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Dedication

To

Mother & Father ,

I could never have done this without your faith, support, and constant encouragement. thank you for teaching me to believe in allah, in myself, and in my dreams .

My Brothers and Sisters

MOHAMED, ASMA, REDUANE, ZINEB , ABD-LATIF, AHMED.

My Grandmothers

The Souls of my Grandparents

My Friends

DOUNIA, ASMA, NOUR, MESOUDA.

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All class of physics 2016

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General introduction

From an environmental point of view hydrogen is the cleanest known fuel, and from an economic point of view hydrogen technology will be able to revolutionize the transport and energy market. Nowadays hydrogen becomes a real alternative to fossil fuel systems[11] . Among the advantages of hydrogen are its low density and small volume heat of combustion but recently none of the existing methods of hydrogen storage is efficient neither in terms of volume energy density , nor mass energy density and gas release rate .from the application point of view it is vital to find the most effective way to store hydrogen and then ,to replace the current fuel systems , For this conduct research to find a practical way to store it in the vehicle in the form of solid hydrides metals, as metal Lighter lithium metal elements can be adopted as the basis for hydrogen storage.

Hydrogen storage is a materials science challenge because, for all six storage methods currently being investigated, materials with either a strong interaction with hydrogen or without any reaction are needed. Besides conventional storage methods, i.e. high pressure gas cylinders and liquid hydrogen, the physisorption of hydrogen on materials with a high specific surface area, hydrogen intercalation in metals and complex hydrides, and storage of hydrogen based on metals and water are reviewed.[13]

Hydrogen can be stored physically as either a gas or a liquid. Storage of hydrogen as a gas typically requires high-pressure tanks (350–700 bar [5,000–10,000 psi] tank pressure). Storage of hydrogen as a liquid requires cryogenic temperatures because the boiling point of hydrogen at one atmosphere pressure is −252.8°C. Hydrogen can also be stored on the surfaces of solids (by adsorption) or within solids (by absorption).

The goal is to pack hydrogen as close as possible, i.e. to reach the highest volumetric density by using as little additional material as possible. Hydrogen storage implies the reduction of an enormous volume of hydrogen gas. At ambient temperature and atmospheric pressure, 1 kg of the gas has a volume of 11 m^3. To increase hydrogen density, work must either be applied to compress the gas, the temperature decreased below the critical temperature, or the repulsion reduced by the interaction of hydrogen with another material.

The second important criterion for a hydrogen storage system is the reversibility of uptake and release. Materials that interact with hydrogen, therefore, as well as inert materials, are important.

The reversibility criterion excludes all covalent hydrogen-lithium compounds because hydrogen is only released if they are heated to temperatures above 800°C.[12]

In the present work, we determine the pair (starting and final hydride) among twelve different reactions, with the purpose of comparing the formation energies in all cases (reactions), and determining which is the best pair achieving good hydrogen reversibility and high hydrogen storage content.

In this work we have 3 chapter :

In the first chapter we will present study about the density functional theory and LAPW method .

In the second chapter will be about the WIEN2k code .

Finally, in the third chapter we will discuss our results .

Chapter I :

Density Functional Theory (DFT)and LAPW method

Chapter I: Density Functional Theory and LAPW method

I.1 Introduction

For the past 30 years density functional theory has been the dominant method for the quantum mechanical simulation of periodic systems. In recent years it has also been adopted by quantum chemists and is now very widely used for the simulation of energy surfaces in molecules.

The Linearized Augmented Plane Wave (LAPW) method has proven to be one of the most accurate methods for the computation of the electronic structure of solids within density functional theory.

A full-potential LAPW-code for crystalline solids has been developed over a period of more than twenty years, in this chapter we will talk about density functional theory and LAPW method.

I.2 Schrödinger's equation and density functional theory (DFT)

I.2.1 Wave functions and Schrödinger's Equation

To study and predict the properties of atomic and molecular systems (including solid state matter), one must use Quantum Mechanics. For molecular systems, the energy shifts caused by the presence of magnetic dipoles of the electrons and nuclei are small compared to chemical binding energies, and can usually be treated successfully by perturbation theory. In addition, because the chemistry focus is on the valence electrons, the core electrons can be treated approximately and thus relativistic effects, which affect mostly the core, can be neglected. For chemistry and the solid state, then, the basic characterization of structure and reactivity can be obtained from the non-relativistic Schrödinger equation without magnetic effects. For the characterization of structure, the time independent Schrödinger Equation suffices, while to study the interaction of molecular systems with electromagnetic radiation, the full time dependent Schrödinger Equation is necessary. The following discussion is restricted to the time independent Schrödinger Equation in the Born-Oppenheimer approximation in which the electronic structure is computed at fixed nuclear positions. For a molecular system, it is:

$$H\,\Psi(x_1,x_2,\ldots,x_N;\,R_1,\ldots,R_{Nn}) = E\,\Psi(x_1,x_2,\ldots,x_N;\,R_1,\ldots,R_{Nn}) \qquad (I.1)$$

Where $x_1,x_2,\ldots,x_N$ represent the spin and cartesian coordinates of the N electrons in the molecule, and $R_1,\ldots,R_{Nn}$ are the nuclear coordinates of the N_n nuclei in the molecule. The Hamiltonian operator is given by:

$$H = Te + Tn + Ven + Vee + Vnn \tag{I.2}$$

Where the kinetic and potential energies of N electrons (e) and N_n nuclei (n) are given by:

$$Te = -\frac{\hbar^2}{2m_e}\sum_{\mu=1}^{N_e}\nabla_\mu^2 \tag{I.3}$$

$$Tn = -\frac{\hbar^2}{2}\sum_{k=1}^{N_n}\frac{\nabla_k^2}{m_k}$$

$$Ven = -\sum_{\mu=1}^{N_e}\sum_{k=1}^{N_n}\frac{Z_k e^2}{4\pi\varepsilon_0 |\vec{r}_\mu - \vec{R}_k|}$$

$$Vee = \sum_{\mu=1}^{N_e}\sum_{\nu>\mu}^{N_e}\frac{e^2}{4\pi\varepsilon_0 |\vec{r}_\mu - \vec{r}_\nu|}$$

$$Vnn = \sum_{j=1}^{N_n}\sum_{k>j}^{N_n}\frac{Z_k Z_j e^2}{4\pi\varepsilon_0 |\vec{R}_j - \vec{R}_k|}$$

The solutions to this equation must be obtained with several important restrictions. First, the wavefunction Ψ must be normalizable, and, second, it must be antisymmetric with respect to the exchange of any pair of electron spin-coordinates x_i, x_j because electrons are Fermions. This requirement is equivalent to the usually stated Pauli Exclusion Principle: no two electrons of the same spin can occupy the same space point at the same time. Equivalently, $\Psi(x_1,x_{1,\ldots}) = 0$. This implies that two electrons of the same spin are automatically kept away from each other by the antisymmetry requirement and they do not move independently of each other. Their motion is correlated, regardless of the fact that they are electrically charged objects.[1]

I.2.2 Theory of Hohenberg and Kohn

Can we obtain the ground state properties of the molecular system without explicitly constructing the very complex wavefunction? In 1964, Hohenberg and Kohn demonstrated that, surprisingly, the answer is YES. The reason this is of fundamental importance is that the electron density, for any molecular system, is a function of only three spatial coordinates (for a given set of nuclear positions)! Let's define it:

$$\rho(r_1) = N \int |\Psi(\vec{x}_1, \vec{x}_2, \ldots, \vec{x}_N ; \vec{R}_1, \ldots, \vec{R}_{Nn})|^2 \, d\sigma_1 d\vec{x}_2 \ldots d\vec{x}_N \qquad (I.4)$$

This is the integral over all electron cartesian and spin coordinates, except the Cartesian ones of electron 1, of the probability distribution defined by the wavefunction, multiplied by the number of electrons in the system. The integral of the density over all space equals N. The Hohenberg-Kohn theorems are deceptively simple:

Theorem 1: The external potential, Ven is determined, up to an additive constant by the electron density. Since $\rho(r_1)$ determines the number of electrons N, then the density also determines the ground state wavefunction and all other electronic properties of the system.

Proof: Prove by contradiction. Assume that there exist two different external potentials V=Ven +Vnn and V'=Ven' +Vnn' which both give the same electron density $\rho(r_1)$.

Then we have two Hamiltonians, H and H' with the same ground state density and different Ψ and Ψ'. Now we use the variational principle, taking Ψ' as a trial function for the H Hamiltonian, to obtain:

$$E_0 < \langle \Psi'|H|\Psi'\rangle = \langle \Psi'|H'|\Psi'\rangle + \langle \Psi'|(H-H')|\Psi'\rangle \quad = E_0' + \langle \Psi'|(V-V')|\Psi'\rangle \qquad (I.5)$$

In addition, we can take the Ψ as a trial function for the H' Hamiltonian, to obtain:

$$E_0' < \langle \Psi|H'|\Psi\rangle = \langle \Psi|H|\Psi\rangle + \langle \Psi|(H'-H)|\Psi\rangle = E_0 + \langle \Psi|(V'-V)|\Psi\rangle \qquad (I.6)$$

Now we recognize that the expectation value of the difference in the external potentials differ only in sign because we assumed that the electron density is the same. When we add the two equations, we then obtain the contradiction:

$$E_0 + E_0' < E_0' + E_0 \qquad (I.7)$$

Thus we conclude there exists a unique map between the external potential V and the ground state density. This implies that all the energies, including the total energy, is a functional of the density. We write this as E = E[ρ]. The density determines the Hamiltonian, and thereby, the wavefunction.

Theorem 2: Variational Principle

Suppose we have a trial density ρ'. Then this density defines its own wavefunction Ψ', and the expectation value of the true Hamiltonian satisfies the variational principle:

$$\langle \Psi'|H|\Psi'\rangle = T[\rho] + Vee[\rho] + \int \rho(\vec{r}) V(\vec{r}) d\vec{r} = E[\rho'] \geq E_0[\rho_0] = \langle \Psi_0|H|\Psi_0\rangle \qquad (I.8)$$

Thus, the correct density is the one that produces the minimum energy.[2]

I.2.3 The Kohn-Sham Equations

The KS method relies on the introduction of a fictitious reference systems of non-interacting electrons that is constructed to have the same electron density as the system of interest. These electrons must move in a complex potential that takes into account the actual forms of electron correlation and the difference between the kinetic energy functional of the reference system and the real system. The reference system of ficticious non-interacting particles has a rigorous solution in terms of single electron wavefunctions, or molecular orbitals. These are called the Kohn-Sham orbitals. Thus, we can express the kinetic energy exactly for the reference system as the sum of the expectation value of the Laplacian for each “electron”.

$$T_S[\rho_S] = -\frac{1}{2}\sum_{j=1}^{N} < \chi_j \,|\, \nabla_j^2 \,|\, \chi_j > \qquad \text{(I.9)}$$

provided that the density of the real system, $\rho = \rho_S = \sum_{j=1}^{N}\sum_{\sigma} |\chi_j(\vec{r},\sigma)|^2$. Then, the energy functional of the real system is written as:

$$E[\rho] = T_S[\rho] + J[\rho] + Vnn + Exc[\rho] \qquad \text{(I.10)}$$

Where all the unknown pieces are collected into the Exchange Correlation energy,

$$Exc[\rho] = T[\rho] - T_S[\rho] + Eee[\rho] - J[\rho]. \qquad \text{(I.11)}$$

The above expression for the Exchange-Correlation energy includes the error in the kinetic energy, the correlation effects, and also the correction for the self –interaction of the electron that has been included in the classical Coulomb integral J.

Now we must apply the variational principle and the variables to be adjusted are the KS orbitals themselves. In practice, this is done just like in the HF method, a basis set expansion is used to represent the KS orbitals. Thus, similar computational engines are required for both DFT and HF theory and it is not then a surprise that computational packages have them often both available as options. We write the entire energy functional in terms of the KS orbitals:

$$E[\rho]=-\frac{1}{2}\sum_{j=1}^{N}\langle\chi_j\,|\nabla_j^2|\,\chi_j\rangle+\frac{1}{2}\sum_{j=1}^{N}\sum_{i=1}^{N}\iint\langle\chi_j\chi_i\,|\frac{1}{r_{12}}|\,\chi_j\chi_i\rangle+Exc[\rho]-$$
$$\sum_{a=1}^{Nn}\sum_{j=1}^{N}Z_a\langle\chi_j\,|\frac{1}{r_{a1}}|\,\chi_j\rangle+\sum_{a=1}^{Nn}\sum_{b=1}^{Nn}\frac{Z_aZ_b}{r_{ab}} \qquad \text{(I.12)}$$

The setting the functional derivative of this expression to zero yields the equations that the KS orbitals must satisfy to provide the same density for both systems:

$$\{-\frac{1}{2}\nabla_j^2-\sum_{a=1}^{Nn}\frac{Z_a}{r_{aj}}+V_{KS}(x_j)\}\chi_j=\varepsilon_j\chi_j \qquad \text{(I.13)}$$

Where the effective KS potential in which the non-interacting particles move contains the classical electrostatic interaction, the Exchange-Correlation potential and the electron nucleus attraction.

$$V_{KS}(\vec{r}_1)=\int\frac{\rho(\vec{r}_2)}{r_{12}}d\vec{r}_2+Vxc(\vec{r}_1) \qquad \text{(I-14)}$$

I.2.4 Approximations for the Exchange-Correlation Functional

The simplest approximation that one can make is to imagine that at every point in space we can use the value of the density that the uniform electron gas would have at that point, and allow it to vary from point to point. This is called the Local Density Approximation (LDA) (Figure I.1). In more detail, we write:

$$E_{xc}^{LDA}[\rho]=\int\rho(\vec{r})\varepsilon_{xc}(\rho(\vec{r}))d\vec{r} \qquad , \qquad \varepsilon_{xc}(\rho(\vec{r}))=\varepsilon_x(\rho(\vec{r}))+\varepsilon_c(\rho(\vec{r})) \qquad \text{(I.15)}$$

Where the $\varepsilon_x(\rho(\vec{r}))=-\frac{3}{4}\left(\frac{3\rho((\vec{r}))}{\pi}\right)^{1/3}$ is the Dirac/Slater Exchange energy of the gas. The Coulomb correlation piece is obtained from interpolations of the Monte Carlo data of Ceperly and Alder (1980). The typical LDA approximation is the SWVN implementation that implies Slater Exchange plus Coulomb correlation obtained by Vosko, Wilk & Nussair (1980). Perdew & Wang (1992) made a more accurate implementation.

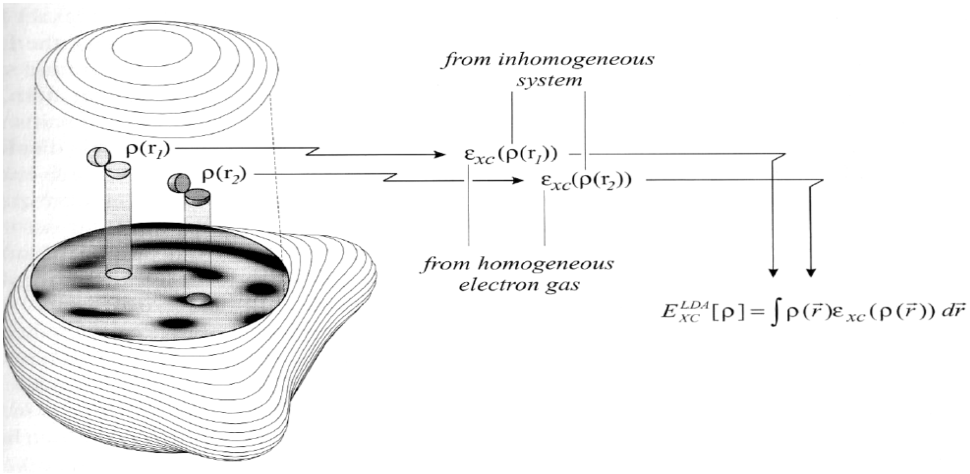


Figure I.1: Schematic of the LDA (Koch and Holthausen).

The LDA by its self does not contain sufficient accuracy for chemical applications. It is necessary to include terms that explicitly take into account the spatial variation of the density. This the formulation of functionals within the Generalized Gradient Approximation (GGA) is what made good accuracy density functional theory possible. As above, approximations are made separately for the Exchange and Coulomb portions.

I.2.5 Solution to the Kohn-Sham equations

We can solve the Kohn-Sham equations self-consistently, in the same spirit as we solved the Hartree-Fock equations in the previous section (Figure I.2). The first step is to pick a suitable exchange functional.

1. Choose and appropriate atomic basis χ_P .
2. We write the variational ansatz as:

$$\psi_K = \sum_P C_{KP}\mathcal{X}_P \quad \text{(I.16)}$$

3. We compute the density as:

$$n(r) = \sum_k |\psi_k(r)|^2 \quad \text{(I.17)}$$

4. We replace the density in the Kohn-Sham equations to find the new eigenfunctions and eigenvalues. Thsi means funding the coefficients C_{KP} .
5. Go to 3 to compute the new density and iterate until convergence is achieved.

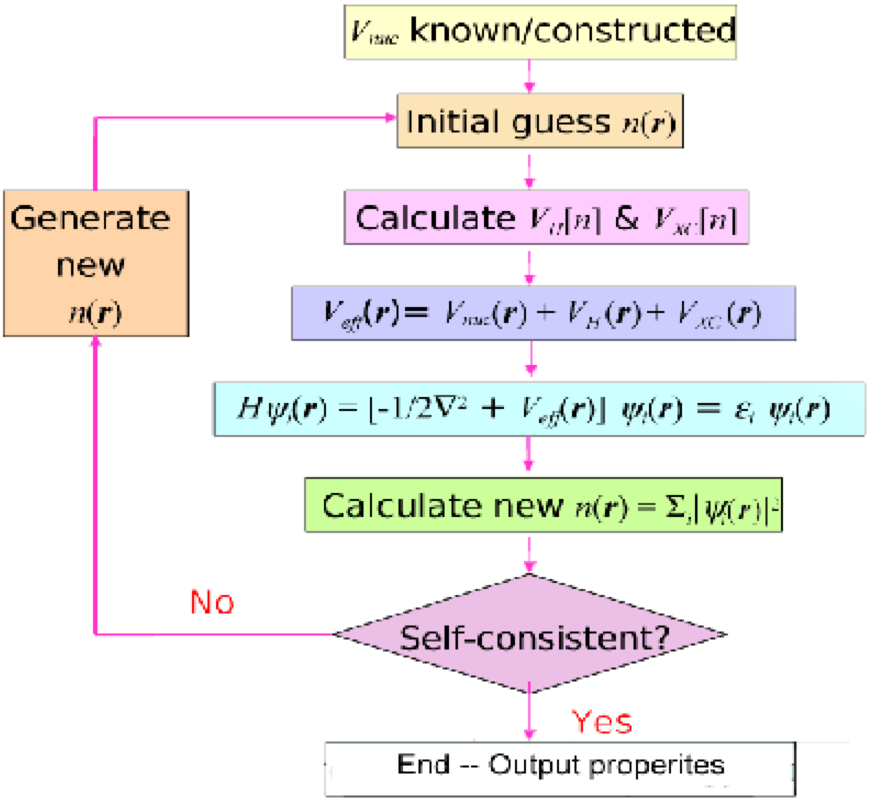


Figure I.2: Numerical solution of kohn-sham equation for atom

I.3 Full potential APW methods

Recently, the development of the Augmented Plane Wave (APW) methods from Slater's APW, to LAPW and the new APW+lo was described by Schwarz and al. 2001.

I.3.1 The LAPW method

The linearized augmented plane wave (LAPW) method is among the most accurate methods for performing electronic structure calculations for crystals. It is based on the density functional theory for the treatment of exchange and correlation and uses e.g. the local spin density approximation (LSDA). Several forms of LSDA potentials exist in the literature , but recent improvements using the generalized gradient approximation (GGA) are available too. For valence states relativistic effects can be included either in a scalar relativistic treatment or with the second variational method including spin-orbit coupling .Core states are treated fully relativistically .

Like most ``energy-band methods``, the LAPW method is a procedure for solving the Kohn-Sham equations for the ground state density, total energy, and (Kohn-Sham) eigenvalues (energy bands) of a many-electron system (here a crystal) by introducing a basis set which is especially adapted to the problem.

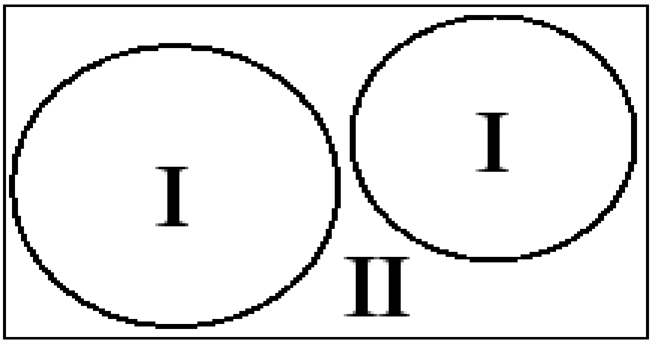


Figure I.3: Partitioning of the unit cell into atomic spheres (I) and an interstitial region (II)

This adaptation is achieved by dividing the unit cell into (I) non-overlapping atomic spheres (centered at the atomic sites) and (II) an interstitial region. In the two types of regions different basis sets are used:

- inside atomic sphere t of radius R_t a linear combination of radial functions times spherical harmonics $Y_{lm}(r)$ is used (we omit the index ***t*** when it is clear from the context)

$$\phi_{kn} = \sum_{lm}[A_{lm}\, u_l\,(r\,, E_l) + B_{lm}\,\dot{u}_l(r, E_l)]Y_{lm}\,(\hat{r}) \qquad (I.18)$$

where $u_l(r,E_l)$ is the (at the origin) regular solution of the radial Schroedinger equation for energy E_l (chosen normally at the center of the corresponding band with l-like character) and the spherical part of the potential inside sphere $t\ \dot{\mu}_l\ (r, E_t)$ is the energy derivative of $\boldsymbol{u_l}$ taken at the same energy E_l. A linear combination of these two functions constitute the linearization of the radial function; the coefficients A_{lm} and B_{lm} are functions of k_n (see below) determined by requiring that this basis function matches (in value and slope) the corresponding basis function of the interstitial region;$\mathcal{U}_l$ and $\dot{\mathcal{U}}_l$ are obtained by numerical integration of the radial Schroedinger equation on a radial mesh inside the sphere.

- (II) in the interstitial region a plane wave expansion is used

$$\phi_{kn} = \frac{1}{\sqrt{w}} e^{ik_n r} \qquad (I.19)$$

where $k_n=k+K_n$; K_n are the reciprocal lattice vectors and ***k*** is the wave vector inside the first Brillouin zone. Each plane wave is augmented by an atomic-like function in every atomic sphere.

The solutions to the Kohn-Sham equations are expanded in this combined basis set of LAPW's according to the linear variation method

$$\psi_{\mathrm{K}} = \sum_{\eta} C_n \, \phi \mathrm{K}_n \qquad \text{(I.20)}$$

and the coefficients $\boldsymbol{c_n}$ are determined by the Rayleigh-Ritz variational principle. The convergence of this basis set is controlled by a cutoff parameter $R_{mt}K_{max}= 6$ - 9, where R_{mt} is the smallest atomic sphere radius in the unit cell and K_{max} is the magnitude of the largest K vector.

In order to improve upon the linearization (i.e. to increase the flexibility of the basis) and to make possible a consistent treatment of semicore and valence states in one energy window (to ensure orthogonality) additional (k_n independent) basis functions can be added. They are called "local orbitals" (Singh 91) and consist of a linear combination of 2 radial functions at 2 different energies (e.g. at the ***3s*** and ***4s*** energy) and one energy derivative (at one of these energies):

$$\phi_{\iota m}^{\iota o} = \left[A_{\iota m}\, u_{\iota}\left(r\,, E_{1,l}\right) + B_{lm}\, \dot{u}_l\left(r, E_{1,l}\right) + C_{lm}\, u_l\left(r, E_{2,L}\right)\right] Y_{lm}(\hat{r}) \qquad \text{(I.21)}$$

The coefficients A_{lm}, B_{lm}, and C_{lm}, are determined by the requirements that ϕ^{LO} should be normalized and has zero value and slope at the sphere boundary.[17]

I.3.2 The APW+lo method

Sjöstedt, Nordström and Singh (2000) have shown that the standard LAPW method with the additional constraint on the PWs of matching in value AND slope to the solution inside the sphere is not the most efficient way to linearize Slater's APW method. It can be made much more efficient when one uses the standard APW basis, but of course with $u_l(r,E_l)$ at a fixed energy E_l in order to keep the linear eigenvalue problem. One then adds a new local orbital (*lo*) to have enough variational flexibility in the radial basisfunctions

$$\phi \mathrm{K}_n = \sum_{\iota m}\left[A_{\iota m}\,, \mathrm{K}_{\eta}\ \mu_{\iota}(r, E_{\iota})\right] Y_{\iota m}(\hat{r}) \qquad \text{(I.22)}$$

$$\phi_{\iota m}^{\iota o} = \left[A_{\iota m}\, u_{\iota}\left(r\,, E_{1,l}\right) + B_{lm}\, \dot{u}_l\left(r, E_{1,l}\right)\right] Y_{lm}(\hat{r}) \qquad \text{(I.23)}$$

This new *lo* (denoted with lower case to distinguish it from the LO given above) looks almost like the old ``LAPW"-basis set, but here the A_{lm} and B_{lm} do not depend on $\boldsymbol{k_n}$ and are determined by the requirement that the *lo* is zero at the sphere boundary and normalized.

Thus we construct basis functions that have ``kinks" at the sphere boundary, which makes it necessary to include surface terms in the kinetic energy part of the Hamiltonian. Note, however, that the total wavefunction is of course smooth and differentiable.

As shown by Madsen et al. (2001) this new scheme converges practically to identical results as the LAPW method, but allows to reduce ``RKmax" by about one, leading to significantly smaller basis sets (up to 50 %) and thus the corresponding the computational time is drastically reduced (up to an order of magnitude). Within one calculation a mixed ``LAPW and APW+lo" basis can be used for different atoms and even different ***l***-values for the same atom (Madsen et al. 2001). In general one describes by APW+lo those orbitals which converge most slowly with the number of PWs (such as TM 3d states) or the atoms with a small sphere size, but the rest with ordinary LAPWs. One can also add a second ``lo" at a different energy so that both, semicore and valence states, can be described simultaneously. [18]

Chapter II :

WIEN2k code

Chapter II: WIEN2k code

II.1 Introduction

The program package WIEN2k allows to perform electronic structure calculations of solids using density functional theory (DFT). It is based on the full-potential linearized augmented plane-wave LAPW method, one among the most accurate schemes for band structure calculations. WIEN2k is an all-electron scheme including relativistic effects and has many features. It has been licensed by more than 2000 user groups[28]. in this chapter we will talk about VIEN2k code.

II.2 WIEN2k

The WIEN2k package is a computer program written in Fortran which performs quantum mechanical calculations on periodic solids. It uses the full-potential (linearized) augmented plane-wave and local-orbitals [FP-(L) APW+lo] basis set to solve the Kohn–Sham equations of density functional theory ,WIEN2k was originally developed by Peter Blaha and Karlheinz Schwarz from the Institute of Materials Chemistry of the Vienna University of Technology. The first public release of the code was done in 1990.[3] Then, the next releases were WIEN93, WIEN97, and WIEN2k.[4]

II.3 Applications

- Energy bands and density of states
- Total energy, forces, and equilibrium geometries
- electric field graidients, hyperfine fields, isomer shifts
- spin polarized calculations (ferromagnetic or antiferromagnetic)
- spin-orbit coupling
- optical properties
- x-ray emission and absorption spectra, electron energy loss spectra (EELs)
- Fermi surfaces
- LDA, GGA, meta-GGA, LDA+U, orbital polarization

II.4 Steps of WIEN2k calculations

We assume that WIEN2k is properly installed and configured for your site and that you ran userconfig lapw to adjust your path and environment.

II.4.1 Starting the w2web server

Start the user interface w2web on the computer where you want to execute WIEN2k (you may have to telnet, ssh,.. to this machine) with the command. At the first startup of this server, you will also be asked to setup a username and password, which is required to connect to this server.[24]

II.4.2 Creating a new session

First you have to create a new session (or select an old one). Enter “LiH” and click the “Create” button.

II.4.3 Creating the “master input“ file case.struct

To create the file LiH.struct start the struct-file generator using “Execution StructGen” . As a first step specify the number of atoms (2 for LiH) and fill in the data given into the fields.

Title	LiH
Lattice	B (body centre)
A	3.491
B	3.491
C	3.491
α ,β , γ	90°
Atom	Li(0,0,0)
Atom	H(0.5,0.5,0.5)

Table(II-1) The parameters of Li-H structure

Click “Save Structure” (Z will be updated automatically) and “set automatically RMT and continue editing ” **.**

II.4.4 Initialization of the calculation (init lapw)

We describe the initial utility programs. These programs are used to set up a calculation (Figure II.1).

- **NN (nearest neighbor distances)**

This program uses the case.struct file in which the atomic positions in the unit cell are specified, calculates the nearest neighbor distances of all atoms, and checks that the corresponding atomic spheres (radii) are not overlapping.

- **View outputnn**

check for overlapping spheres, coordination numbers and nearest neighbor distances.

- **x sgroup**

This program uses information from case.struct (lattice type, lattice constants, atomic positions) and determines the space group as well as all point groups of non-equivalent sites. It uses the nuclear charges Z or the "label" in the 3rd place of the atomic name (Li1, Li2) to distinguish different atoms uniquely. It is able to find possible smaller unit cells, shift the origin of the cell and can even produce a new struct file case.struct_sgroup based on your input case.struct with proper lattice types and equivalency. It is thus most usefull in particular for ``handmade" structures.

- **x symmetry**

This program uses information from case.struct (lattice type, atomic positions). If NSYM was set to zero it generates the space group symmetry operations and writes them to case.struct_st to complete this file. Otherwise (NSYM > 0) it compares the generated symmetry operations with the already present ones. If they disagree a warning is given in the output

- **view LiH.outputs**

check the symmetry operations (they have been written to or compared with already available ones in LiH.struct by the program symmetry) and the point group symmetry of the atoms (You may compare them with the “International Tables for X-Ray Crystallography“).

- **Instgen_lapw**

You are requested to generate an input file LiH.inst and can define the spinpolarization of each atom.

- **x lstart**

lstart is a relativistic atomic LSDA code originally written by Desclaux (69, 75) and modified for the present purpose. Internally it uses Hartree atomic units, but all output has been converted to Rydberg units. lstart generates atomic densities which are used by dstart to generate a starting density for a scf calculation and all the input files for the scf run: in0, in1, in2, inc and inm (according to the atomic eigenvalues). In addition it creates atomic potentials (which are truncated at their corresponding atomic radii and could be used to run lapw1) and optional atomic valence densities, which can be used in lapw5 for a difference density plot. The atomic total energies are also printed, but it can only be used for cohesive energy calculations of light elements. Already for second-row elements the different treatment of relativistic effects in lstart and lapwso yields inconsistent data and you must calculate the atomic total energy consistently by a supercell approach via a ``band structure calculation (Put a single atom in a sufficiently large fcc-type unit cell).

- **x kgen**

is program generates the k-mesh in the irreducible wedge of the Brillouin zone (IBZ) on a special point grid, which can be used in a modified tetrahedron integration scheme (Blöchl et al 1994). kgen needs as interactive input the total number of k-points in the BZ. If this is set to zero, you are asked to specify the divisions of the reciprocal unit-cell vectors (3 numbers, be careful not to "break" symmetry and choose them properly according to the inverse lenght of the reciprocal lattice vectors) for a mesh yourself. If inversion symmetry is not present, it will be added automatically unless you specified the ``-so" switch (for magnetic cases with spin-orbit coupling). The k-mesh is then created with this additional symmetry. If symmetry permits, it further asks whether or not the k-mesh should be shifted away from high symmetry directions. The file case.klist is used in lapw1 and case.kgen is used in tetra and lapw2, if the EF switch is set to TETRA, i.e. the tetrahedron method for the k-space integration is used.

- **x dstart**

This program generates an initial crystalline charge density case.clmsum by a superposition of atomic densities (case.rsp) generated with lstart. Information about LM values of the lattice harmonics representation and number of Fourier coefficients of the interstitial charge density are taken from case.in1 and case.in2. In the case of a spin-polarized calculation it must also be run for the spin-up charge density case.clmup and spin-down charge density case.clmdn.[6]

II.4.5 Programs for running an SCF cycle

The second step is the SCF calculation (Figure II.1). This step consists of the cyclic form under program.[5]

- **LAPW0 (generates potential)**

lapw0 computes the total potential V_{tot} as the sum of the Coulomb V_c and the exchange-correlation potential V_{xc} using the total electron (spin) density as input. It generates the spherical part (l=0) ascase.vsp and the non-spherical part as case.vns. For spin-polarized systems, the spin-densities case.clmup and case.clmdn lead to two pairs of potential files. These files are called: case.vspup, case.vnsupand case.vspdn, case.vnsdn.

- **LAPW1 (generates eigenvalues and eigenvectors)**

lapw1 sets up the Hamiltonian and the overlap matrix (Koelling and Arbman 75) and finds by diagonalization eigenvalues and eigenvectors which are written to case.vector. Besides the standard LAPW basis set, also the APW+lo method. is supported and the basis sets can be mixed for maximal efficiency. If the file case.vns exists (i.e. non-spherical terms in the potential), a full-potential calculation is performed.For structures without inversion symmetry, where the hamilton and overlap matrix elements are complex numbers, the corresponding program version lapw1c must be used in connection with lapw2c. Since usually the diagonalization is the most time consuming part of the calculations, two options exist here. In *WIEN2k* we include highly optimized modifications of LAPACK routines. We call all these routines ``full diagonalization'', but we also provide an option to do an ``iterative diagonalization'' using a new preconditioning of a block-Davidson method .

- **LAPW2 (generates valence charge density expansions)**

lapw2 uses the files case.energy and case.vector and computes the Fermi-energy (for a semiconductor E_f is set to the valence band maximum). for each occupied state and each k-vector; then the corresponding (partial) charges inside the atomic spheres are obtained by integration. In addition ``Pulay-corrections`` to the forces at the nuclei are calculated here.

For systems without inversion symmetry you have to use the program lapw2c (in connection with lapw1c). The partial charges for each state (energy eigenvalue) and each k-vector can be written to files case.help031, case.help032 etc., where the last digit gives the atomic index of inequivalent atoms (switch -help_files). Optionally these partial charges are also written to case.qtl (switch -qtl). For meta-GGA calculations energy densities are written to case.vrepval(switch -vresp). In order to get partial charges for bandstructure plots, use -band, which sets the ``QTL option and uses ``ROOT'' in case.in2. Several other switches change the input file case.in2 temporarely and are described there.

- **LCORE (generates core states)**

lcore is a modified version of the Desclaux (69, 75) relativistic LSDA atomic code. It computes the core states (relativistically including SO, or non-relativistically if ``NREL'' is set in case.struct) for the current spherical part of the potential (case.vsp). It yields core eigenvalues, the file case.clmcor with the corresponding core densities, and the core contribution to the atomic forces.

- **MIXER (adding and mixing of charge densities)**

In mixer the electron densities of core, semi-core, and valence states are added to yield the total new (output) density (in some calculations only one or two types will exist). Proper normalization of the densities is checked and enforced (by adding a constant charge density in the interstitial). As it is well known, simply taking the new densities leads to instabilities in the iterative SCF process. Therefore it is necessary to stabilize the SCF cycle. In *WIEN2k* this is done by mixing the output density with the (old) input density to obtain the new density to be used in the next iteration.

The file case.scf is product after the convergence of cycle scf and contains the total energy which calculated (in the final file).[15]

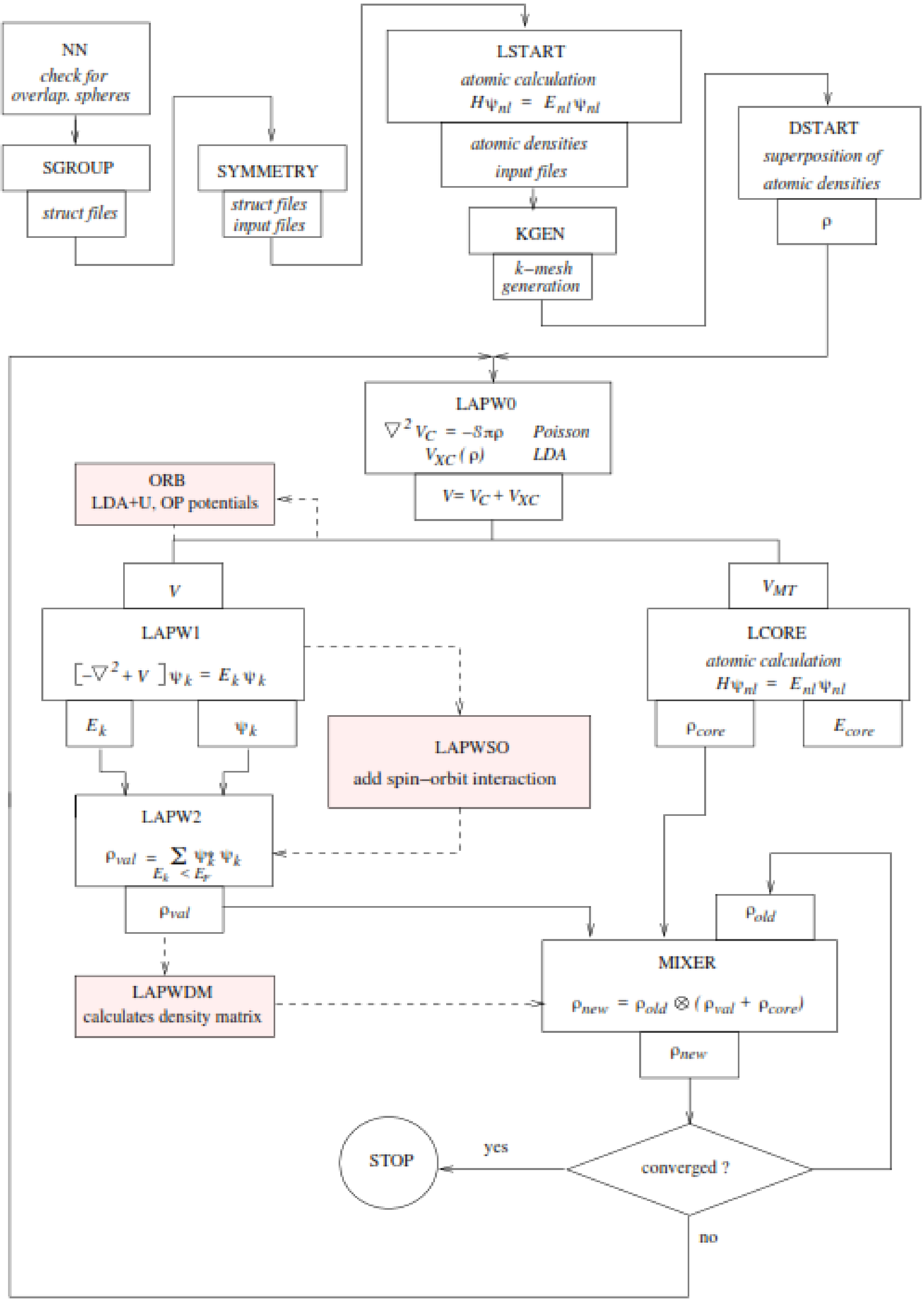


Figure II.1: Organization WIEN2k software modules[6]

II.5 Calculating properties

Once the SCF cycle has converged one can calculate various properties like Density of States (DOS), band structure.

II.5.1 Density of States (DOS) [5]

Select “Density of States (DOS)” from the “Tasks” menu and click on the buttons one by one:

- Calculate partial charges
- Create LiH.int
- Calculate DOS (x tetra).
- Preview output using “dosplot”

Chapter III :

Results and discussion

Chapter III: results and discussion

III.1 Introduction

The understanding of basic material properties of metal hydrides is of great interest in improving storage performance since the stability of metal hydrides is key to rationally investigate and design potential hydrogen-storage materials. The objective of this work is to obtain the pair (starting and final hydride) among the Li-H systems, achieving good hydrogen reversibility and high hydrogen storage content. The first principles calculations were performed using LAPW method within the framework of density functional theory (DFT) [7] as implemented in the Wien2K code [8, 9]. In this way, the exchange-correlation potential for structural and electronic properties was calculated using both a local density approximation (LDA) and the Perdewe Burkee Ernzerhof (GGA) expression [10].

III.2 Structure of Li_229

Lithium is a chemical element with the symbol Li and atomic number 3. It is a soft, silver-white metal belonging to the alkali metal group of chemical elements. Under standard conditions, it is the lightest metal and the least dense solid element. Like all alkali metals, lithium is highly reactive and flammable. For this reason, it is typically stored in mineral oil. The Li_229 compound has body centered cubic structure (Figure III.1). The general properties of Li_229 are shown in table III.1.

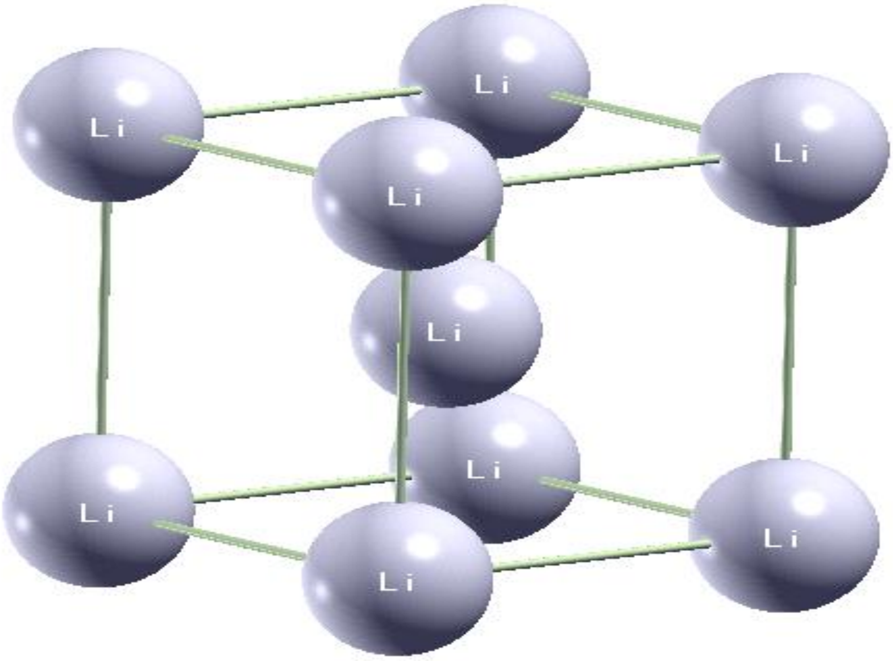


Figure III.1: Structure of the Li_229 compound

Table III.1: Lithium properties[17]

Properties	**Physical and chemical characteristic**
Electron configuration	$1s^22s^1$
Bulk modulus	4.9 GPa
Density	0.534 g/cm^3 near room temperature
Cristal structure	Body-centered cubic

III.3 Creating the structure file of Li_229

To create the file Li_229.struct we start the strut-file generator using (StructGen). As a first step we specify the number of atoms (1 for Li_229) and fill in the data given below in table III.2.

Table III.2: Structure file input of Li_229

Compound	**Lattice**	**Space group**	**Lattice parameter (Å)**	**Wyckoff positions**	**Coordinate of Li**	**Rmt (Bohr)**
Li_229	Cubic	229	3.491	1a	(0, 0, 0)	1.8

III.4 Total energy of Li_229

The total energy of Li_229 was determined by SCF cycle, using the following parameters:

- ✓ Lattice parameter a = 3.491 Å [7].
- ✓ k-points = 3000.
- ✓ $R_{mt}K_{max}$ = 9

The total energy of Li_229 was found to be -15.04392325 Ry.

III.5 Convergence test of Li-H hydrides

We want to use a basis set ($R_{mt}K_{max}$ and k-mesh) that is large enough to be accurate, but only just large enough in order not to waste computer time. Therefore, some testing calculations are necessary before going to real calculations. For all Li hydrides , the procedure will be described to make a fair choice of basis set size and k-point density. Starting with the k-points which we change, from 500 to 4000 with a step of 500 and $R_{mt}K_{max}$ = 7. With the energy criteria of 0.0001 Ry, 3000 k-points are sufficient (Table III.3). Then, the same procedure for the $R_{mt}K_{max}$ parameter which was change from, 5 to 9 with 0.5 as step and 3000 k-points (optimal value). With the same energy criteria, the $R_{mt}K_{max}$ parameter equal to 7 is sufficient (Table III.3).

Table III.3: k-points and $R_{mt}K_{max}$ parameters used in these calculations

k-points	$R_{mt}K_{max}$
3000	7

III.6 Structural properties of Li-H systems

We have proposed the theoretical study of six crystal structures, one of them being LiH_225 with known experimental data. For this compound, we have compared the values obtained with the experimental ones. The five remaining structures have been developed theoretically as potential structures to hydrogen storage. LiH_221, LiH_225, LiH_2_191, LiH_2_194, LiH_4_215 and LiH_4_221 have not yet been synthesized, and there are no references on experimental studies, different from the 225 cubic phase.

For structural properties, we should know the energy, as well as the crystal structure of the crystalline phases LiH_221, LiH_225, LiH_2_191, LiH_2_194, LiH_4_215 and LiH_4_221. Figures III.2-III.6 illustrate the six crystal structures used in our theoretical calculations.

We changed the volume towards the compression and expansion in order to survey the state of equilibrium, and then we drew the curve of total energy as a function of volume according to equation of Murnaghan (Figures III.7-III.12) [11, 12].

The static properties as lattice equilibrium constant (equilibrium volume V_0), bulk modulus, pressure derivative of bulk modulus and ground state energy E_0 were obtained from the total energy and fitted with the Murnaghan equation (Tables III.4 and III.5) [11, 12] .

The lattice parameters for the LiH_225 (a= 3.491 Å) are close to those calculated by the VASP code (a= 3.9978 Å) [13] .

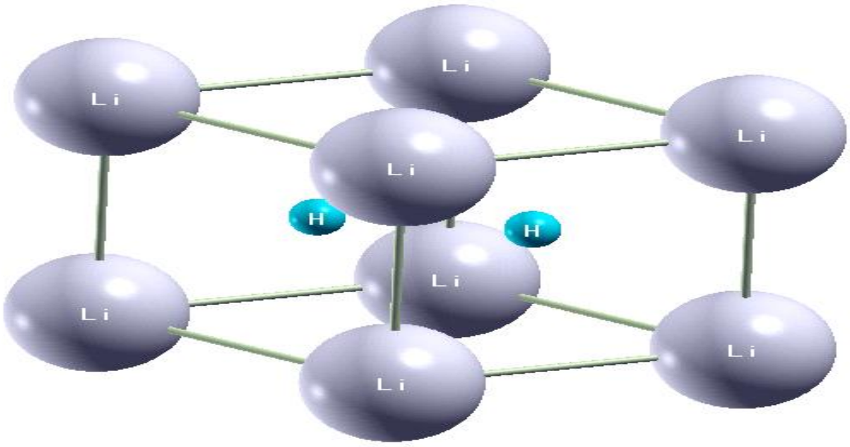


Figure III.2: Structure of the LiH_225 hydride

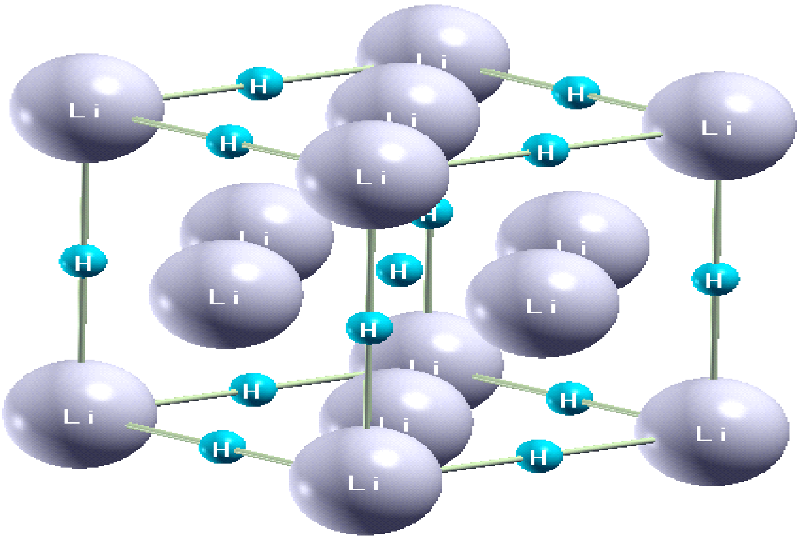


Figure III.3: Structure of the LiH_2_191 hydride

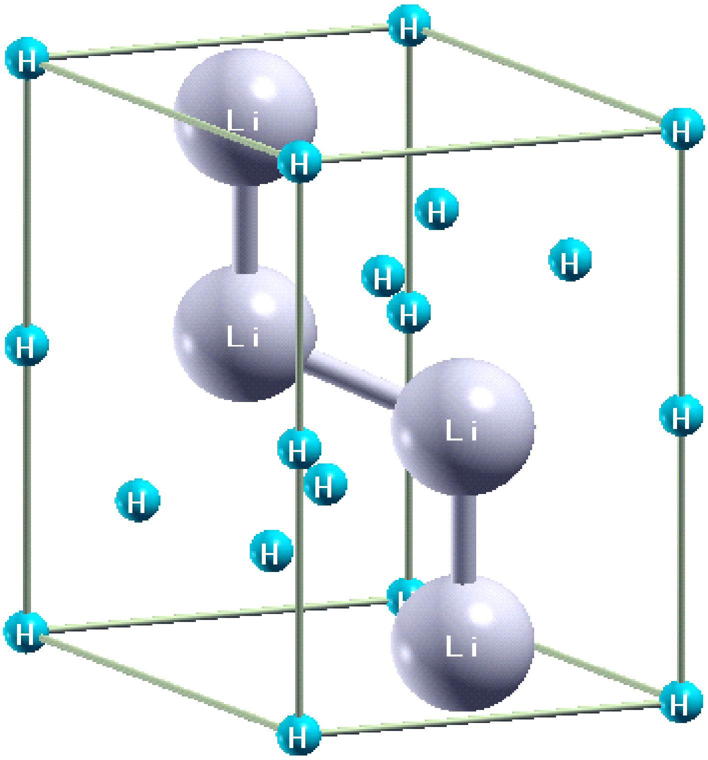


Figure III.4: Structure of the LiH_2_194 hydride

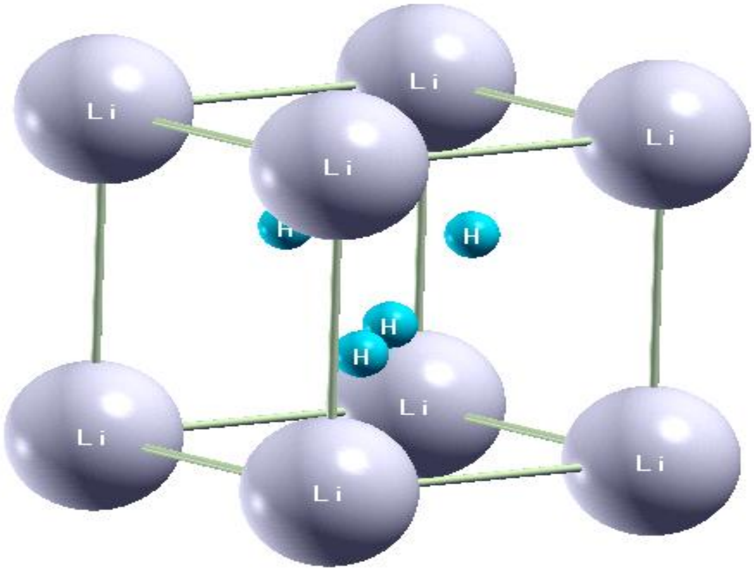


Figure III.5: Structure of the LiH_4_215 hydride

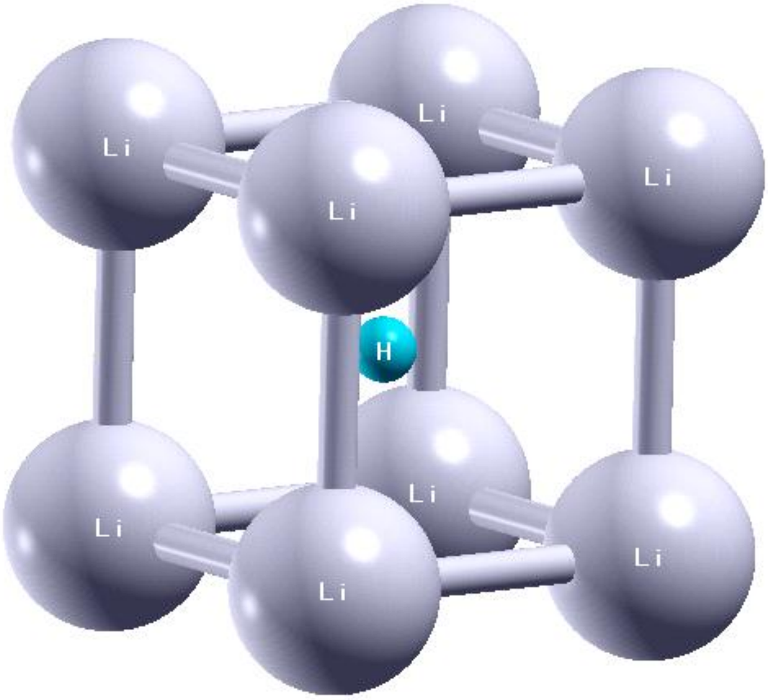


Figure III.6: Structure of the LiH_4_221 hydride

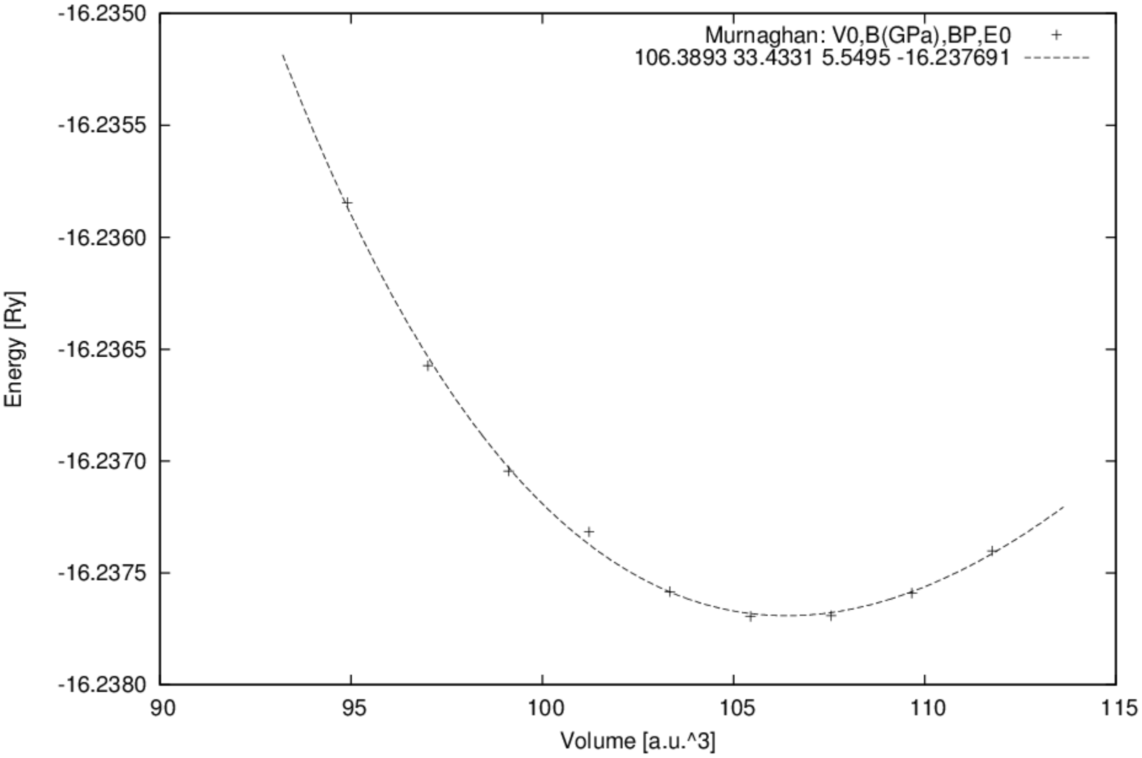


Figure III.7 : Energy versus volume curve for LiH_221

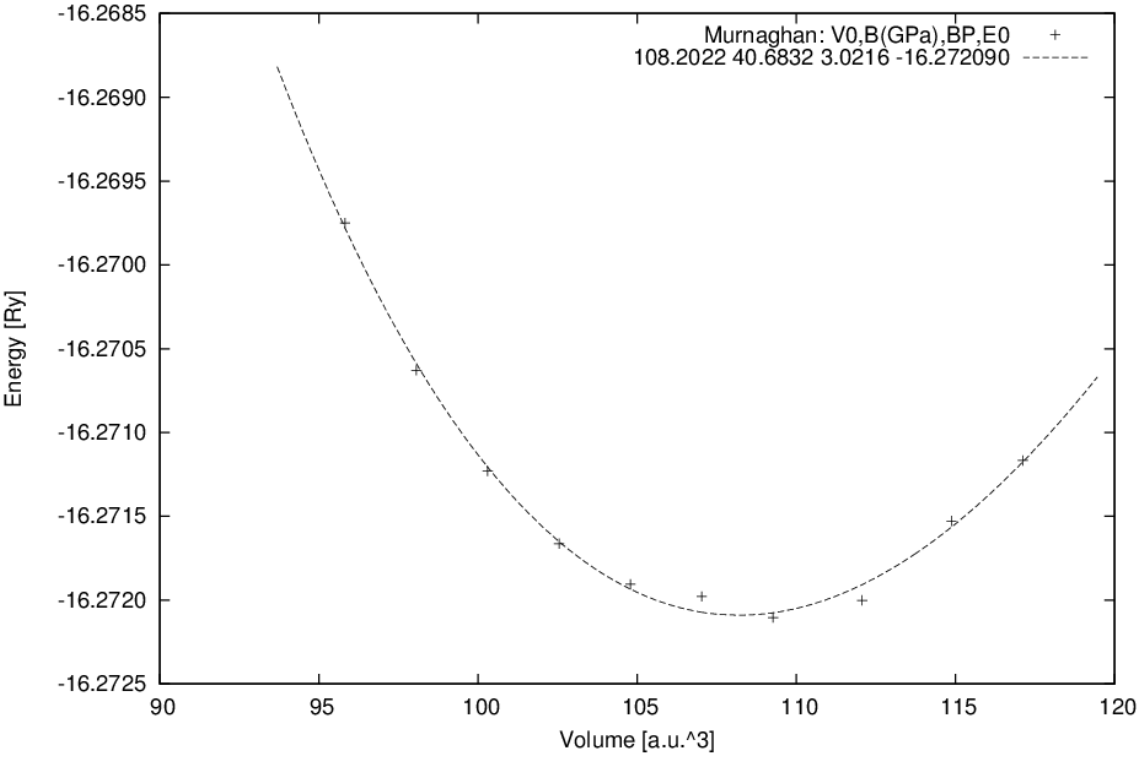


Figure III.8: Energy versus volume curve for LiH_225

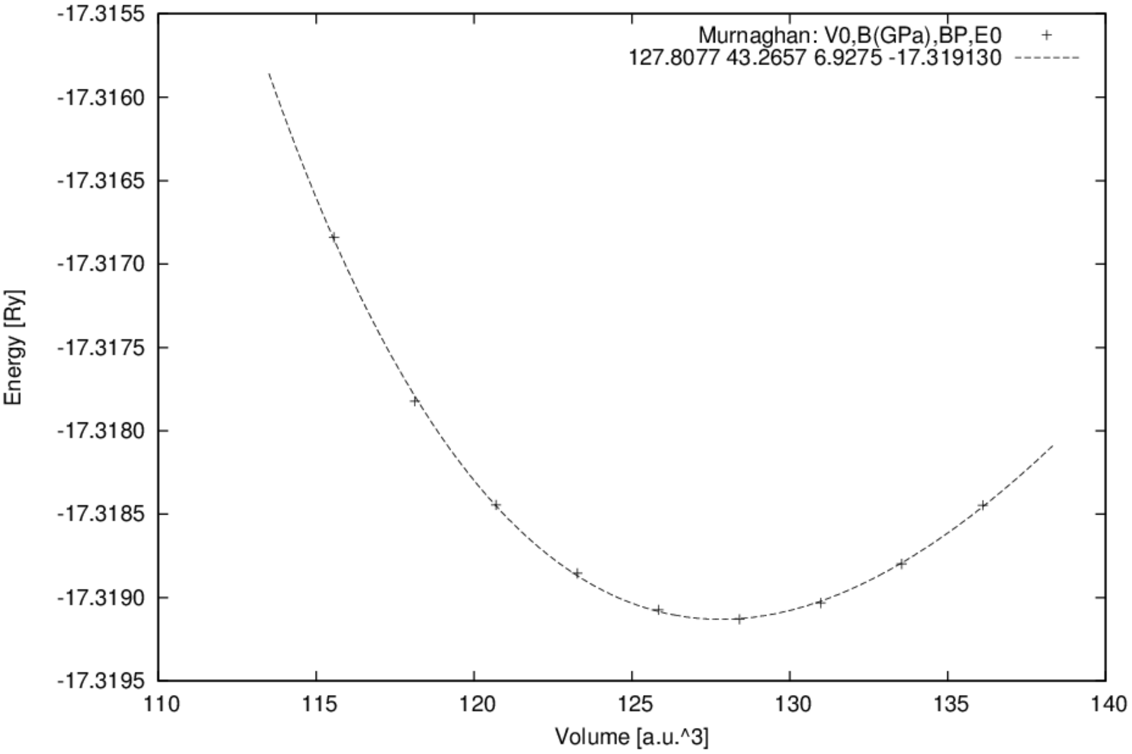


Figure III.9: Energy versus volume curve for LiH_2_191

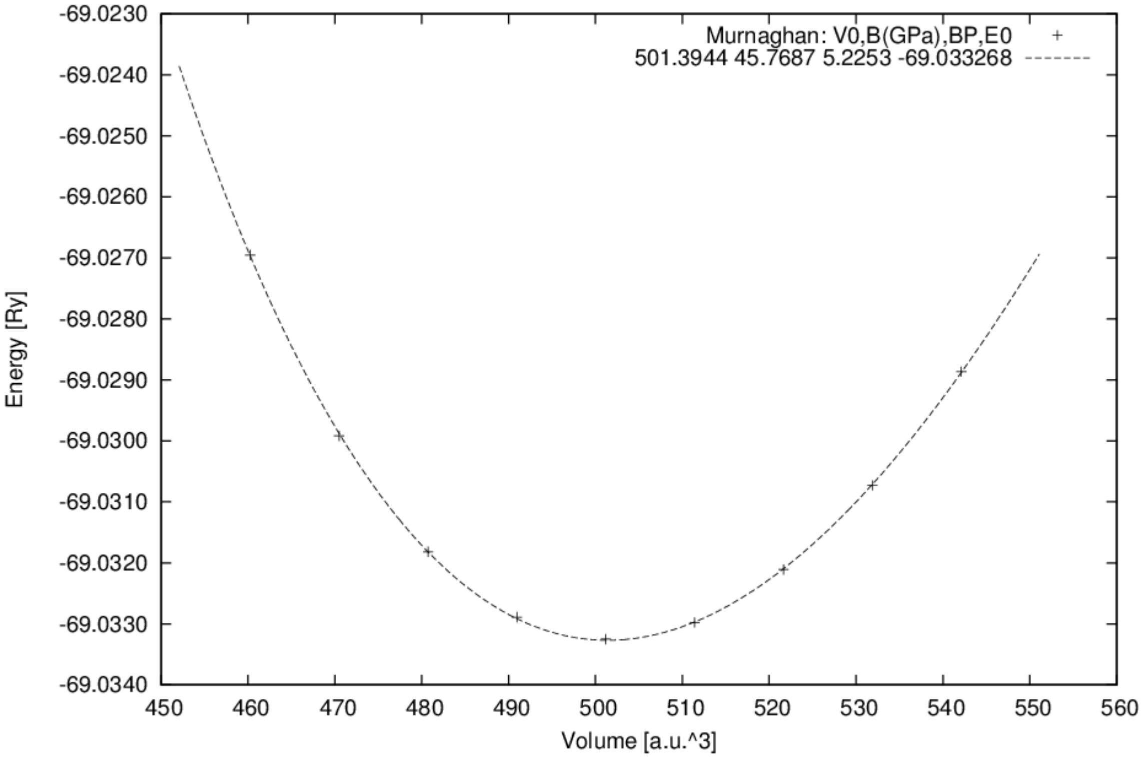


Figure III.10: Energy versus volume curve for LiH_2_194

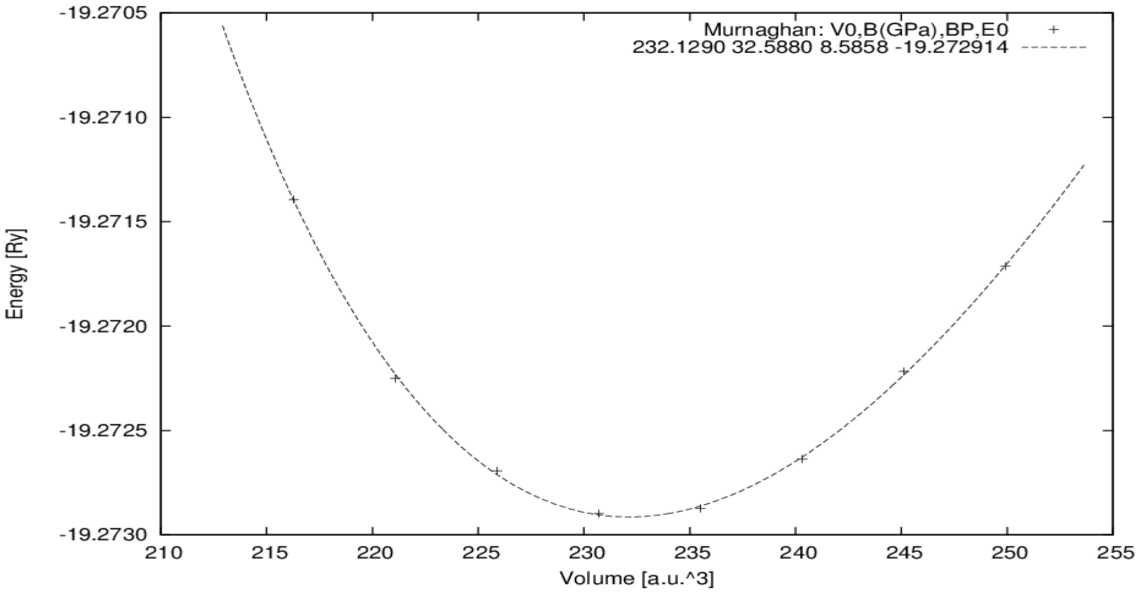


Figure III.11: Energy versus volume curve for LiH_4_215

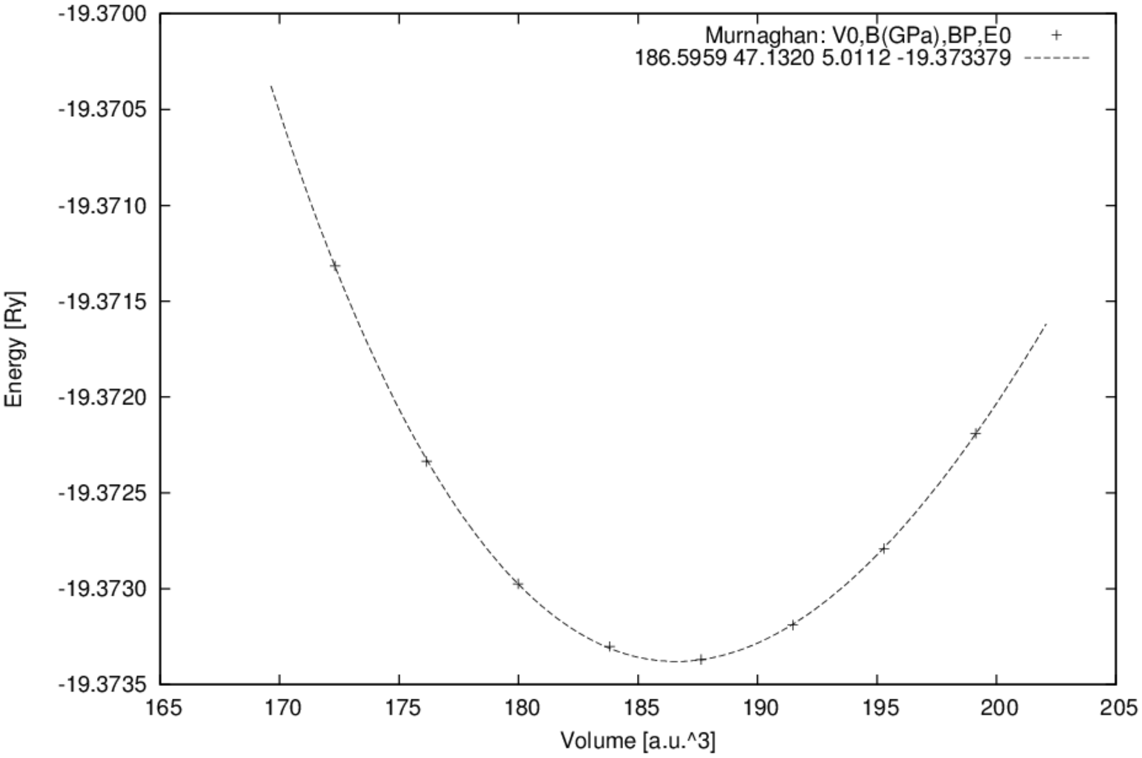


Figure III.12 : Energy versus volume curve for LiH_4_221

Table III.4: Structural parameters of Li-H systems at ground state

Compounds	**Lattice**	**Space Group**	**Wyckoff Positions**		**Lattice parameters (Å)**		
			Li	H	**a**	**b**	**c**
Li_229	cubique	229	1a	/	3.491	3.491	3.491
LiH_221	cubique	221	1a	1b	2.5075	2.5075	2.5075
LiH_225	cubique	225	4a	4b	4.0028	4.0028	4.0028
LiH_2_191	hexagonale	191	1a	2d	2.9493	2.9493	2.5141
LiH_2_194	hexagonale	194	4f	2a 6h	3.9689	3.9689	5.4469
LiH_4_221	cubique	221	1a	1b 3d	3.2522	3.2522	3.2522
LiH_4_215	cubique	215	1a	4e	3.0239	3.0239	3.0239

Table III.5: Volume, bulk modulus, pressure derivative of bulk modulus and total energy of Li-H hydrides at ground state.

compounds	**a_0 (Bohr)**	**B_0 (GPa)**	**B_p**	**E_0 (Ry)**
LiH_221	106.3893	33.4331	5.5495	-16.237691
LiH_225	108.2022	40.6832	3.0216	-16.272090
LiH_2_191	127.8077	43.2657	6.9275	-17.319130
LiH_2_194	501.3944	45.7687	5.2253	-17.269325
LiH_4_221	186.5959	47.1320	5.0112	-19.373379
LiH_4_215	232.1290	32.5880	8.5858	-19.272914

III.7 Hydrogen Partial storage of Li_H systems

III.7.1 Formation energies

The energy of formation E_f may be decomposed into the following terms: $E_{transform}$, is the energy required, to transform the host metal lattice into the arrangement of the metal ions in the metal hydride, $E_{expansion}$, is the energy required to expand the host metal lattice to that of the hydride and finally $E_{hydride}$, is the hydrogen insertion energy in the expanded metal lattice [14].

$$E_f = E_{transform} + E_{expansion} + E_{hydride} \tag{1}$$

The hydrogen absorption process is exothermic ($\Delta H < 0$). The more exothermic the reaction, the more negative the enthalpy, calculated for 1 mol of H_2. The enthalpies are calculated between the hydrides themselves according to the following reaction:

$$2LiH\_221 + H_2 \rightarrow 2LiH_2\_191 \tag{2}$$

$$2LiH\_221 + H_2 \rightarrow 2LiH_2\_194 \tag{3}$$

$$2LiH\_225 + H_2 \rightarrow 2LiH_2\_191 \tag{4}$$

$$2LiH\_225 + H_2 \rightarrow 2LiH_2\_194 \tag{5}$$

$$\frac{2}{3}LiH\_221 + H_2 \rightarrow \frac{2}{3}LiH_4\_221 \tag{6}$$

$$\frac{2}{3}LiH\_221 + H_2 \rightarrow \frac{2}{3}LiH_4\_215 \tag{7}$$

$$\frac{2}{3}LiH\_225 + H_2 \rightarrow \frac{2}{3}LiH_4\_221 \tag{8}$$

$$\frac{2}{3}LiH\_225 + H_2 \rightarrow \frac{2}{3}LiH_4\_215 \tag{9}$$

$$LiH_2\_191 + H_2 \rightarrow LiH_4\_221 \tag{10}$$

$$LiH_2\_191 + H_2 \rightarrow LiH_4\_215 \tag{11}$$

$$LiH_2\_194 + H_2 \rightarrow LiH_4\_221 \tag{12}$$

$$LiH_2\_194 + H_2 \rightarrow LiH_4\_215 \tag{13}$$

From figure III.13, we can observe the average values of enthalpy calculated for all structures.

To obtain the pair (starting and final hydride) among the Li-H systems, achieving good hydrogen reversibility and high hydrogen, we have studied all hydrides in case of partial hydrogen storage as shown from equation (2) to equation (13).

From the equation (2) to that (5), the reversible hydrogen pair stocking one atom of hydrogen is in equation (2).

From the equation (6) to that (9), the reversible hydrogen pair stocking three atoms of hydrogen is in equation (6).

From the equation (10) to that (13), the reversible hydrogen pair stocking two atoms of hydrogen is in equation (10).

According to these results, in the first order the best reversible hydrogen pair is between LiH_221 and LiH_2_191 which stock one atom of hydrogen, in the second order is between LiH_2_191 and LiH_4_221 which stock two atoms of hydrogen and in the third order is between LiH_221 and LiH_4_221 which stock three atoms of hydrogen. On the other hand, for another structures studied, they would be more difficult and expensive to carry out the extraction of H_2 from these structures, therefore, would not be the most recommended structure for one hydrogen storage system. For this reason, the pair among the Li-H systems, achieving good hydrogen reversibility and high hydrogen is between LiH_221 and LiH_4_221.

In addition to that, the first-principles calculations offer an excellent way to predict new compounds for hydrogen storage or to obtain information on metal hydrides that is difficult to access experimentally.

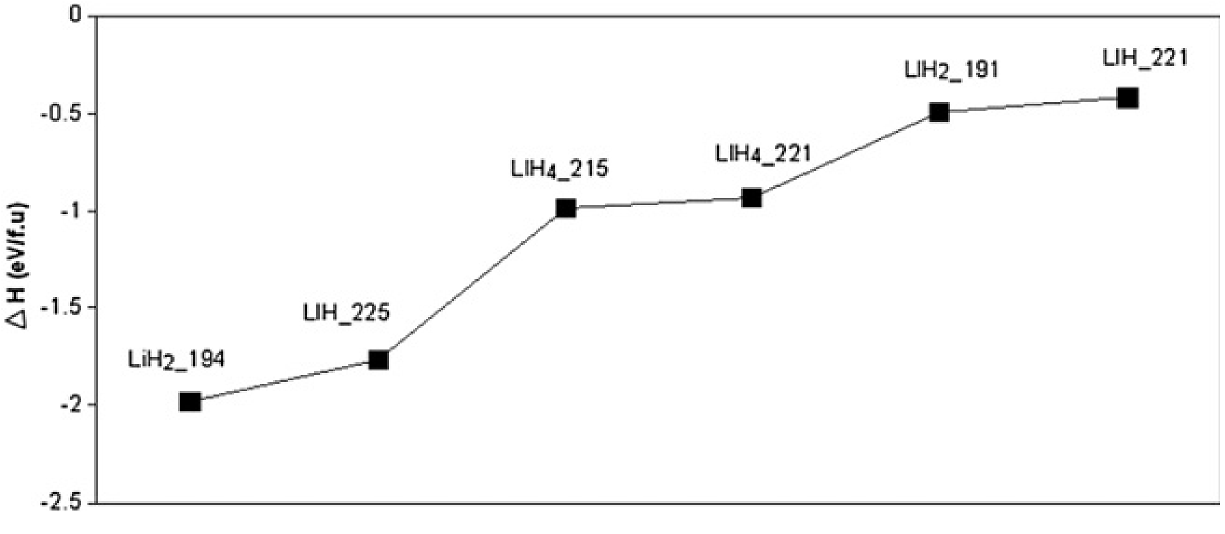


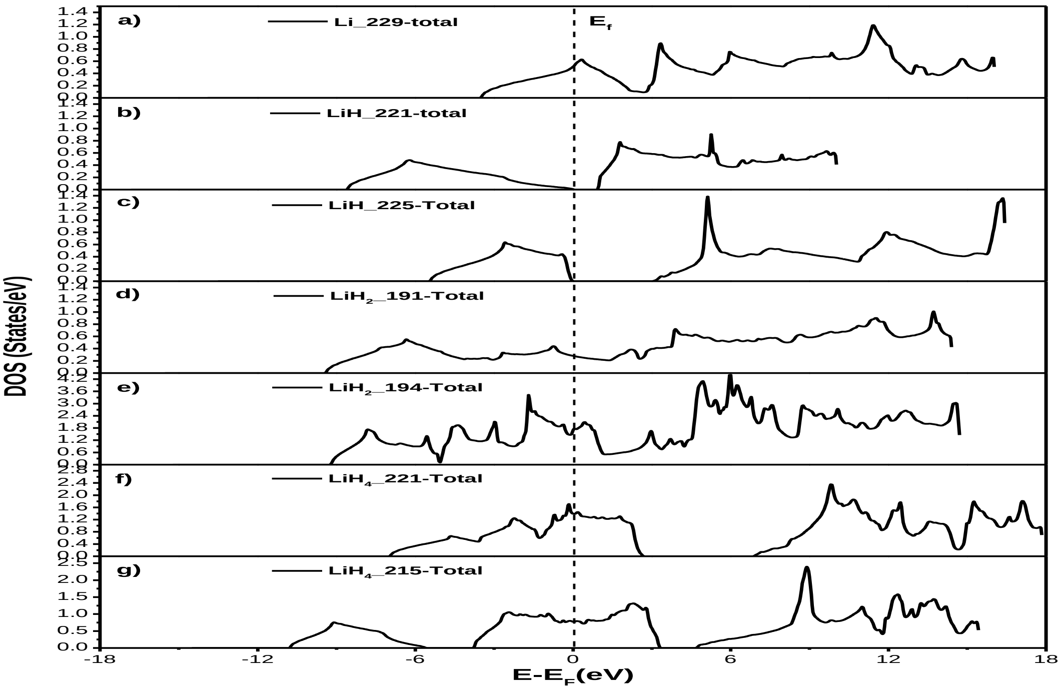
Figure III.13: Average enthalpy for all structures

III-7.2. densities of states (DOS)

The electronic structure of a material contains important information about the characteristics of the materials; it is necessary to determine whether the material is a metal, semiconductor or an insulator.

Fig(III-15)(aef) represents the electronic densities of states (DOS) as a function of energy. We cannot be sure, due to limits of the theoretical calculations performed in the frame of DFT, of the value of the band gap, but what we can say is that some of the compounds are insulators Fig(III-15)((aeb)). For the LiH_225; we observe a wide band above the Fermi level. The broadband in LiH_225 arises from the equivalence of the Li 2s and hydrogen 1s orbital in energy and geometry, allowing for a significant hybridization . [9]

Fig(III-15) (cef) for LiH2_191, LiH2_194, LiH4_215 and LiH4_221 structures have metallic behavior.



Fig(III-14) the electronic densities of states (DOS) as a function of energy

General conclusion

Hydrogen is a chemical element with chemical symbol H and atomic number 1. With an atomic weight of 1.00794 u, hydrogen is the lightest element on the periodic table. Hydrogen is used in Hydrogen storage and fuel and precursor to complex metal hydrides , In nuclear chemistry and physics.

In this work we have studied the partial hydrogen storage in the Li-H hydrides, using the first principles calculations based on density functional theory (DFT). The crystal structure, electronic properties and internal optimization parameters are treated by WIEN2k code and LAPW method. In the first order the best reversible hydrogen pair is between LiH_221 and LiH_2_191 which store one atom of hydrogen, in the second order is between LiH_2_191 and LiH_4_221 which store two atoms of hydrogen and in the third order is between LiH_221 and LiH_4_221 which stock three atoms of hydrogen. On the other hand, for another studied structures pairs, they would be more difficult and expensive to carry out the extraction of H_2 from these structures. Therefore, would not be the most recommended structure for one hydrogen storage system. For this reason, the pair among the Li-H systems, achieving good hydrogen reversibility and high hydrogen is between LiH_221 and LiH_4_221.

In addition to that, the first-principles calculations offer an excellent way to predict new compounds for hydrogen storage or to obtain information on metal hydrides that is difficult to access experimentally.

List of references

[1] W. Koch, M. C. Holthausen, “A Chemist’s Guide to Density Functional Theory”, Wiley-VCH: New York, 2000.

[2] Adrian E. Feiguin , Michigan university 2009-11-04

[3] P. Blaha, K. Schwarz, P. Sorantin, and S. B. Trickey, Comput. Phys. Commun. 59, 399 (1990).

[4] Jump up^ K. Schwarz and P. Blaha, Comput. Mater. Sci. 28, 259 (2003).

[5] User’s Guide, WIEN2k 14.1 (Release 09/08/2014) ,Peter Blaha ,Karlheinz Schwarz ,Georg Madsen ,Dieter Kvasnicka ,Joachim Luitz ,Vienna University of Technology ,Inst. of Physical and Theoretical Chemistry ,Getreidemarkt 9/156, A-1060 Vienna/Austria

[6] SIKEBIR Abdelbaki ,Calcul ab-initio structural et électronique de TiNi , dissertation of academic master ,university of kasdi merbah ourgla ,2013-2014

[7] P Hohemberg, W Kohn, Inhomogeneous Electron Gas, Phys. Rev. B **136** (1964) 864-871.

[8] P Blaha, K Schwarz, J Luitz, G.K.H. Madsen, D. Kvasnicka, WIEN2K, Vienna, Technical University of Vienna, 2001.

[9] K Schwarz, P Blaha, G.K.H. Madsen, Electronic structure calculations of solids using the WIEN2k package for material sciences, Comput. Phys. Commun **147** (2002) 71-76.

J.P. Perdew, K. Burke, M. Ernzerhof, Generalized Gradient Approximation Made Simple, Phys. Rev. Lett. **77** (1996) 3865-3868.

[10] F.D. Murnaghan, The Compressibility of Media under Extreme Pressures, Proc. Natl. Acad. Sci. USA **30** (1944) 244-247.

[11] F.D. Murnaghan, Finite Deformations of an Elastic Solid, Am, J. Math. **59** (1937) 235-60.

[12] J.F. Herbst, L.G. Hector Jr, Energetics of the Li amide/Li imide hydrogen storage reaction, Phys. Rev. B **72** (2005) 125120.

[13] A. Andreasen, Predicting formation enthalpies of metal hydrides, Ris national laboratory report, Ris-R-1484(EN), 2004.

[14] Robertf . Nystrom and Weldong . Brown , Contribution From The Georgeh Erberjo Nes Laboratortyh, university O Chicago Reduction of Organic Compounds by Lithium

[15] Aluminum Hydride. I. Aldehydes, Ketones, Esters, Acid Chlorides and Acid Anhydrides

[16] http://www.qft.iqfr.csic.es/docs/WIEN2k/6Initialization.html, 2016

[17] http://www.webelements.com/lithium/history.html,2014

[18] http://slideplayer.com/slide/5095542/,2016

[19] http://www.wien2k.at/features/3Quick_Start.html,2014

[20] Gunnarsson O, and Johansson P. The Spin-Density-Functional Formalism for Quantum Mechanical Calculations: Test on Diatomic Molecules with an Efficient Numerical Method. Int J Quant Chem 1976 ;10 :307.

[21] Nakamura H, Nguyen-Manh D, Pettifor G. J Alloys Compd 1998;281:81.

[22] First-principles studies of lithium hydride series for hydrogen Storage, R. Napa´n a,*, E.L. Peltzer y Blanca´ a,b , [a] GEMyDE, Group of Study of Materials and Electronic Devices, Electrotechnical Dept., Engineering Faculty, UNLP, La Plata, Argentina , [b] IFLYSIB-CONICET, 59 N_ 789, 1900, La Plata, Argentina

[23] Andreasen A. Predicting formation enthalpies of metal hydrides, Ris national laboratory report, Ris-R-1484(EN); 2004.

[24] Smithson H, Marianetti CA, Morgan D, Van der Ven A, Predit A, Ceder G. First-principles study of the stability and electronic structure of metal hydrides. Phys Rev B 2002;66:144107

Zegait mesouda ,flexible study of the compound Li-H, dissertation of academic master , university of kasdi merbah ourgla ,2014-2015

[25] Landolt-Börnstein , diffusion of hydrogen atom (1); hydrogen (2) ,New Series IV/15A ,DOI: 10.1007/978-3-540-49718-9_144 , Springer 2007

[26] Andreas Züttel , Materials for hydrogen storage , Physics Department, University of Fribourg , Pérolles CH-1700 Fribourg , Switzerland,E-mail: Andreas.Zuettel@unifr.ch, September 2003

[27] A.C.Dillon , K.M.jeunes ,T.A.Bekkedahl ,C.H. Kiang ,D.S.Bethune ,M.J.Heben ,Storage of hydrogen in single-walled carbon nanotubes , ,national renewable energy laboratory ,1617 cole boulevard , golden , Colorado ,80401-3393 ,USA .

[28] Hadi Khalilieh and Nidal Kafri , Evaluation of WIEN2K Performance on MPICH2 vs. MPICH1 ,Department of Computer Science, Al-Quds University, Jerusalem, Palestine

الخلاصة :

الهدف من هذه المذكرة هو دراسة التخزين الجزئي للهيدروجين في هيدريد الليثيوم Li-H حيث باستخدام نظرية الكثافة التابعية (DFT) التي تعتمد على نظريتي هوهانبرغ و كوهن شام بطريقة الامواج الخطية المستوية المتزايدة (LAPW) و بتطبيق برنامج WIEN2k قمنا بحساب الطاقة الكلية ل 6 هيدريدات LiH_221, LiH_225, LiH2_191, LiH2_194, LiH4_215 , LiH4_221 و قمنا بدراسة بنيوية و حددنا ثوابت الشبكة في الحجم المثالي ثم حصلنا على منحنى طاقات التشكل و قمنا بمقارنة الهيدريدات من حيث عدد الذرات المنزوعة و قيمة الطاقة المتشكلة وفق 12 معادلة فوجدنا ان الهيدريد الأفضل هو بين LiH_4_221 و LiH_221 لتخزين الهيدروجين في المواد الصلبة.

الكلمات المفتاحية : تخزين الهيدروجين ، هيدريد الليثيوم ، نظرية الكثافة التابعية (DFT) ، WIEN2k

Ruséme :

Le but de ce mémoire est d'examiner le stockage partiel de l'hydrogène dans l'hydrure de lithium Li-H, où l'utilisation de la théorie de la fonctionnelle de la densité (DFT) qui repose sur la théorie de Hohenberg et Kohen Sham dont les ondes planaire , linéaire augmentée (LAPW) façon, et avec l'application de programme WIEN2k nous avons calculer l'énergie totale pour 6 hydrures LiH_221 , LiH_225, LiH2_191, LiH2_194, LiH4_215, LiH4_221 et nous avons étudié la structure et identifié les constantes de réseau dans la volume d'optimisation et nous avons obtenu la courbe de l'énergie de formation et nous comparons les hydrures en termes de nombre d'atomes dépouillés et l'énergie formée par 12 l'équations Nous avons constaté que l'hydrure enter LiH_221 et LiH_4_221. Il est préférable de stocker l'hydrogène dans cette hydrures.

Mots-clés : stockage de l'hydrogène , hydrure de lithium , théorie de la fonctionnelle de la densité (DFT) , WIEN2k

Abstract :

The objective of this dissertation is to examine the partial storage of hydrogen in lithium hydride Li-H, where using the density functional theory (DFT) that rely on the theory Hohenberg and Kohn Sham with the linear augmented plane wave (LAPW) method, and applying the WIEN2k program.We have calculated the total energy for 6 hydrides LiH_221 , LiH_225, LiH_2_191, LiH_2_194, LiH_4_215, LiH_4_221 and we studied the structural parameters and the lattice constants in volume optimization then we got the formation energies curve and we compare the hydrides in terms of the number of atoms stripped and formed the energy value in accordance with the 12 equation , We find that the hydride achieving good hydrogen reversibility and high hydrogen content is between the LiH_221 and LiH_4_221 compounds.

Keywords: hydrogen storage, lithium hydride, density functional theory (DFT), WIEN2k