunction for

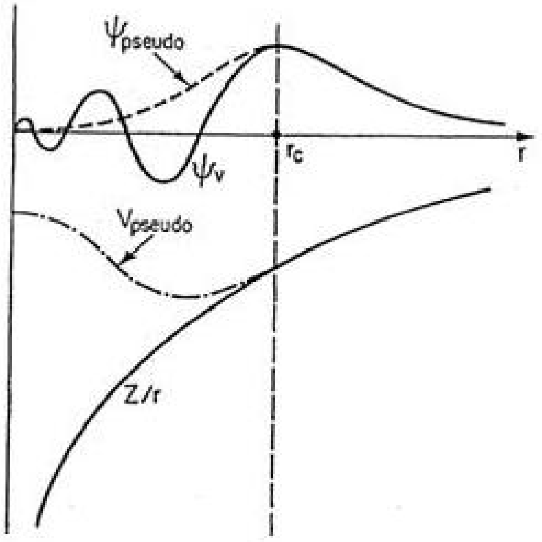

Figure 3.1: Schematic illustration of pseudopotential approach

any given angular momentum. Usually there is one angular momentum that is harder than the others (in transition metals, the d state, in second-row elements N, O, F, the p state), and one should concentrate on this one and push outwards its r_c as much as possible. In addition, one should try to have not too different r_c for different angular momenta.

In CASTEP two forms of the pseudo-potential are implemented: the ultra-soft pseudopotential and the norm-conserving pseudo-potential. The ultra-soft pseudo-potential calculations are performed at a low $E_{cut-off}$ while for the norm-conserving pseudo-potential implementation of a larger cut-off energy is needed and it makes computationally more expensive. Therefore, in all calculations performed in this thesis are based on ultra-soft pseudo-potential proposed by Vanderbilt [31].

3.3.1 The ultrasoft pseudopotentials

An additional step in the development of even softer pseudopotentials was taken by Vanderbildt when he introduced the concept of ultrasoft pseudopotentials . The idea of ultrasoft pseudopotentials as put by Vanderbilt is that the relaxation of the norm-conserving condition can be used to generate much softer potentials.

The idea behind the ultrasoft pseudopotential is in a sense similar to the orthogonalized plane wave method (OPW)[32] method, because the Kohn-Sham wave function is divided into a soft delocalized contribution and a rapidly oscillating augmentation charge localized in the core region. In this scheme the pseudo-wave-functions are allowed to be soft as possible within the core region, so that the cutoff energy can be reduced dramatically. Technically, this is achieved by introducing a generalized orthonormality condition. The electron density given by the squared moduli of the wave functions has to be augmented in the core region in order to recover the full electronic charge. The electron density is thus subdivided into (i) a smooth part that extends throughout the unit cell, and (ii) a hard part localized in the core regions. The augmented part appears in the density approach is applied to wavefunctions. Ultrasoft potentials is much softer than the norm conserving potential. The ultrasoft potentials generation algorithm guarantees good scattering properties over a pre-specified energy range, which results in much better transferability and accuracy of pseudopotentials. It usually also treats "shallow" core states as valence by including multiple sets of occupied states in each angular momentum channel. This also adds to high accuracy and transferability of the potentials, although at a price of computational efficiency.

3.4 CASTEP calculations

Geometry optimization: The geometry optimization process allows to find the most stable structure corresponding to the energy minimum. CASTEP performs geometry optimization using an iterative process. The atomic coordinates and the cell parameters are modified until a defined convergence tolerance of the calculated stresses and forces is reached.

By default, CASTEP uses the BFGS geometry optimization method. The main advantage of the new BFGS minimizer[33] is the ability to perform cell optimizations, including optimization at fixed external stress. It is important to set up the calculation correctly in order to achieve the best performance of the minimizer.

Band structure: Extended periodic systems may be characterized by their energy bands. These are analagous to orbital eigenvalues in molecular systems. Unlike the orbital eigenvalues, the energy of each band will vary at different points in the cell. The bands are plotted in the so-called reciprocal space of the cell. In fact, there are a limited number of symmetry-unique directions in reciprocal space, so only a finite number of points are needed to characterize the bands. By observing the energy gaps between bands at various points, it is possible to draw conclusions about the nature of a material, i.e., whether it is an insulator, a conductor, or a semiconductor.

Density of states: Another way of characterizing the electronic structure of a material is by the density of states (DOS). The DOS counts the relative number of energy levels in each energy range. In a molecule, there are distinct energy eigenvalues, so, strictly speaking, the DOS has a value of 1 at each of these values and a value of 0 elsewhere. For a crystal, by contrast, the energy levels are a continuum, with more or less energy values squeezed into an energy range. Examining the DOS also allows us to see whether a system is conducting or insulating. In addition, the partial density of states (PDOS) allows us to characterize the DOS in terms of particular atomic orbitals, s, p, d, or f.

The Mulliken bond population and total charge density distributions: Mulliken charge analysis[33] is one of the most common methods of population analysis for assigning partial charges of individual atoms in a molecule. Bond population is an important parameter which suggests the nature of bonding between two atoms in a molecule. The method is able to calculate the net electron transferred from the surface to the adsorbant upon adsorption or to the transition state of a surface reaction. The distribution of electrons in a molecule and the properties related to the charge distribution can provide enormous help in interpreting the chemical surface processes.

Chapter 4

Results and discussion

Density functional theory (DFT) is widely using in solid-state chemistry and materials science for the calculation of electronic, bonding, and structural properties of solids. DFT has became very successful tool in predicting and explaining a wide variety of materials ground-state phenomena. In this present work, we studied the structural, electronic and bonding properties of Li_3X (X= P, As) compounds at ambient conditions using density functional theory. We perform the full structural optimizations for the unit cell and atomic positions of Li_3X (X= P, As) compounds and as discussed in detail in the subsequent sections. The ground state structural parameters such as lattice constants, internal parameters are calculated based on local density approximation(LDA) using CASTEP program. Geometry optimization for the compounds is achieved by using the Broyden-Fletcher-Goldfard-Shannon (BFGS) minimisation method which minimizes a real valued function evaluated for the system after each SCF convergence and obtained the equilibrium geometry. Since all the calculations are performed using plane wave pseudo potentials, it would be necessary to check the convergance of plane wave cut-off energy and k-point grid. We have calculated the total energies for each cut-off energy starting from an initial guess at a fixed k-point set. It was found that for the cut-off energy of 650 eV the change in energy was in milli electron volts, hence we chose this cut-off energy for further calculation. Now by fixing this cut-off energy we have performed the k-point sampling test. For the k-point set of 10x10x7 we find the change in energy in milli electron volts. These set of 650 eV and 10x10x7 has been used for all further calculations.

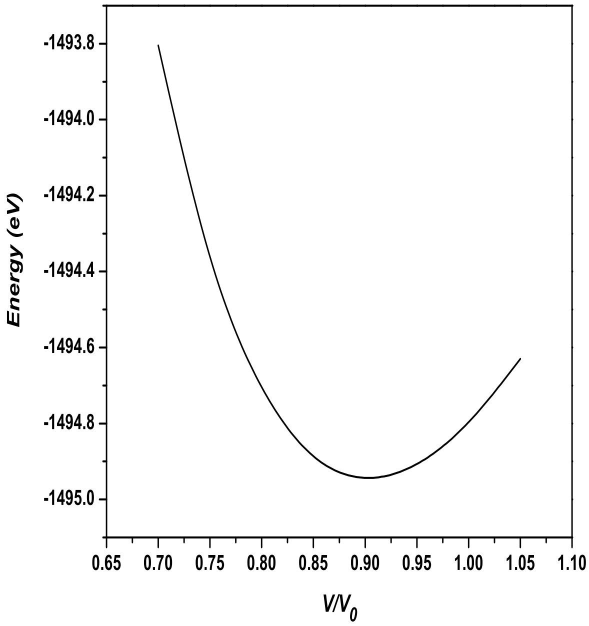

Figure 4.1: Total energy as a function of V/V_0 for Li_3P

The electronic configuration of each element is as follows:

Li: $1s^2\ 2s^1$

P : $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^3$

As: $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^{10}\ 4s^2\ 4p^3$

4.1 Li$_3$P

4.1.1 Geometry optimization

As a first step of our calculations we have optimized the experimental crystal structure of Li$_3$P. This is done by calculating the total energies for different volumes and fitting the results into Birch-Murnaghan equation of state. The crystal structure with minimum total energy has been taken as the theoretical crystal structure(optimized crystal structure) and it is used for further calculations. The optimized lattice parameters, volume and internal parameter are presented in Table 4.1 along with experiment. It is observed that our calculated lattice parameters are underestimated by 3-4% compared to experimental data. This discrepancy can be expected from density functional calculations based on local density approximation. Total energy as a function of V/V$_0$ for Li$_3$P is shown in Fig 4.1. We have also calculated the bulk modulus(B) of the compound Li$_3$P and it is obtained to be 44.9 GPa.

Parameter	Present work	Experiment
a(Å)	4.112	4.264
c(Å)	7.350	7.579
Volume(V)$(Å)^3$	107.68	119.33
u	0.584	0.583
B(GPa)	44.9	–

Table 4.1: The calculated and experimental parameters of Li$_3$P

4.1.2 Band structure

The energy band structure of Li$_3$P is shown in Fig 4.2. The Fermi level is set to be zero of the Y-axis. From the obtained energy band structure one can clearly observes that the the valence band maximum and conduction band minimum are located at Γ and K points in the

Brillouin zone, implies that this compound has an indirect band gap with a magnitude of 0.45 eV. This clearly shows the semiconducting nature of Lithium phosphide. The contribution of various electronic states in the valence band and the conduction band can be known by their total and partial density of states (DOS).

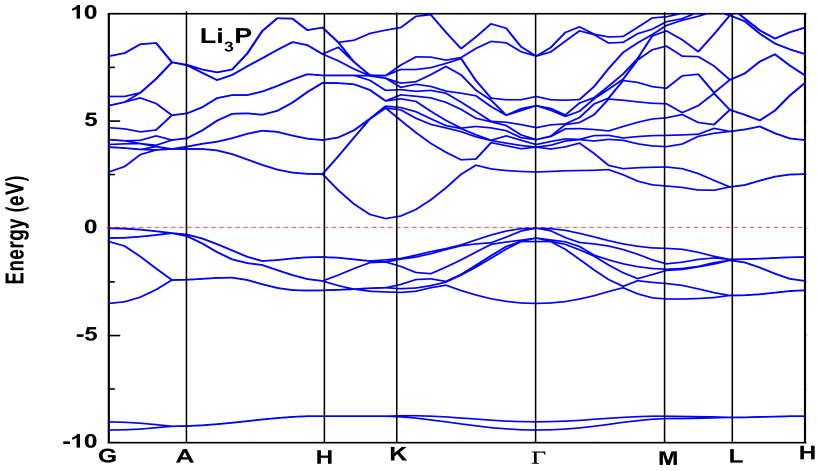

Figure 4.2: Band structure of Li_3P

4.1.3 Density of states

The total and partial density of states of Li_3P are shown in Fig 4.3. From figure, we can clearly observe that in the valence band near the Fermi level, the states are dominated by p-electrons of the P atom. The states near the Fermi level between -3.5 eV to 0 eV are due to p-states of pnictide element P and s-states of Li with a small contribution below the Fermi level. We can also observe that there is an overlap between s-states of Li and p-states of the P, leads to existence of covalent bonding in Li_3P. In the conduction band, above the Fermi level the peaks are entirely dominated by the s-states of metal atom Li, which implies that the electrons from the metal atom can be act as free electrons in this pnictide compound. The contribution of states from P atom are very less in the conduction band, see Fig 4.3.

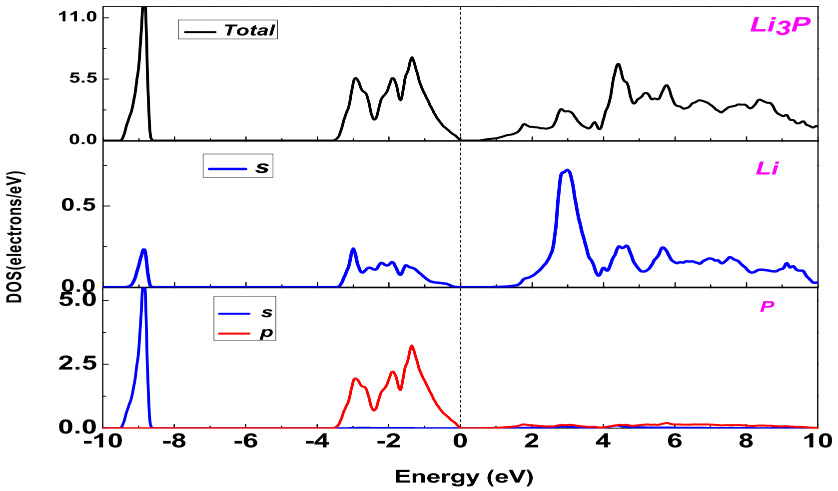

Figure 4.3: Density of states of $\mathrm{Li_3P}$

4.1.4 Nature of bonding

The nature of chemical bonding in Li_3P compound is evaluated by using Mulliken bond population analysis. Bond population is an important parameter which suggests the nature of bonding between two atoms in a molecule. A high value of the bond population indicates a covalent bond, where as a low value indicates an ionic nature. Positive and negative values indicate bonding and anti-bonding states respectively. For Li_3P, we have obtained a Mulliken atomic charge of $0.60|e|$ on Li atom and $-1.85|e|$ on P atom. The calculated avarage Li-P bond population found to be 0.65 and -0.13. This indicates that nature of the bond is mainly covalent and some ionic nature is also exists. The charge density distributions of Li_3P along (100) and (010) planes are shown in Fig 4.4. From these plots, we can clearly understand that there is considerable charge sharing between Li and P atoms which indicates that the boniding between them is partly covalent and partly ionic.

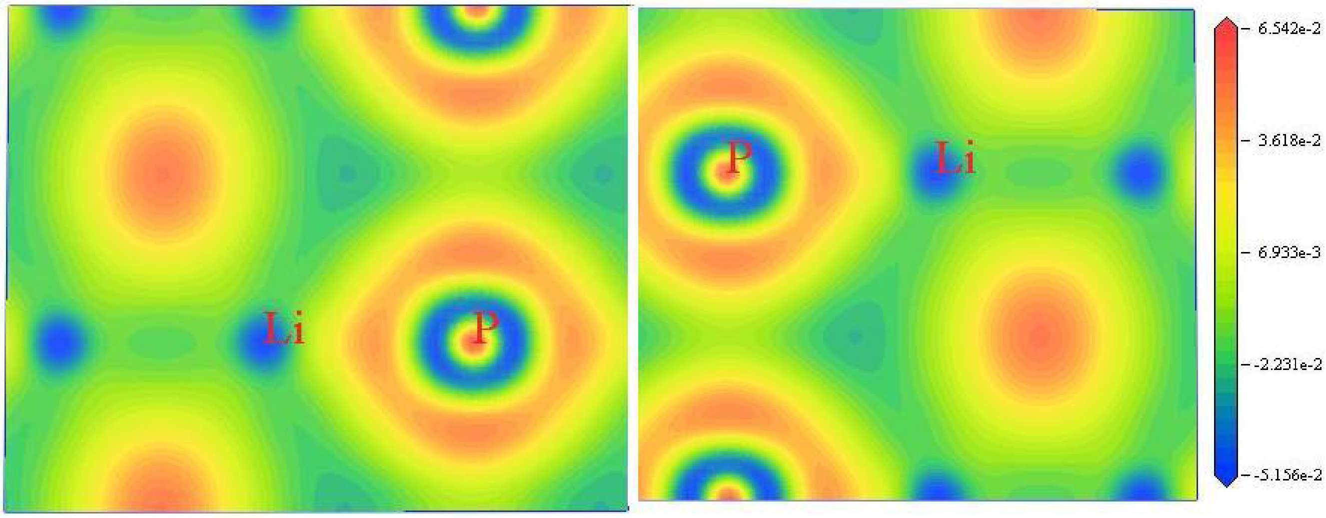

Figure 4.4: Charge density distribution of Li_3P along (100) and (010) plane

4.2 Li_3As

4.2.1 Geometry optimization

Parameter	Present work	Experiment
a(Å)	4.230	4.397
c(Å)	7.555	7.824
Volume(V)$(\AA)^3$	117.13	131.00
u	0.585	0.583
B(GPa)	40.0	–

Table 4.2: The calculated and experimental parameters of Li_3As

For Li_3As compound also, we have optimized the experimental crystal structure by calculating the total energies for different volumes and then the results are fitted into Birch-Murnaghan equation of state. The crystal structure with minimum total energy has been taken as the theoretical crystal structure and it is used for further calculations. The optimized lattice parameters, volume and internal parameter are presented in Table 4.2 along with experiment. Here also, it is observed that our calculated lattice parameters are underestimated by 3-4% compare to experimental data, this is due to the typical behavior of LDA for the exchange correlation functional. Total energy as a function of of V/V_0 for Li_3As is shown in fig 4.5. And also, we calculated the bulk modulus(B) of the compound Li_3As and it is obtained to be 40.0 GPa.

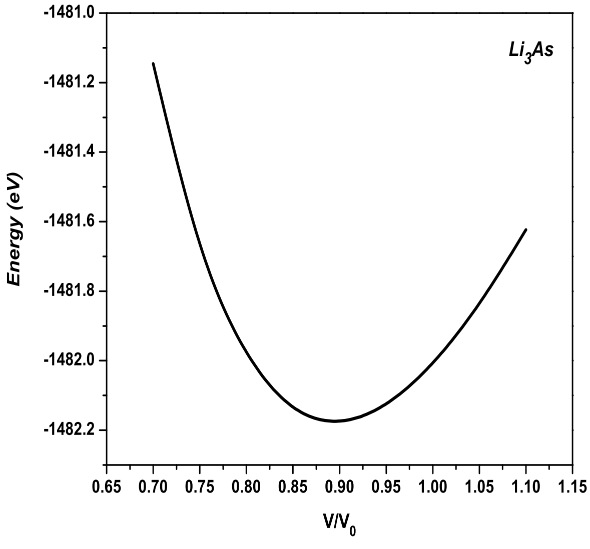

Figure 4.5: Total energy as a function of V/V_0 for Li_3As

4.2.2 Band structure

Since these Li_3P, Li_3As compounds are isostructural compounds, we can expect a similarity in their properties. So,we can expect a similarity in the band strucure of these compounds. The energy band structure of Li_3As compound is shown in Fig 4.6. The Fermi level is set to be zero of the Y-axis. The obtained band structure of Li_3As is similar to the band structure of Li_3P. For this compound also, the valence band maximum and conduction band minimum are located at Γ and K points, implies that this compound has an indirect band gap with a magnitude of 0.40 eV. So,we can say that it is also an indirect band gap semiconductor.

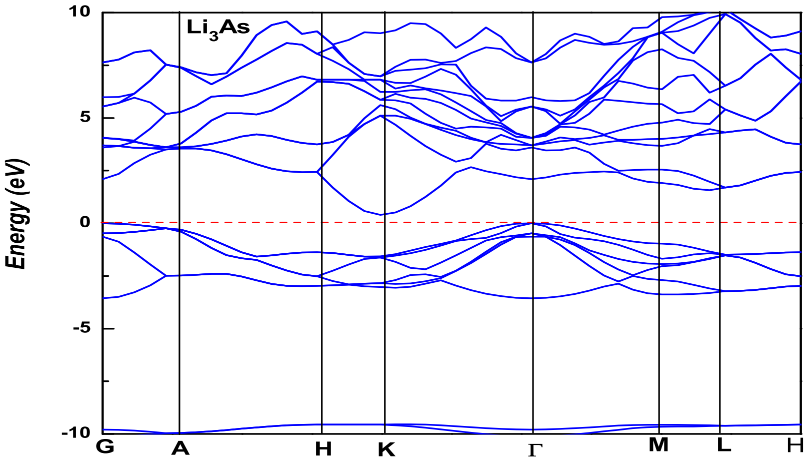

Figure 4.6: Band structure of Li_3As

4.2.3 Density of states

The total and partial density of states are shown in Fig 4.7. In the valence band, the peaks near the Fermi level are dominated by *p*-states of As and there is also some contribution from the s-states of Li between -3.5 eV to 0 eV . The states near the Fermi level between -3.5 eV to 0 eV there is a overlapping between *s*-states of Li and *p*-states of As and therefore we can expect a covalent nature bonding. Around -9 eV to 10 eV ,the *s*-states of As atom are dominating where as there is no states contributions from the metal atom Li in this energy region. So over all in this Li_3As compound the bonding is mainly ionic and there is a small covalent nature also present. This result we can observe quantitatively from the study of Mulliken bond population and charge density distributions in the next section(4.2.4). In the conduction band, bands are mainly derived from the *s*-states of metal atom Li above the Fermi level. And also in the conduction band there is a contribution from the *s*-states of As.

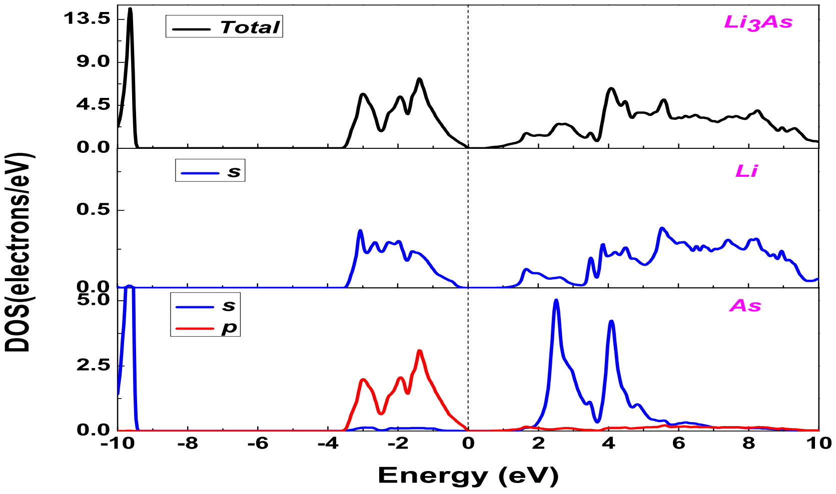

Figure 4.7: Density of states of Li$_3$As

4.2.4 Nature of bonding

In case of Li$_3$As, the Mulliken population analysis shows that a charge of 0.52$|e|$ on Li atom and -1.61$|e|$ on As atom. If we see the overlap bond population between Li and As, it takes a negative value of -1.73 which indicates that the bonding is ionic in nature. The charge density distributions of Li$_3$As along (100) and (010) planes are shown in Fig 4.8. From these charge distribution plots also we can observe the same. So from the study we observe that the bonding in Li$_3$P and Li$_3$As is of quite different in nature. In Li$_3$P, the sharing of electrons between Li and P atoms is observed to be dominating where as in Li$_3$As the charge transfer is more as the population value takes more negative. This shows that the ionic nature is increasing in this pnictides going from Li$_3$P to Li$_3$As.

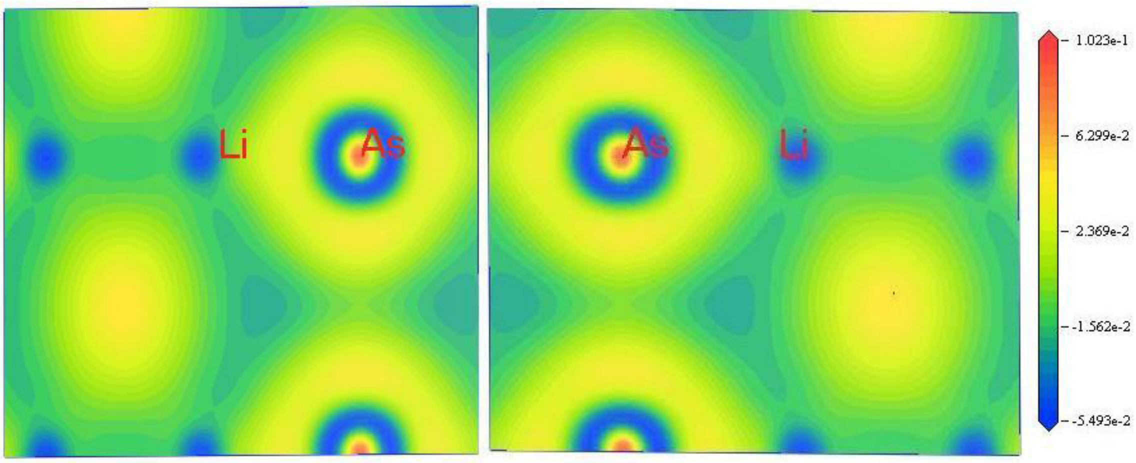

Figure 4.8: Charge density distribution of Li$_3$As along (100) and (010) plane

Chapter 5

Conclusions

In the present work, we studied the electronic band structure, density of states and bonding properties of lithium pnictide superionic conductor compounds Li_3P, Li_3As. All the calculations that are reported in this work are done based on local density approximation(LDA) using CASTEP program. We have done structural optimization for the unit cell of each compound and determined the theoretical equilibrium crystal structure. We calculated the ground state properties such as the lattice constants and internal parameter and they are in good aggrement with experiment. The band structure and density of states of Li_3P, Li_3As compounds are plotted. From the band structure and density of states it is concluded that, these compounds are indirect band gap semiconductors. To understand the nature of bonding, we plotted the charge density distribution plots along various planes. In addition to this charge density distributions, we also studied the Mulliken bond population analysis to understand the nature of bonding. This shows that the ionic nature is increasing in this pnictides going from Li_3P to Li_3As.

Chapter 6

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