



The Effect of GGA + U on the Structural and Electronic Properties of LiH

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ABSTRACT

In this paper, the electronic and structural (Lattice Constant) properties of LiH are calculated, using density functional theory. The Kohn-Sham equations were solved using full potential-linearized augmented plane wave (FP-LAPW). Generalized Gradient Approximation (GGA) and GGA + U approximations are used as the exchange - correlation potential in this study. It was found that adding Hubbard – U term to GGA improved calculated structural property, energy band structure results are in better agreement with the experimental data.

Keywords: Exchange correlation , FP- LAPW, GGA and GGA+U

1. INTRODUCTION

Ionic hydrides have gained a new wave of interest in the last ten years, mainly in connection with the hydrogen storage problem, where, for example, alkali and alkaline earth borohydrides and aluminohydrides seem to play a significant role (Colognes and Zoppi, 2006). The simplest ionic hydrides can be formed by H through the reaction with an alkali metal (Colognesi and Zoppi, 2006).

and H (0.5, 0.5, 0.5), and lattice parameter 4.083Å (Kittel, 1986).

LiH is predicted to change its structure, out only at very high pressure (P~600 Pa), (Barrera *et al*, 2005).

The electronic and structural properties have been calculated using the plane wave pseudo potential code ESPRESSO (Wen Yu *et al*, 2007), but result was in poor agreement with experimental result. Brock *et al*, 2007, have also used LDA and GGA as exchange – correlation potential, and it was found, as usual, DFT severally underestimated the band gap with LDA, giving smaller values than that of GGA.

The Electronic structure, volume optimization, bulk modulus and elastic constraints of LiH have been calculated using the full potential augmented plane method. The obtained results show some common features in the electronic structure of other ALKH; but there were clear differences which could not be explained, using empirical trends (Novakovic *et al*, 2007).

It is relevant to reiterate that all these methods gave results that show several common features in the compound, but they differ in comparison with experimental data. In the present work, an improved method has been employed, using full-potential linearized augmented plane wave (FP-LAPW) method as embodied in WIEN2K code, with Generalized Gradient Approximation (GGA) and GGA + U, used as

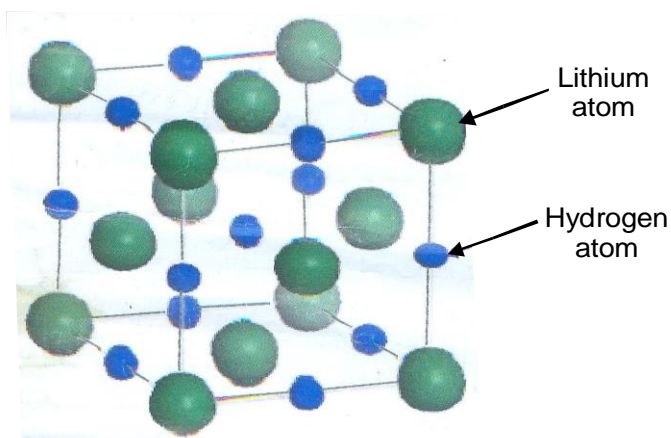


Figure 1: Crystal Structure of LiH (Structure of Rock Salt NaCl Crystal. Larger spheres represent Lithium atoms and the smaller ones, the hydrogen.

As the lightest alkali, Lithium hydride has a simple rock salt structure. It also has a like NaCl – type structure, Li (o, o, o)

exchange – correlation potential, where U is the Hubbard correction term.

2. THEORETICAL BASIS

One of the trials of Density Functional Theory (DFT) is band gap problem. It has some severe problems of reproducing electronic structure accurately, starting with the problem that it does not undertake electron counting correctly.

This results in its failure to render an accurate description of electronic structure of molecular system (Becke, 1988). Furthermore, the presence of electron self-interaction error in the external potential is another problem; since it is ground state theory, the Kohn-Sham eigen value, generally cannot be assigned to the excitation energy of the system.

In DFT, only the highest occupied eigenvalue can be assigned the physical interpretation: it is exactly the chemical potential of the system, (Kummel and Kronik, 2008). However, the interpretation of the Kohn-Sham eigen values as the excitation energies (like the Hartree – Fock method) leads to surprising good results.

But one of the most crucial issues which came from the interpretation is the underestimation of the band-gap in DFT. One of the reasons, as mentioned above, is self-interaction error, and the solution to this problem proceeds to the usage of orbital semi-empirical functions for selected orbitals. Such functions partly cancel this error and allow improvement of calculation of the band-gaps (Kummel and Kronik, 2008).

There exist variety of implementation of such methods, but this work will discuss only two of them which are useful in our calculations.

Exact and Hybrid Functional

One of the possibilities to cancel self-interaction error is to add exchange term to exchange correlation function. Thus, the total energy will have the following form (Novak *et al*, 2006; Blaha *et al*, 2006);

$$E = EGGA [\rho(r)] + \alpha (E_x^{HF}[\Psi_{sel}] - E_x^{GGA}[\rho_{sel}]) \quad (1)$$

where ρ_{sel} and Ψ_{sel} the density and the wave function of the selected orbitals, $E_x^{HF}[\Psi_{sel}]$ and $E_x^{GGA}[\rho_{sel}]$ are the Hartree – Fock and GGA exchange energy for selected orbitals. The α parameter defines the fraction of exact functional, and in other cases called hybrid functional. A special case $\alpha = 0.25$ and GGA-PBE exchange correction functional is commonly devoted as PBE0.

The GGA+U

The GGA+U exchange correlation method relies on the combination of LDA or GGA functional with the Hubbard

Hamiltonian which describes the repulsion of the electrons in the nearest neighbour approximation.

The total ground state energy is corrected in the following way (Chioncel *et al*, 2003; Botton *et al*, 1998, Anisimoy *et al*, 1995).

$$E_{GGA+U}[\rho(r), (\rho_\sigma)] = E_{GGA+U}[\rho(r)] + \Delta E_{GGA+U}[\rho, \alpha, U, J] \quad (2)$$

where ρ_σ is an occupation matrix of the selected orbital with occupancies $n_{m\sigma}$ (m is a momentum quantum number and σ is the spin, U and J are averaged coulomb and exchange parameters (Chioncel *et al*, 2003; Botton *et al*, 1998).

$$\Delta E_{GGA+U} = \frac{U}{2} \sum_{m\sigma} n_{m\sigma} n_{m'\sigma'} - \frac{J}{2} \sum_{m \neq m'\sigma} n_{m\sigma} n_{m'\sigma'} \quad (3)$$

Equation (3) can be rewritten in terms of the orbital occupation ρ_σ matrix as follows (Chioncel, 2003):

$$\Delta E_{GGA+U} = - \frac{U-J}{2} \sum_{\sigma} [\text{Tr}(\rho_\sigma \rho_\sigma) - (\text{Tr}(\rho_\sigma))^2] + \frac{U}{2} \sum_{r \neq r'} \text{Tr} \rho_\sigma \text{Tr} \rho_{\sigma'} \quad (4)$$

Where $\text{Tr} \rho_\sigma = \sum_m n_{m\sigma}$

The total number of electrons in the selected orbital is

$$N_{el} = \sum_{\sigma} \text{Tr} \rho_\sigma$$

Double Counting Corrections

Equations (3) and (4) contain double counting, thus, additional correction should be added. Two corrections should be added. Two of such corrections methods are:

- (a) Around Mean Field (AMF)
- (b) The Fully Localized Limit (FLL)

Computational Methods

Computations were done by generalized and exact density approximation (GGA and GGA + U), using full potential linearized augmented plane wave (FP-LAPW) with WIEN2K code.

In this method, the unit cell is partitioned into (Muffin-tin) spheres and interstitial regions, where different basis sets were used to describe the Kohn-Sham orbitals: the plane wave basis was used in the interstitial region and an expansion of spherical

harmonics times the radial function was used inside the atomic sphere.

The Hubbard-U correction, in fully localized limit, referred to GGA+U, was applied to the empty up orbital of hydrogen and hybrid functional GGA-PBE exchange correlation functional commonly PBE0, which corresponds to the case $\alpha = 0.25$, using Eq. (1), applied to S orbital of hydrogen.

For GGA + U, the value of $U - J = 8.98\text{eV}$ was determined by adding and removing one electron from the system of two hydrogen atoms separated by 2 \AA . In our calculations, the muffin-tin radii of Li and H were chosen to be 1.8 and 2.0 a.u. respectively.

To initiate calculations, preliminary selections, based on literature about H and Li metal ionic radii were done, and then for GGA+U, the tests were performed with the band-gap and lattice constant to determine the most optimal muffin-tin radius (RMT) for the hydrogen. The RMT for Li is fixed as the difference, the shortest M-H bond length and RMT radius of hydrogen.

For Brillouin zone integration, 500 k – points in the unit cell were chosen. The charge density was Fourier expanded to $G_{\text{max}} = 20\text{Ry}$. The cut-off energy, which defines the separation of the core and valence states, was chosen as -6Ry (Blaha *et al*, 2002). The states below this energy were described by the Local Orbital (LO), while other states by LAPW – the details are found in literatures (Cottenier, 2002; Anderson 1975). For suitable convergence, the cut-off parameter Rk_{max} , which

defines the separation of the core and valence states, was chosen as -6Ry (Blaha *et al*, 2002). For apt convergence, the cut-off parameter Rk_{max} radii and varied from 7.5 to 9.

It is noteworthy to mention that implementation of the orbital dependent functional in WIEN 2K required calculation to be spin polarized. However, the resulting spin-up and spin-down electron density was the same. Thus, the results of band structure and density of states were shown as if calculations were done for the non spin-polarized case.

3. RESULTS AND DISCUSSION

Structural properties (lattice constants)

At first step calculations, the structure was optimized with respect to the lattice parameters and internal ionic position, and atoms remained in their high symmetry positions. The lattice constants of the compound were calculated using FP-LAPW approach based on the density functional theory implemented in WIEN 2k code, using GGA and GGA+U approximation, as presented in Table 1.

It was observed that there was very good agreement between the present GGA calculations and those reported before (Novakovic *et al*, 2007), and these results compared favourably with plane wave calculation.

It was also noticed that with GGA+U, for hydrogen, the lattice parameters were systematically over estimated by 6%.

Table 1: Calculated lattice constant \AA using GGA, GGA+U, compared to experiment and other references.

Compound	Method	Present	Lattice constant	\AA
		Work	Other calculations	experiment
	GGA	4.01	4.02 ^a , 40.2 ^b	4.07 ^c , 4.08 ^d
LiH	GGA+U	4.36		

Ref^a : Brocks *et al* (2007), using GGA

Ref^b : Novakovic *et al*, (2007), using GGA

Ref^c : Wyckoff (1963), experiment

Ref^d : Loubeyre (1998), experiment

Electronic Structure

The valence band of LiH consists of hydrogen 1s orbitals, while the conduction states consist of empty metal s, p orbitals, as shown in Fig. 2. The valence band has more dispersed characters as shown in Fig. 3. This dispersion, however, is an indication for non-ionic contribution to atomic bonding as in Ref. (Novakovic *et al*, 2007). Direct interaction between

hydrogen ions takes place due to small separation H and additionally orbital overlap Li and hydrogen if present below the Fermi level.

It was noticed that, below the Fermi level, the maximum energy difference (on DOS scale) between the peaks was 0.1 $1/\text{eV}$ scale, the shift between GGA+U and GGA was 0.5eV.

The calculated direct band gaps as shown in table 2 and were compared with theoretical and experimental data. It was also observed that the application of PBE+U enlarges the band gap by 0.82eV. Our band gap result compares with the

experimental data (Ichikawa *et al*, 1981), but it is smaller than this calculated by GW method (Brocks *et al*, 2007).

Taking into account the usual overestimation of the band gaps by GW method, one can conclude that our value is reasonable.

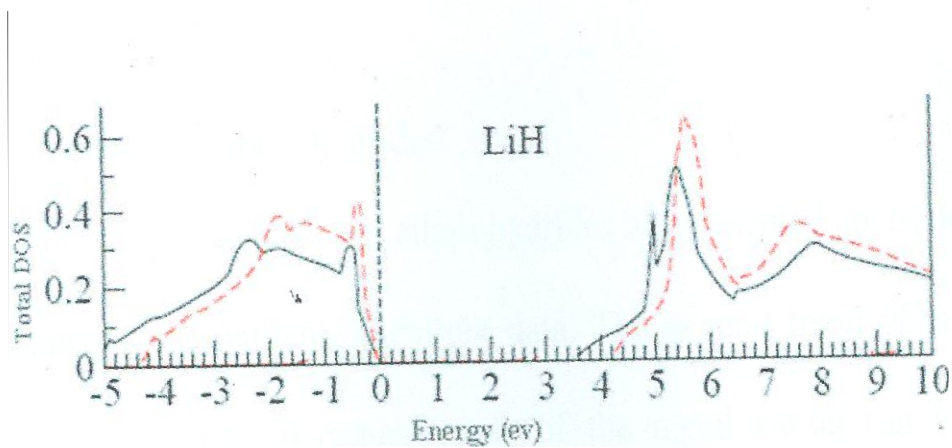


Fig. 2: The total density of state of LiH. Solid lines correspond to GGA exchange correlation functional and dash lines for GGA+U.

Vertical dashed lines indicate the Fermi-level.

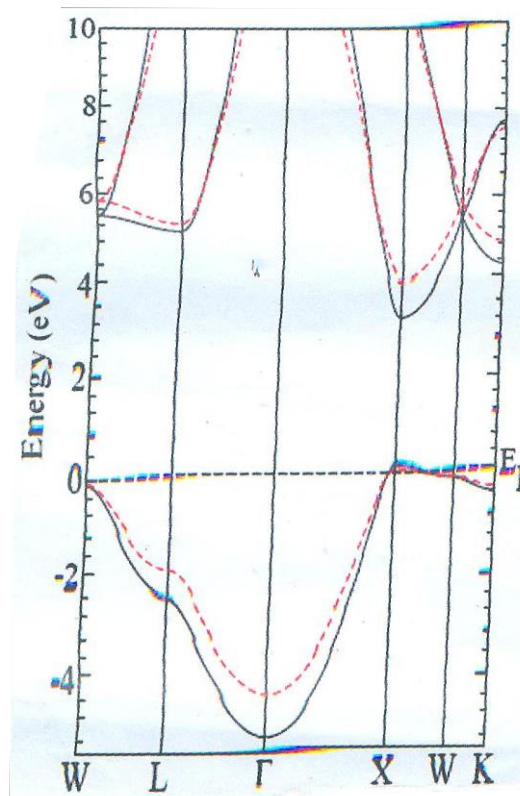


Fig. 3: The band structure of LiH.

Table 2: Direct (Eg) band gap of LiH

Compound	Method	Present	Direct Band gap (eV)	
			Work	Other calculations
	GGA	3.03	3.03 ^a	4.99 ^c , 4.40 ^c
	GGA+U	3.85	3.00/4.54 ^b	4.20 ^d

- Ref^a : Novakovic *et al*, (2007), using GGA
 Ref^b : Brocks *et al*, (2007), using GGA/GW
 Ref^c : Novakovic *et al*, (2007), experiment
 Ref^d : Ichikawa *et al*, (1981), experiment

4. CONCLUSION

In this paper, the electronic and the structural calculations for LiH have been presented. The FP-LAPW was used, within GGA and GGA+U as implemented in WIEN 2k code. A good agreement with the experimental result was obtained by applying GGA+U formation. It was also observed that the present GGA calculations agreed reasonably with other methods, though they were smaller than experimental data. Calculations with GGA+U functional enlarge the band-gap to values close to experimental ones.

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