



Electronic and Structural Properties of α -MgH₂ Using GGA and GGA+U Approximation

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$$\text{Min} \sum_{i=1}^n w_i x_i$$

$$\text{s.t. } A_{(n+w) \times n} X_{n \times 1} \geq b_{(n+w) \times 1}$$

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ABSTRACT

In this paper, the electronic and the structural (lattice constant) properties of α -MgH₂ are calculated, using density functional theory. The Kohn-Sham equations were solved using the full potential-linearized augmented plane wave (FP-LAPW). Generalized Gradient Approximation (GGA) and GGA+U approximations are the exchange-correlation potential used in this study. It was found that adding Hubbard-U term to GGA improved calculated structural property, energy band structure results and are in better agreement with the experimental data.

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Introduction

MgH₂ under several pressure conditions undergoes structural phase transitions. It was found that the ground state α -MgH₂ (TiO₂) rutile type transforms in orthorhombic γ -MgH₂ (α -PbO₂) at 0.39 GPa (Fjellvag *et al.*, 2002), and the subsequent phase from γ to β -MgH₂ (which is a modified CaF₂-type structure) (see Fig. 1) occurs at 3.84 GPa (Araujo *et al.*, 2005).

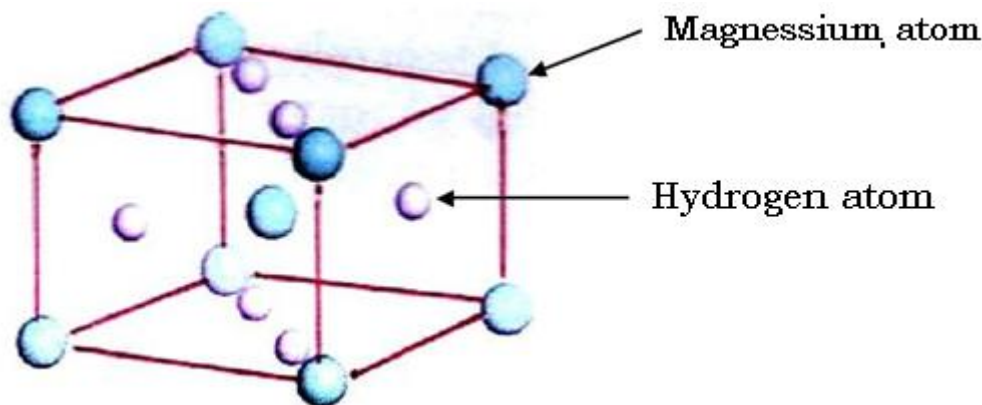


Fig 1: Crystal structure of α -MgH₂ (P42/mnm) (Fjellvag *et al.*, 2004). Larger spheres represent Magnesium atoms and the smaller ones, the hydrogens

In isoelectronic MgH₂, the estimated band-gap is monotonically reduced on increasing pressure (Fjellvag, 2004). Among metal hydrides, the magnesium hydrogen system has occupied a special place. Magnesium reacts reversibly with hydrogen to form MgH₂. It is considered to be one of the most important candidates for the reversible storage of hydrogen due to its light – weight, low cost, and high storage capacity (wt.7.6% of hydrogen) (Arwin *et al.*, 2003).

The large scale utilization of hydrogen as a fuel crucially depends on the development of compact hydrogen storage materials with a high mass content of group I-III mass in the upper rows of periodic table meets this requirement.

All the theoretical calculations published so far, using either Local Density Approximation (LDA) or Generalize Gradient Approximation (GGA) predicts band-gap between 3.1 and 4.2 for α -MgH₂ (Arwin *et al.*, 2003). α -MgH₂ has the rutile structure i.e. space group P42/mnm in tetragonal system.

In this work, the electronic structure and the structural property (lattice constants) of α -MgH₂ are determined by generalized gradient and exact density approximation (GGA and GGA+U), using full-potential linearized augmented plane wave (FP-LAPW) method in frame of density functional theory (DFT).

Band gap and orbital dependent functionals

We are aware that one of the challenges of Density Functional Theory (DFT) is band gap problem. It has some profound problems of reproducing electronic structure correctly, beginning with the problem that it does not undertake electron counting correctly. This results in its failure to provide an accurate description of the electronic structure of molecular system (Becke, 1988). In addition the presence of electron self interaction error in the external potential is another major problem of DFT since in ground state theory the Kohn-Sham eigen values generally cannot be assigned to the excitation energy of the system.

In DFT only the highest occupied eigen value 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 the surprisingly good results. But one of the most important issues which come 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 to this problem proceeds to the usage of the orbital semi-empirical functionals for selected orbitals. Such functionals partly cancel this error and allow improvement of the calculation of the band-gaps (Kummel and Kronik, 2008).

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

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 (Novak *et al.*, 2006; Blaha *et al.*, 2006):

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

where ρ_{sel} and ψ_{sel} are 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 the selected orbitals. The α parameter defines the fraction of exact functional, and other cases called hybrid functional.

A special case of $\alpha = 0.25$ and GGA–PBE exchange correction functional is commonly denoted 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 neighbor approximation.

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

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

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 a spin), U and J are averaged coulomb and exchange parameters.

The first term in equation (1) is the GGA total energy and the second one is the Hubbard correction and is determined from the following expression (Chioncel *et al.*, 2003; Botton *et al.*, 1998):

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

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

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

Where $T_r \rho_{\sigma} = \sum_m n_{m\sigma}$. The total number of electrons on the selected orbital is (Chioncel *et al.*, 2003) $N_{el} = \sum_{\sigma} T_r \rho_{\sigma}$.

Double Counting Corrections

Equations (3) and (4) contain double counting of electrons, thus, additional correction should be added. Two of such correction 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 *p* orbital of hydrogen and hybrid functional GGA-PBE exchange correlation functional commonly called PBE0, which corresponds to the case $\alpha = 0.25$ was applied to *s* orbital of hydrogen.

For GGA+*U*, the value of $U-J = 0.66\text{Ry}$ (8.98eV) was determined by adding and removing one electron from the system of two hydrogen atoms separated by 2Å. In our calculations, the muffin-tin radii of Mg and H were chosen to be 1.5 and 1.8 au, respectively.

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

For Brillouin zone integration, 500 *k*-points in the unit cell were chosen. The charge density was Fourier expanded to $G_{max} = 20\text{Ry}$. 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 literature, (Cottenier, 2002; Andersen 1975). For suitable convergence, the cut-off parameter Rk_{max} which limits the expansion of the basis set for the sphere of radius *R* to a maximum value of *k* was different for different values of the RMT radii, and varied from 7.5 to 9.

It is noteworthy to mention that implementation of the orbital dependent functional in WIEN2K requires 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-polarised case.

Results and Discussion

Structural properties (lattice constants)

From Table 1, it can be seen that application of GGA+*U* functional affects calculated lattice parameters of α -MgH₂. The volume of the unit cell is systematically larger than for GGA. For GGA+*U*, the lattice constants are larger than experimental ones, in agreement with general tendency of GGA calculations to overestimation of the lattice constants (Blaha *et al.*, 2009).

The calculated lattice constants using PBE0, though not indicated in the table, shows that they are between those of GGA and GGA+*U* ($a = 4.60\text{\AA}$, $c = 3.304\text{\AA}$), and this is in good agreement with the experimental values $a = 4.50\text{\AA}$ and $c = 3.01\text{\AA}$ in Table 1.

It is relevant to mention that this additional calculation was done to check the applicability of this functional for calculations of electronic property in α -MgH₂.

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

Compound	Method	Present work	Lattice constant \AA	
			other calculations	experiment
	GGA	5.54,3.02	4.52 ^a ,3.01 ^a	4.50 ^d ,3.01 ^d
MgH ₂	GGA+U	4.66,3.08	4.55 ^b ,3.04 ^b	
			4.43 ^c ,2.97 ^c	

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

Ref^b: Lam and Yu (1981), using LDA

Ref^c: Hector *et al.* (2007), using GGA

Ref^d: Cox *et al.* (2004), experiment.

Electronic structure

α -MgH₂ is insulating with the band-gap exceeding $3eV$. The valence band consists mainly of the occupied states of the hydrogen as shown in Fig. 2. The conduction band consists mostly of the empty s , p and d states of the metal atoms. Application to the corrected functional, shifts the conduction states towards higher energies. The character of the valence band, however, does not change, basically with GGA+ U functional. The valence band consists mainly of the occupied s states of the hydrogen and this indicates complex band structure of the compound as shown in Fig. 3 and the complexity is a reflection of complex structures. The character of the valence band does not change in general, with GGA+ U functional.

The calculated direct and indirect band-gaps are shown in Tables 2 and 3 and compared with calculated theoretical and experimental data.

Here, other calculations are available, and the present GGA agree reasonably with them, however, they are smaller than experimental data. Calculations with GGA+ U functional enlarge the band-gaps approximately 0.3 to $0.69eV$ to values close to experimental ones. On the other hand, the band-gaps are systematically smaller than those available and calculated in GW, and that can be attributed to overestimation of band-gaps in GW method.

The band-gaps for MgH₂ calculated with PBE0 functional are $E_g = 4.84$ and $E_{ig} = 3.91eV$, however this might have been coincidental as this approach fails to describe properly thermodynamics of metal hydrides.

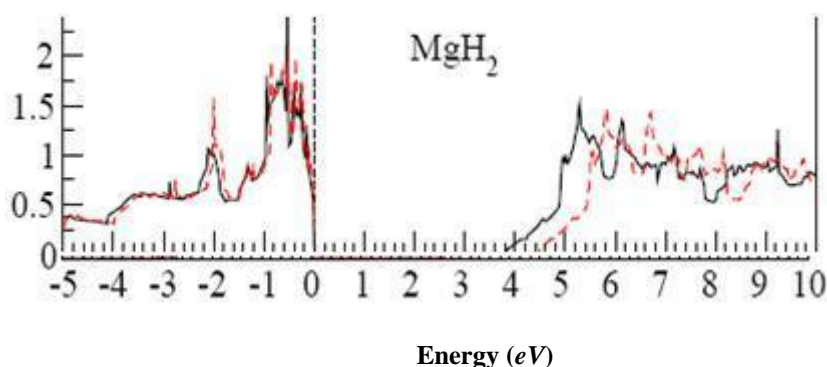


Fig. 2: The total density of state α -MgH₂. solid lines correspond to GGA exchange correlation functional and dash lines GGA+U. Vertical dashed lines indicate the Fermi-level

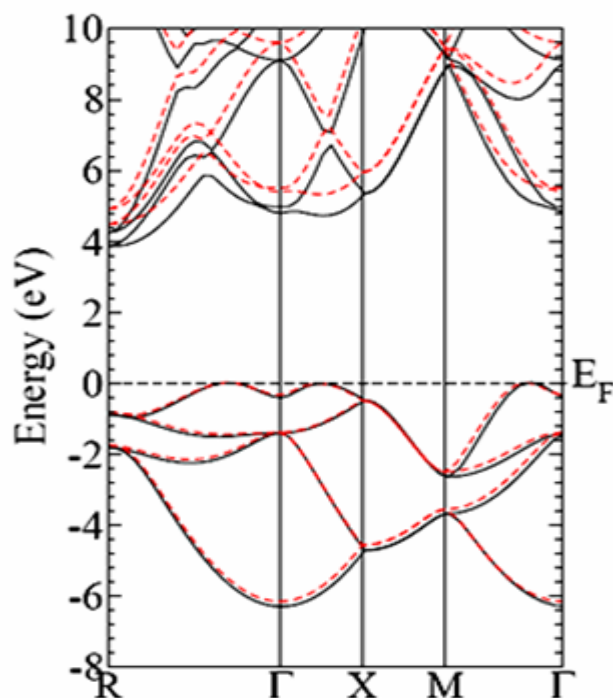


Fig 3: Band structure of α -MgH₂

Table 2. Direct (E_g) band gap of α -MgH₂

Compound	Method	Present work	Direct Bandgap (eV)	
			other calculations	experiment
α -MgH ₂	GGA	4.70	6.19 ^a	5.60 ^c
	GGA+U	5.27	6.52 ^b	5.40 ^d

Ref^a: Brooks *et al.* (2007), using GW

Ref^b: Araujo *et al.* (2005), using GW

Ref^c: Arwin *et al.* (2003), experiment

Ref^d: Fischer *et al.* (1996), experiment

Table 3. Indirect band gap (E_{ig}) of α -MgH₂

Compound	Method	Present work	Indirect Bandgap (eV)	
			other calculations	experiment
α -MgH ₂	GGA	3.84	3.72/5.32 ^a	3.40 ^d
			5.58 ^b	
			5.00 ^c	

Ref^a: Brooks *et al.* (2007), using GGA/GW

Ref^b: Araujo *et al.* 2005, using GW

Ref^c: Lamard Yu (1981), using LDA

Ref^d: Fischer *et al.* (1996), experiment

Conclusion

In this paper the electronic and structural calculations for α -MgH₂ have been presented. The FP-LAPW was used, within the GGA and GGA+U, as implemented in WIEN2K code. A good agreement with experimental result was obtained by applying the GGA+U formalism. It was found that the calculated lattice constants were in agreement with the experimental values. It was also observed the present GGA calculations agreed reasonably well 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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