



# Improved Electronic Band (*Lattice Constants*)

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## Abstract

Some structural and electronic properties of NaH in Rock-salt structure with space group,  $Fm\bar{3}m$ , in cubic (FCC) system, have been evaluated. The calculated quantities include: electronic band structure, lattice constant and density of state using the exchange correlation potentials (GGA and GGA +U). The effects of these exchange correlation potentials on the quantities mentioned have been discussed. The results obtained are reasonable, and in agreement with other calculated methods, but no experimental data on electronic band structure of this compound have been recorded in literature.

## Keywords

Exchange-Correlation functional, Band structure, GGA, GGA + U, WIEN2k code

## 1. Introduction

Density Functional Theory (DFT) is one of the most computational methods for studying electronic properties of materials [1]. The hydride metals, one of which is sodium hydride (NaH), are attractive because of their atomic or electronic properties (optical, electrical, thermal etc.) [2]. NaH is a group I metal hydride in the periodic table, with space group,  $Fm\bar{3}m$ , in crystal structure, FCC (NaCl).

Previous works have been done on electronic and structural properties of NaH. [3]. These researchers studied the electronic structure, and optical properties of light weight hydrides, including NaH, using LDA and GGA as exchange correlation potentials, thus comparing them. However, there was no experimental data for NaH, and this is confirmed with the data available in literature.

In 2012, the structural stability, thermodynamic, electronic and optical properties of NaH with Rock Salt (B1) structure and Cesium Chloride (B2) structure, under high pressure were investigated using non-conserving pseudo potential and applied GGA [4].

In this present work, an improved XC, GGA + U, is applied to the structural property (Lattice Constant), and electronic properties of NaH.

## 2. Theoretical Consideration

The band-gap problem is one of the tribulations of Density Functional Theory (DFT). Its inability to accurately shoulder electron structure counts is the first of several challenging issues with its precise electronic reproduction. As a result, it fails to provide a precise description of the molecular system [5].

Furthermore, since the Kohn-Sham eigenvalues are primarily independent of the system's excitation energy in ground state theory, the presence of self-interaction error in the external potential poses an additional challenge.

Since the highest occupied eigenvalue in DFT precisely represents the system's chemical potential, only this eigenvalue can be given a physical interpretation [6]. On the other hand, the Hatree-Fock approach and the analysis of the Kohn-Sham eigenvalues as the excitation energies yield really good findings.

One of the causes is self-interaction error, which is addressed above. For selected orbitals, orbital semi-empirical functions are used to solve this problem. These functions allow for an improvement in the band-gap calculation and partially rectify this issue. Although there are many ways to implement these techniques, just two will be discussed in this study because they are important to our calculations:

### 2.1 Exact and Hybrid Functional

Incorporating the exchange correlation function results in a unique chance of reversing the self-interaction mistake. Consequently, the total energy will look like this: ([7, 8]);

$$= E_{GGA+U}[\rho(r)] + \alpha(E_{XHF}[\psi_{sel}] - E_{XGGA}[\rho_{sel}], \dots \dots \dots (1)$$

$E_{(X^{\wedge}HF)}[\psi_{sel}]$  and  $E_{(X^{\wedge}GGA)}[\rho_{sel}]$  are the Hartree-Fock and GGA exchange energy for selected orbitals, where  $\rho_{sel}$  and  $\psi_{sel}$  are the density and wave function of the selected orbitals. The fraction of exact functional, also known as hybrid functional in other situations, is defined by the  $\alpha$  parameter. PBE0 is a typical notation for the GGA-PBE exchange correlation functional with an uncommon case of  $\alpha = 0.25$ .

## 2.2 The GGA + U

The Hubbard Hamiltonian, which represents the repulsion of the electrons adjacent to the neighbor approximation, as well as the composition of the LDA and GGA functional are both necessary for the GGA + U exchange correlations. The following process is used to rectify the total ground state energy:[10, 9]:

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

where  $U$  and  $J$  are averaged, and  $\rho_{\sigma}$  is an occupation matrix of the chosen orbitals with occupancies  $n_{m\sigma}$  (where  $\sigma$  is the spin and  $m$  is the momentum quantum number). Exchange parameters and Coulomb: [10, 9]:

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

Equation (3), however, can be rewritten in terms of the orbital occupation matrix,  $\rho$ , as follows:[10]:

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

where,  $T_r \rho_{\sigma} = \sum_m n_{m\rho}$  The total number of electrons on the selected orbital ([10]) is

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

## 2.3 Double Counting

Equations (3) and (4) exemplify double counting; therefore, additional alteration should be made:

- Around Mean Field (AMF)
- The fully localization limit (FLL) and these are found in Literature
- Computational Methods

Generalized and exact density approximations (GGA and GGA + U) were used in the computations, together with full potential linearized augmented plane wave (FP-LAPW) and WIEN 2K code.

By using this method, the unit cell is split into (Muffin-tin) spheres and interstitial regions. The plane wave basis was used in the interstitial region; while an expansion of spherical harmonics times the radial function was used inside the atomic sphere to describe the Kohn-Sham orbitals.

The hybrid function, GGA-PBE exchange correlation functional, also known as PBE0, corresponds to the case  $\alpha = 0.25$  using Eq. (1) and is applied to the hydrogen s orbital. The Hubbard-U correction, in fully localized limit, referred to as GGA + U, was applied to the empty p orbital of hydrogen.

As for GGA + U, the value of  $U - J = 8.84$  was determined by adding and removing one electron from the system of two separated by  $2\text{\AA}$ .

In our calculations, the muffin-tin radii of Na and H were chosen to be 2.38 and 2.0 a.u. respectively. In order to find the greatest muffin-tin radius (RMT) for the hydrogen, preliminary calculations were done using the band-gap and lattice constant, based on literature about the ionic radii of H and Na metals. Five hundred K-points within the unit cell were selected for the Brillouin Zone integration.  $G_{\max}=20\text{Ry}$  was the charge density after Fourier expansion.

The cut-off energy, which defines the separation of the core and the valence states, was chosen as 6 Ry [8]. The cut-off parameter for germane convergence, RK<sub>(max)</sub>, varied for different values of RMT radius, ranging from 7.5 to 9. This parameter limits the extension of the basis set for sphere of radius  $R$  to maximum value of  $K$ .

It is noteworthy to note that spin polarization is required for the computation in order to implement the orbital dependent functional in WIEN2K; yet, the obtained spin-up and spin-down electron densities were identical. As a result, the density of states and band structure results were presented as though they were for a non-spin polarized scenario.

## 3. Results and Discussion

### 3.1 Lattice Constants

The arrangement was maximized. The lattice parameters for GGA +U were found to be consistent with the experimental outcome reported in [11]. It was also noted that the GGA computation of [7] agreed with the current work.

**Table 1** Lattice constants ( $\text{\AA}$ ) for NaH, with results compared with literature

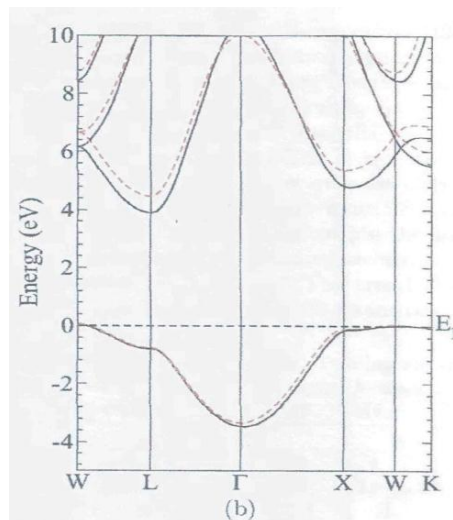
Structure	Structural Parameter	Compound	Method	Present Calculations	Other Calculations	Experimental Calculation
FCC	$\text{\AA}$	NaH	GGA+U	4.93	4.83[3]	4.85[11]
			GGA	4.84	4.84[7]	
					4.85[12]	

However, it was noted that the hydrogen lattice parameter calculation using GGA+U was only one percent overestimated. This was due to the fact that the lattice parameters that were revealed are measured outside of the zero point vibration sway. Taking into account the general tendency of GGA calculations to overestimate Lattice parameters, it could be concluded that the GGA +U method utilized is consistent with [12].

### 3.2 Electronic Band Structure and Density of States

#### 3.2.1 Electronic Band Structure

The electronic band structure for NaH, with space group  $Fm\bar{3}m$ , in crystal structure, FCC (NaCl), was calculated, using GGA and GGA +U, as exchange, correlation, potentials and is graphically represented in Figure 1.

**Fig. 1** Band Structure of NaH for GGA (solid lines) and GGA +U (dashed lines).**Table 2** Direct Band Gaps,  $E_g$ , of NaH.

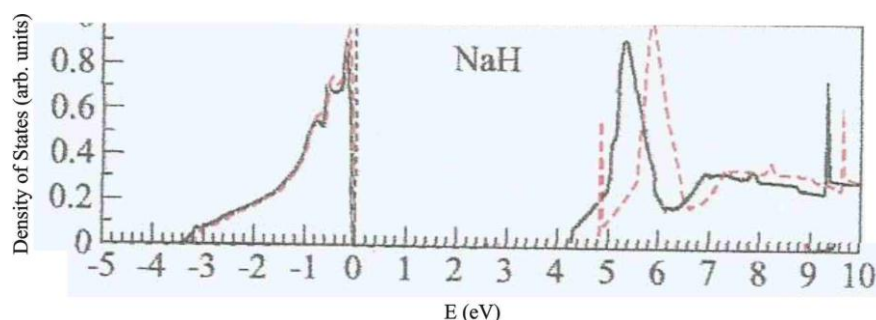
Structure	Structural Parameter	Compound	Method	Present Calculation	Other Calculation	Experimental Calculation
FCC	A	NaH	GGA +U	3.87	3.50 [13]	
			GGA	4.44	4.70 [7]	
					3.77 [7]	
					3.79 [3]	

The adoption of the GGA +U technique was shown to increase the band gap by 0.87 eV, making this material more offensive. Additionally, it was discovered that our work's GGA +U computation is 0.8 eV lower than that of [3], which is caused by the GW method's constitutional tendency on overestimating the band gap.

It is apropos to mention that band gaps of our present calculation are parallel to the GGA approximation of [7]. No experimental data on energy gap structure of NaH have been recorded in Literature.

#### 3.2.2 Density of States of NaH

The density of states of NaH is presented in Fig. 2, with the solid indicating GGA-exchange correlation, the dotted lines depicting the GGA +U approximation, and the vertical dash lines delineating the Fermi-level:

**Fig. 2** Density of states of NaH, with the features explicated above.

Hydrogen 1s orbitals make up the valence band, and empty Na, s, and p orbitals make up the conduction band. As a result, this characteristic, along with a wider band gap, fairly describes the compound's ionic structure.

#### 4. Conclusion

The lattice constant of our present GGA +U result was in consonance with the experimental value, also the GGA lattice constant calculation in the study was in agreement with the GGA calculation literature value. Besides, the GGA +U calculation was over by one percent only, which was symptomatic of Lattice constant being measure out of the sway of Zero vibration.

It may be concluded that our current GGA + U computation is consistent with the literature, despite the tendency of the GGA + U approach to overestimate the lattice parameters. It was observed that the application of GGA + U increased the band gap by 0.87 eV in relation to the electronic band structure of NaH, hence increasing the material's insulating properties. According to the density of states calculation, the conduction band was made up of empty Na, s, and p orbitals, and the valence band was made up of hydrogen 1s orbitals. As a result, this characteristic contributes to the compound's ionic structure together with a wide band gap.

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