GGA + U Study of α-BeH₂: Dependence on the Effective U Parameter with WIEN2K Codes.

Uko Ofe [a*], Michael U. Onuu[b], Igbo Michael[a]

[a]Department of Science Laboratory Technology, Akanu Ibiam Federal Polytechnic Unwana, Afikpo, Ebonyi State, Nigeria

[b]Department of Physics/Geology/Geophysics, Federal University Ndufu – Alike, Ikwo, Ebonyi State, Nigeria.

[a]Email: ukoofe@yahoo.com

[b]Email:michaelonuu@yahoo.com

Abstract

In this paper, the electronic and the structural (Lattice constant) properties of α-BeH₂, which is the ground state of BeH₂, in orthorhombic crystal system, with space group (Ibam) are calculated using density functional theory. The Kohn-Sham equations were solved; using the Full-potential linearized augmented Plane-wave (FP-LAPW) method. With the apt choice of $U_{eff} = U – J$, and orbital dependent functional, there was a palpable improvement using GGA + U approximation, as exchange – correlation potential on structural properties(lattice constants), and, results were in better agreement with experimental and other existing methods.

Keywords: Exchange – correlation; FP-LAPW; GGA; GGA+ U and WIEN2K Code.

1.   Introduction

Metal hydrides are of great scientific and technological interest in view of their potential applications, e.g. for hydrogen storage, in fuel cells and internal combustion engines as electrodes of rechargeable barriers and energy conversion devices [1].

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* Corresponding author

E-mail address: ukoofe@yahoo.com

At higher pressure α-BeH$_2$ successively experiences structural transitions (i) α- to β - BeH$_2$ at 7.07GPa; (ii) β – to r – BeH$_2$ at 51.41GPa; (iii) r – to δ – BeH$_2$ at 86.56 GPa; and (iv) δ – to Є – BeH$_2$ at 97.55GPa [1], and this explicates why BeH$_2$ behaves differently from the rest alkaline earth dihydrides.
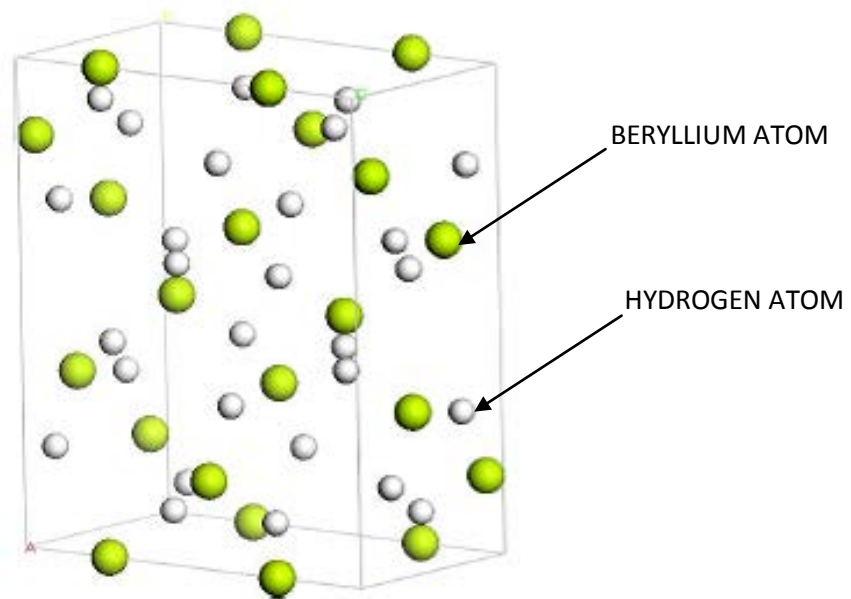

Fig. 1: Crystal Structure of α-BeH$_2$ with Ibam space group

Within all structural polymorphs, beryllium hydride remains insulating, despite that, the band gap contracts notably in β – BeH$_2$ to recapture the original form of α – BeH$_2$ at high pressures.

The electron structure and structural stability of BeH$_2$ have been studied, using first principle calculation [13]. The density functional theory (DFT) total energy calculations for α-BeH$_2$ have been performed, using the Vienna *ab initio* simulations package (VASP) with projected – augmented – wave (PAW), pseudo potentials [15] and plane waves, although all these methods were in agreement with experimental of Cox et al, 2004, but are, in general, computationally expensive. In this present work, an enriched method has been employed, using full –potential linearized augmented plane wave (FP – LAPW) methods embodied in WIEN 2K code, with Generalized Gradient Approximation (GGA) and GGA+U, used as exchange – correlation potential, where U is Hubbard correction term.

2.   Theoretical Considerations

One of the pathological problems of DFT is replication of electronic structure precisely, since it does not take electron counting accurately. This, however, results in its inability to provide an exact description of electronic structure of the molecular system [2]. Moreover, the tangibility of self interaction in the external potential is another crucial problem of DFT. Self interaction error (SIE) in DFT appears from the fact the residual interaction in the coulomb part and that in the exchange do not cancel each other exactly.

As it is ground state theory, the highest occupied Eigenvalue can be assigned the physical interpretation: It is exactly the chemical potential of the system [3]. However, the construction of Kohn – Sham Eigenvalues as the excitation energies (Like Hartree- Fock method) leads surprisingly to good results. Nonetheless, one of the most consequential 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 solution of this problem results in the usage of orbital. Such functional partly annuls this error and permits enhancement of calculation of the band gaps [4].

There exist a class of implementations of such methods but this work will examine only two of them, which are valuable in our calculation.

2.1 *Exact exchange and hybrid functional*

One of the new approaches designed to solve the problem of self – interaction error (SIE) is to add exchange term to the exchange – correlation function; hence, the total Energy will have the form [5,6]:

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

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 of the selected orbitals. The α– parameter delineates the fraction of the exact functional, and other cases hybrid functional. A special case of α = 0.25 and GGA – PBE exchange correction functional is commonly denoted by PBED.

2.2 *The GGA + U*

The GGA + U exchange correlation is used to treat specifically the complex interaction in the system studied for it gives more comprehension and leans on the combination LDA or GGA functional with the Hubbard Hamiltonian which describes the repulsion of electron in the nearest neighbor approximation. The total ground energy is corrected in the following way [7, 9]:

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

Where ρ_σ is occupation matrix of selected orbital with occupancies $n_{m\sigma}$ (m is the momentum quantum number and σ the spin), U and J are averaged and exchange parameter [7][9]:

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

Equation (3), however, can be modified in terms of the occupation matrix ρ_σ as follows [7]:

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

Where

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

the total number of electrons on the selected orbitals [7].

Incontrovertibly, equations (3) and (4) contain double counting of electrons; hence, additional correction should be added. Based on the underlying implementation of the double counting corrections a few adjustments of GGA + U exist in literature, two of which are to be illuminated in this work:

(i)   Around mean field (AMF);

(ii)   Fully localized limit (FLL).

2.3   Around Mean Field (AMF)

This scheme, the average electron occupancy $n_{av,\sigma}$ is given by

$$n_{\sigma u, \sigma} = \frac{N_{el,\sigma}}{2l+1} = \frac{T_r \rho_\sigma}{2l+1} = \frac{\sum_m n_{m\sigma}}{2l+1} \tag{5}$$

The formula above explicates a uniform orbital occupancy limit where the selected orbitals have the same occupancy and changes from this limit is described by effecting the following reconstructions in the equations (3) – (5) [7,9]:

$$n_{m\sigma} \rightarrow n_{m\sigma} - n_{au,\sigma}, \rho_\sigma \rightarrow \rho_\sigma - \delta_{mm'} n_{av,\sigma} \tag{6}$$

Hence eqn. (3) becomes:

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

Now, the substituting equation, in terms of the occupation matrix ρ_σ gives [7]:

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

2.4 Fully Localized Limit (FLL)

The aforementioned approximation is unsuitable for strongly localized electrons [7], but in fully localized limit, it means that occupancies of either $n_{m\sigma}$ or $n_{m\sigma} = 1$ are possible. In this case, the double counting correction can be expressed in terms of total number of electrons [8], and equation (3) yields

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

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

in this approximation equation (4) becomes

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

For efficient use of this approximation, the values of U and J parameters (or their difference $U_{eff} = U - J$) is invariably known, and this relates to energies required to move the electrons between the neighboring orbitals (this will be specified in method of our calculations).

It is pertinent to mention, at this point, that the choice of U_{eff} strongly influences the calculated observables.

These parameters can be determined by string of calculations with one electron added to and removed from the regime [10]:

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

where $\varepsilon_{nl}\sum(n\uparrow, n\downarrow)$ is the Kohn-Sham Eigenvalue of nl orbital with the occupancy of $(nl\uparrow, nl\downarrow)$ and $n = nl\uparrow + nl\downarrow$ is a total occupancy of this orbital before adding or removing electrons.

With these approximations, the total energies for ground state and energy levels related to the orbitals of interest are ameliorated.

3. Computational Methods

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

In this method, 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 functional GGA – PBE exchange correlation functional commonly called PEBO, which corresponds to the case α = 0.25 was applied to S orbital of hydrogen. For GGA + U, the value of U – J = 8.98eV was determined by adding and removing one electron from system of two hydrogen atoms separated by 2Å. The muffin – tin radii of Be and H were chosen as R_{MT}^{Be}= 1.38 and R_{MT}^{H} = 1.4 a.u. respectively.

To initiate calculation, preliminary selections based on literature about H⁻ and Be metallic ionic radii were done, then GGA + U tests were performed with respect to band gap and lattice constants to determine most optional muffin – tin radius (RMT) for the hydrogen. The RMT for Be is set as the difference between the shortest M – H bond length and RMT radius of hydrogen. For Brillouin Zone integration, 100 K – points in the unit cell were chosen. The charge density was Fourier expanded to G_{max} = 20R_y. The cut-off energy, which defines the separation of the core and valence states, was chosen as -6R_y [16]. To ensure high accuracy, the K – point densities and plane wave cut – off energy are increased until convergence.

The states below this energy were described by the local orbital (LO), while other states by LAPW – the details are found in Literature [11,12]. For suitable convergence, the cut-off parameter RK_{max} , which limits the expansion of the basis set for sphere of radius R different for different values of RMT radii, and varied from 7.5 to 9.

It is important to mention that 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 equal. 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 compared to other calculations, and it was noticed that the present GGA calculations over estimated the volume of the unit cell, while application of GGA + U affected the calculated lattice parameters, thereby making the volume of the cell systematically larger than that of GGA as shown in the table 1.

4.2   Electronic band structure and Density States

The band structure for orthorhombic phase space group Ibam of α – BeH$_2$ was calculated along the high symmetry directions in the first Brillouin Zone as shown in Fig.1. The band structure is complex, which depicts inextricable, complex crystalline structure.

Table 1: Lattice Constant (Å) for α – BeH₂. (Results were compared with available experimental data.)

Compound	Method	Present work	Other calculations	Experiment
α – BeH$_2$	GGA + U	9.17, 4.24, 7.78	8.63[a], 3.91, 7.43	9.08[b], 4.16, 7.71
	GGA	9.00, 4.16, 7.64		

- Source: [17]; using GGA

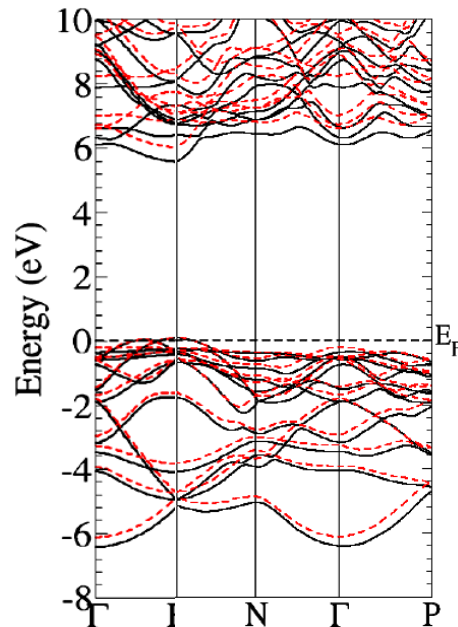*Table 2: Direct band gap (Eg) for α – BeH₂ (eV)*

Compound	Method	Present work	Other calculations	Experiment
α – BeH$_2$	GGA + U	6.05	-------	-------
	GGA	5.63	-------	-------

Table 3. Indirect band gap (Eg) for α – BeH₂ (eV)

| Compound	Method	Present work	Other calculations	Experiment
α – BeH$_2$	GGA + U	6.05	5.51c	-------
	GGA	5.63	8.27c	-------

- Source: [18]; using GW

- Source: [18]; using GGA

Fig. 2: Band structure of α – BeH$_2$. Solid lines indicate the band structures
for GGA functional and dashed lines for GGA + U functional.

The calculated direct and indirect band gaps are shown in tables 2 and 3, and results are compared with calculated theoretical data. Unfortunately there were no available experimental data for further comparisons, but the present GGA data agree reasonably with the existing ones.

It was observed that application of GGA + U shifted, the conduction states towards higher energies, thus making the compound more insulating, but the valence band did not change. The band gaps, however, are systematically smaller than those available, and, calculated in GW method, and that is attributed to the overestimation of band – gaps inherent in GW method.

Figure 3 shows the total density of states of α – BeH$_2$. It was noticed that the compound is an insulator with maximum band gap exceeding 5eV. The valence band consists mainly of the occupied S states of hydrogen, while the conduction band consists mostly of empty s, p and d states of Be atoms.
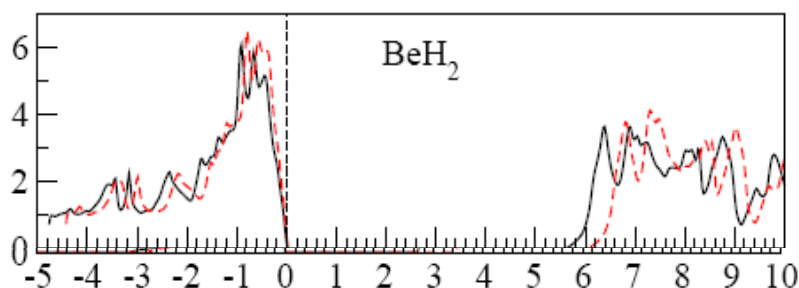
Fig. 3: Total Density of states of α – BeH$_2$. Solid Lines correspond to GGA exchange-correlation functional and dashed lines GGA+U. Vertical dashed line indicates the Fermi level.

5.   Conclusion

A detailed GGA+U study of α-BeH$_2$ in orthorhombic crystal system, with space group Ibam was carried out by means of GGA and GGA+U. The palpable effect of GGA+U on the calculated properties was observed.

GGA+U method affected the calculated lattice parameters, thus making the volume of the cell systematically larger than that of GGA.

It was also observed that application of GGA+U shifted the conduction states towards higher energies, thus making α-BeH$_2$ more insulating.

The total density of states calculation revealed that α-BeH$_2$ is an insulator with the band gap greater than 5eV.

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