

## Electronic and Structural Properties of $\text{CaH}_2$ Using GGA and GGA + U Approximation with WIEN 2K Codes

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**ABSTRACT:** In this paper, the electronic and the structural (lattice constant) properties of  $\text{CaH}_2$ , in orthorhombic phase, with  $P_{nma}$  space groups, are calculated using density functional theory. The Kohn-Sham equations were solved using the full-potential linearized augmented plane wave (FP-LAPW) method. Generalized Gradient Approximation (GGA) and GGA+U approximation were used as exchange-correlation potential with the suitable choice of  $U_{eff} = U - J$ , and the orbital dependent functional. It was found that adding Hubbard-U term to GGA improved calculated structural property, energy band structure results, and are in good agreement with experimental results.

**KEYWORDS:** Exchange, correlation, FP-LAPW, GGA, GGA+U, WIEN 2K.

### 1 INTRODUCTION

Hydrides compounds are often used as portable sources of hydrogen gas. Calcium is an essential metal for living organism and non-toxic [9]. Its primary commercial application, in its metallic form, is as a reducing agent in the production of other metals. In iron and steel production it is added to melt, remove oxygen, sulphur and carbon. The various calcium compounds have wide applications in food, pharmaceutical and cosmetics [9].

Metal hydrides are promising option for efficient on-board storage of hydrogen in future electric cars.  $\text{CaH}_2$  is in group II hydrides in the periodic table. It is isomorphous and crystallizes with orthorhombic lattice (at low pressure and temperature below  $600^\circ\text{C}$ ), exhibiting the  $P_{nma}$  space group [14]. Each unit cell contains four  $\text{CaH}_2$  molecules with two sites of non-equivalent hydrogen;  $\text{CaH}_2$  forms ionic structure with physical properties that are quite different from its metallic hydride [14].

Previous works have been done on the electronic and structural properties of  $\text{CaH}_2$ , using *ab initio* Hartree-Fock or the pseudo-potential method in connection with the CRYSTAL 95 program, but because of its orthorhombic symmetry, no calculations of the band structure have been undertaken in its real structure [8]. Indeed on its bands have been determined in a hypothetical structure of FCC  $\text{CaF}_2$ - type [8]. Their band structure, with this method, over-estimated the energy band gap ( $E_g$ ) between around 10 eV, which is almost twice larger than the experimental one (in order of 5 eV)[15].

In this present work, an improved method has been employed, using full-potential linearized augmented plane wave (FP-LAPW) method as embodied in WIEN 2K code, with Generalized Gradient Approximation (GGA) and GGA+U, used as exchange-correlation potential, where U is the Hubbard correction term.

## 2 THEORETICAL CONSIDERATIONS

One of the challenges of Density Functional Theory (DFT) is its profound problem of reproducing electronic structure correctly, beginning with the problem that it does not tackle electron counting accurately. This results in its failure to provide an exact description of the electronic structure of the molecular system [3]. In addition, the existence of self-interaction error in the external potential is another critical problem of DFT. Since it is ground state theory, Kohn-Sham eigenvalues 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 [8]. However, the interpretation of the Kohn-Sham eigenvalues as the excitation energies (like the Hartree-Fock method) leads to the astonishingly good results although one of the most important issues which came from the interpretation is the underestimation of the band-gap in DFT.

One of the reasons, as mentioned above, is the self interaction error, and the solution of this problem proceeds to the usage of orbital semi-empirical functions for selected orbitals. Such functional partly cancels this error and allows enhancement of calculation of the band-gaps [11]. There exist a variety of implementations of such methods, but this work will discuss only two of them, which are useful in our calculation.

### 2.1 EXACT EXCHANGE AND HYBRID FUNCTIONAL

One of the possibilities to cancel self interaction error is to add exchange term to the exchange-correlation function. Thus, the total energy will have the following form [12]:

$$E = E_{GGA}[\rho(r)] + \alpha(E_X^{HF}[\psi_{sel}] - E_X^{GGA}[\rho_{sel}]) \quad (1)$$

where  $\rho_{sel}$  and  $\psi_{sel}$  are density and the wave function of the selected orbitals;  $E_X^{HF}[\psi_{sel}]$  and  $E_X^{GGA}[\rho_{sel}]$  are the Hartree-Fock energy for the selected orbitals. The  $\alpha$ -parameter defines the fraction of the exact functional, and other cases called hybrid functional. A special case of  $\alpha = 0.25$  and GGA-PBE exchange correction functional is commonly denoted by PBEO.

### 2.2 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 electrons in the nearest neighbour approximation. The total ground state energy is corrected in the following way,[6]:

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

where  $\rho_\sigma$  is an occupation matrix of selected orbital with occupancies  $n_{m\sigma}$  ( $m$  is a momentum quantum number and  $\sigma$  is the spin),  $U$  and  $J$  are averaged coulomb and exchange parameters [6]:

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

Equation (3), however, can be rewritten in terms of the orbital occupation matrix  $\rho_\sigma$  as follows [6]:

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

Where

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

The total number of electrons on the selected orbital is [6]:

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

Equations (3) and (4) contain double counting of electrons; thus additional correction should be added. Hinging on the implementation of the double counting corrections, a few adjustments of GGA + U exist in literature, two of which to be highlighted in this work:

- (i) Around mean field(AMF)
- (ii) Fully localized limit(FLL)

### 2.3 AROUND MEAN FIELD (AMF)

In this method, the average electron occupancy  $n_{av,\sigma}$  is given by

$$n_{av,\sigma} = \frac{N_{el,\sigma}}{2l+1} = \frac{T_r \rho_\sigma}{2l+1} \quad (5)$$

The above formula delineates a uniform orbital occupancy limit where the selected orbitals have the same occupancy and the changes from this limit is described by causing the following reconstruction in eqns.(3) - (5), ([5], [6]):

$$n_{m\sigma} \rightarrow n_{m\sigma} - n_{av,\sigma}, \rho_\sigma \rightarrow \rho_\sigma - \delta_{mm'} n_{av,\sigma}$$

Thus eqn. (3) becomes:

$$\Delta E_{GGA+U}^{AMF} = \frac{U}{2} \sum_{m\sigma \neq m'\sigma'} (n_{m\sigma} - n_{av,\sigma'}) (n_{m'\sigma'} - n_{av,\sigma'}) - \frac{J}{2} \sum_{m \neq m', \sigma} (n_{m\sigma} - n_{av,\sigma'}) (n_{m'\sigma} - n_{av,\sigma}) \quad (7)$$

Now, the confirming equation, in terms of the occupation matrix  $\rho_\sigma$  gives [6]:

$$\Delta E_{GGA+U}^{AMF} = \frac{-U-J}{2} \sum_{\sigma} T_r (\rho_\sigma - \delta_{mm'} n_{av,\sigma}) (\rho_\sigma - \delta_{mm'} n_{av,\sigma}) \quad (8)$$

### 2.4 FULLY LOCALIZED LIMIT (FLL)

The former approximation is not valid for strongly localized electrons [6],, but in fully localized limit, it means that occupancies of either  $n_{m\sigma} = 0$  or  $n_{m\sigma} = 1$  are possible. In this case, the double counting correction can be expressed in terms of total number of electrons[1], and eqn. (3) becomes:

$$\Delta E_{GGA+U}^{FLL} = \frac{U}{2} \sum_{m\sigma \neq m'\sigma'} (n_{m\sigma} n_{m'\sigma'}) - \frac{J}{2} \sum_{m \neq m', \sigma} n_{m\sigma} n_{m'\sigma} - \left( \frac{U}{2} N_{el} (N_{el} - 1) - \frac{J}{2} \sum_{\sigma} N_{el2\sigma} (N_{el,\sigma} - 1) \right) \quad (9)$$

where  $N_{el,\sigma} = T_r \rho_\sigma$  and  $N_{el2\sigma} = \sum_{\sigma} N_{el,\sigma}$ .

In this approximation eqn. (4) becomes [6], [12]:

$$\Delta E_{GGA+U}^{FLL} = \frac{-U-J}{2} \sum_{\sigma} [T_r (\rho_\sigma \cdot \rho_{\sigma'}) - T_r (\rho_\sigma)]. \quad (10)$$

For effective use of this approximation, the values of  $U$  and  $J$  parameters (or their difference

$U_{eff} = U - J$ ) must be known, and this is related to energies required to move the electrons between the neighboring orbitals (this will be specified in method of our calculations).

These parameters can be determined by series of calculations with one electron added to and removed from the system (Anisimov *et al.*, 1991):

$$U_{eff} = [\epsilon_{nl}^\uparrow (\frac{n+1}{2}, \frac{n}{2}) - \epsilon_{nl}^\uparrow (\frac{n}{2}, \frac{n-1}{2})] - [\epsilon_{nl}^\downarrow (\frac{n+1}{2}, \frac{n-1}{2}) - \epsilon_{nl}^\downarrow (\frac{n}{2}, \frac{n-1}{2})] \quad (11)$$

where  $\epsilon_{nl} \sum n^\uparrow, n_\downarrow$  is the Kohn – Sham eigenvalue of  $nl$  orbital with the occupancy of  $(nl^\uparrow, n_\downarrow)$  and  $n = (nl^\uparrow + nl_\downarrow)$  is a total occupancy of this total orbital before adding or removing electrons. With these approximations, the total energies for ground state and energy levels related to the orbit of interest are improved.

### 3 COMPUTATIONAL METHODS

Computations were done by generalized gradient and exact density approximation (GGA and GGA + U), using the full potential linearized augmented plane wave (FP – LAPW) with WIEN 2K Codes in frame of density functional theory.

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 the expansion of spherical harmonics times the radial function was used inside the atomic sphere. The Hubbard– $U$  correction, in fully localized limit, referred to as GGA + U, was applied to the empty  $p$  orbital of hydrogen, and hybrid function. GGA – PBE exchange correlation functional, commonly called PBEO, corresponds to the case  $\alpha = 0.25$ , using eqn. (1), was applied to  $s$  orbital of hydrogen.

For GGA + U, the value of  $U - J = 8.98 \text{ eV}$ , was determined by adding and removing electrons from the system of two hydrogen atoms separated by  $2\text{\AA}$ , using eqn. (11).

In this calculation, the Muffin – tin radii of Ca and H were chosen to be

$$R_{MT}^{Ca} = 1.9 \text{ and } R_{MT}^H = 2.2 \text{ a.u., respectively.}$$

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

For Brillouin zone integration, 300 K – points in the unit cell were chosen. The cut – off energy, which defines the separation of the core and valence states, was chosen as  $-6\text{Ry}$  [13]. The states below this energy were described by the local orbital (LO), while other states by LAPW [7].

For suitable convergence, the cut – off parameter  $Rk_{max}$ , which limits the expansion of the basis set for the sphere of radius  $R$  to maximum value of  $k$  was different for different values of RMT radii, and varied from 7.5 to 9.

The implementation of the orbital dependent functional in WIEN 2K requires calculation to be spin – polarized. However the resulting spin – up and spin – down electron density was the same. Thus, the result of the band structure and density of states were performed for non – spin polarized case.

### 4 RESULTS AND DISCUSSIONS

#### 4.1 LATTICE CONSTANTS

The structure was optimized. The calculated lattice parameters for GGA + U were in agreement with the experimental data (Table 1). The application of GGA functional affects the calculated lattice parameters. It was also found that the volume of the unit cell was more systematical than for GGA. It was also observed, for this functional, that the lattice parameters were larger than the experimental ones, and this was a result of the general tendency of GGA calculations to overestimate lattice constant [17].

**Table 1. Lattice constants for  $\text{CaH}_2$ . Results are compared with available experimental data.**

Compound	Method	Present Work	Other Calculation	Experiment
$\text{CaH}_2$	GGA + U	6.00,	5.58 <sup>a</sup> ,	6.00 <sup>b</sup> ,
		3.62, 6.94	3.35 <sup>a</sup> ,	3.60 <sup>b</sup> ,
			5.75	6.81 <sup>b</sup> ,
	GGA	6.26,		
		3.87, 7.31		

a. [7] using GGA

b. [16] experiments.

#### 4.2 ELECTRONIC BAND STRUCTURE AND DENSITY OF STATES

The band structure for the orthorhombic phase of  $\text{CaH}_2$ , with space group Pnma, was calculated along the high symmetry directions in Brillouin zone as shown in Fig.2. The band structure plot is complex, and this indicates a complex crystalline structure. It was noticed that the application of  $\text{GGA} + U$  shifted the conduction bands towards higher energies, thus enlarging the band gaps by about 0.09 eV: values close to experimental ones (as shown in Tables 2 and 3). It was further observed that the valence band remain unchanged.

Figure 1 shows the total density of states of  $\text{CaH}_2$ . The compound, it was noticed, was insulating with band gap exceeding 3 eV.

**Table 2. Direct band gap ( $E_g$ ) for  $\text{CaH}_2$  (eV)**

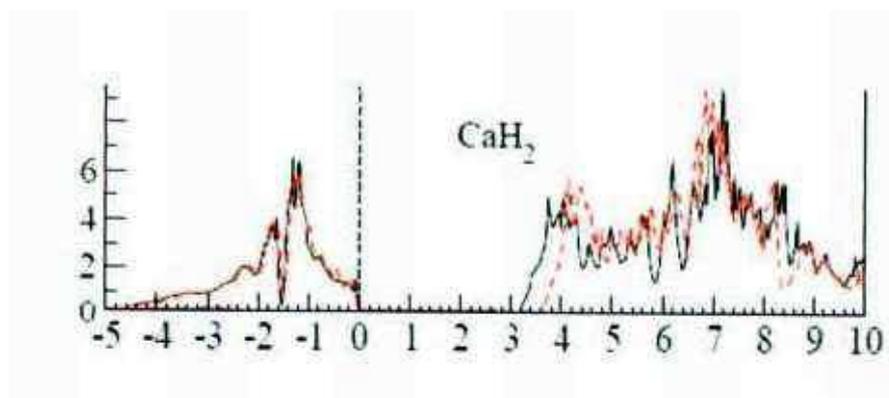
Compound	Method	Present Work	Other Calculation	Experiment
$\text{CaH}_2$	GGA+U	4.17	-	5.00 <sup>a</sup>
	GGA	4.22	-	-

**Table 3. Indirect band gap ( $E_g$ ) for  $\text{CaH}_2$  (eV)**

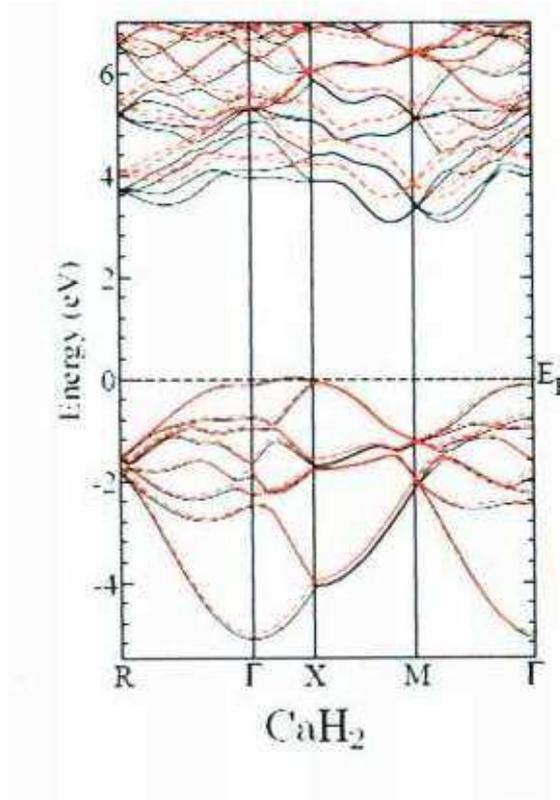
Compound	Method	Present Work	Other Calculation	Experiment
$\text{CaH}_2$	GGA+U	3.53	10.0 <sup>b</sup>	2.51 <sup>c</sup>
	GGA	3.04	-	-

a. [8], using A-F

b. [15] experiment.



**Figure 1: Total density of state of  $\text{CaH}_2$ . Solid lines correspond to GGA exchange-correlation functional and dash lines for GGA + U. Vertical dashed lines indicate the Fermi level.**



**Figure 2: Band structure of  $\text{CaH}_2$ . Solid lines indicate the band structures for GGA functional and dashed lines are for GGA + U functional.**

It was observed that the valence band consisted mainly of the occupied states of hydrogen while the conduction band consisted of mostly empty  $s$ ,  $p$  and  $d$  states of the Ca atom.

## 5 CONCLUSION

A detailed study of the electronic and structural properties (lattice constants) of  $\text{CaH}_2$  in its orthorhombic structure was carried out by means of GGA and GGA + U methods. For the calculated lattice constants it was observed that GGA has the tendency to underestimate the cell, while GGA + U method overestimated the volume of the unit cell systematically more than the former method.

The total density of states calculation revealed that  $\text{CaH}_2$  is an insulator with band gap exceeding 3 eV.

It was also observed that the valence band consisted mainly of occupied states of hydrogen, while the conduction band consisted of empty  $s$ ,  $p$  and  $d$  states of the Ca atom. It was also noticed that GGA + U shifts the conduction states toward higher energies while the valence band did not change with application of GGA+U.

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