GGA + U Study of the Optical Properties of LiH

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Abstract

In this paper, the optical properties of Lithium hydride (LiH), in rocksalt structure, with space group, Fm3m, in cubic (FCC) system, have been discussed. The theoretical background of the relation between the dielectric function, and, other optical constants has been examined. The real and imaginary parts of the dielectric function have also been scrutinized. The consequences of the exchange correlation potentials (GGA and GGA + U) applied to the absorption peaks and edges of the compound have also been spoken of. It was observed, at the application of GGA + U and GGA to the first absorption edge matched together; but there was overt difference in fine structure at higher energies due to the presence of the former exchange correlation approximation.

Subject Areas

Applied Physics, Modern Physics, Particle Physics

Keywords

Dielectric Function, Optical Properties, GGA + U and GGA Approximations

1. Introduction

The Alkali hydrides compounds XH (X = Li, Na, K, Rb and Cs) are very simulating compounds in that they have the simplest electronic band structure. Alkali hydrides with complex hydrides are besides interesting for their capacity to store hydrogen [1]. The electronic band structure, and structural property (lattice constant) of LiH, in rock salt structure, with space groups Fm3m, in cubic (FCC) system have been examined, using density functional theory, employing the full-potential linearized augmented plane wave (FP-LAPW) [2]. Generalized gradient approximation and GGA + U were used as exchange correlation poten-

tials, with WIEN2k code; detailed method of calculation of the observables was explicated in [3]. To comprehend the optical properties of solids, their electronic band structure provides a more perspicuous explanation. [2] has studied the dielectric function of LiH in RS structure by first-principles density and all electronic GW approximation, with the latter known for its unconscionable computational cost. Confirming with [1], the optical properties for the family of alkali hydride compounds have been done for only the LiH and the NaH compounds, in RS structure, using GGA as the exchange correlation (XC).

In this present work, the optical properties of LiH are to be investigated, using full-potential linearized augmented plane wave (FP-LAPW), using GGA and GGA + U approximations with WIEN2k codes in the framework of density function theory (DFT) [4].

2. Theoretical Consideration

Dielectric Function

The optical properties can be derived from the dielectric function $\varepsilon(\omega)$ computed by density functional theory (DFT). Dielectric function is a three-dimensional tensor, which hinges on the symmetry of the crystal, and is calculated directly from the Kohn-Sham energy eigenvalues, ε_k. In the Random Phase Approximation (RPA), the function, $\varepsilon_{ij}(\omega)$, can be expressed as [5]

$$\varepsilon_{ij} = \delta_{ij} - \frac{1}{v\omega^2} \sum_{n,k} \left(\frac{-\delta F(\varepsilon)}{\delta \varepsilon_{n,k}} \right) P_{i;n,n,k} P_{j;n,n,k}$$

$$- \frac{4\pi}{v\omega_2} \sum \frac{P_{i;c,v,k} P_{j;c,v,k}}{\left(\varepsilon_{c,k} - \varepsilon_{v,k} \right) \left(\varepsilon_{c,k} - \varepsilon_{v,k} \right)^2} \tag{1}$$

where V is a unit cell Volume, $P_{n,m,k}$ are momentum matrix elements between the bands n and m, for the point K of the crystal. $F(\varepsilon)$ is a Fermi-Dirac distribution function:

$$F(\varepsilon) = \frac{1}{\exp\left(\dfrac{\varepsilon - \varepsilon_F}{K_B T} \right) + 1} \tag{2}$$

where K_B is Boltzmann constant.

3. Optical Properties of LiH

3.1. Imaginary and Real Parts of the Dielectric Function

The imaginary part, $\varepsilon_2(\omega)$, for the dielectric function $\varepsilon(\omega) = \varepsilon_1(\omega) + i\varepsilon_2(\omega)$, can be calculated using momentum matrix [6]. The corresponding eigenfunction of each of the occupied and unoccupied state contributes to the matrix elements. The real parts $\varepsilon_1(\omega)$ of the dielectric function can be derived from the imaginary part $\varepsilon_2(\omega)$ by Krong-Kramers relationship [6].

The imaginary part of the dielectric function is indicative of real transfer between occupied and unoccupied states, thus the imaginary part then handles the

attenuation, while the real part accounts for refraction; explicitly, the real part indicates scattering and loss in optical processes. At this point, it is apt to maintain that the conduction band is the imaginary part, while the valence band is the real part of the dielectric function.

3.2. Refractive Index and Extinction Coefficient

The refractive index is one of the principles defining the characteristics of an optical material, while the extinction coefficient, *K*, illustrates the exponential decay of the amplitude of the electromagnetic waves. The refractive index and the extinction coefficients are intrisically related, for they are derived from the same physical process. The refractive index and the extinction coefficient are tensors, and expressed as in Equations (3) and (4) below:

$$n_{ii}(\omega) = \sqrt{\frac{|\varepsilon_{ii}(\omega)| + Re\varepsilon_{ii}(\omega)}{2}} \tag{3}$$

and

$$k_{ii}(\omega) = \sqrt{\frac{|\varepsilon_{ii}(\omega)| - Re\varepsilon_{ii}(\omega)}{2}} \tag{4}$$

where $n_{ii}(\omega)$ is the refractive index, and $k_{ii}(\omega)$ is the extinction coefficient.

3.3. Reflectivity and Absorption Coefficient

In optical experiments, $n_{ii}(\omega)$ and $k_{ii}(\omega)$ cannot be measured explicitly. The observables are reflectivity $R_{ii}(\omega)$, and the absorption coefficient $A_{ii}(\omega)$. The absorption coefficient describes how the intensity of light decays. It can be shown in Literature on electromagnetism that these quantities can be expressed as in Equation (5):

$$R_{ii}(\omega) = \frac{(n_{ii}(\omega) - 1)^2 + k_{ii}^2(\omega)}{(n_{ii}(\omega) + 1)^2 + k_{ii}^2(\omega)} \tag{5}$$

and

$$A_{ii}(\omega) = \frac{2\omega k_{ii}(\omega)}{c} \tag{6}$$

4. Computational Methods

To determine the optical properties of LiH, a self-scheme was used by solving the Kohn-Sham equation, employing FP-LAPW method, in the frame work of density theory along with GGA and GGA + U functionals [4] by WIEN2K codes, details of which are discussed in electronic and structural properties, using GGA and GGA + U as exchange correlation potentials [3].

5. Results and Discussion

Absorption Edge for GGA and GGA + U Functional

The calculated complex dielectric function for LiH is depicted in **Figure 1**. The
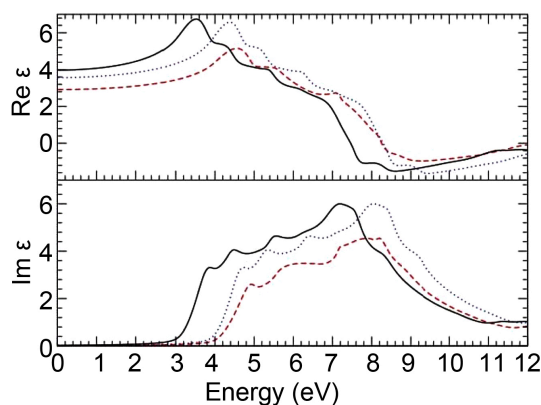
Figure 1. Real and imaginary parts of the dielectric function of LiH.

familiar method in the GGA calculations of scissor operation, shifting the empty conduction bands (imaginary part of the dielectric function) upwards to correspond with the experimental scissor operation was observed [7]. It was recognized that the first absorption edge for GGA and GGA + U match together, albeit, the fine structure at higher energy slightly differ for the improved XC. It was, also, noticed that first absorption peak (transition at point X) was in good agreement with that calculated by [2], which was 9 eV (approximately). The discrepancies noticed at other peaks due to the application of GGA + U.

The imaginary part of the dielectric function obtained in this way depicts the absorption spectra of LiH. The black lines are for the GGA-PBE calculations, where the scissor operation was employed to correct the band gap error of this exchange-correlation functional [8].

6. Conclusion

The dielectric function of Lithium hydride (LiH), which is the underlying quantity relating to its electronic structure, and outlines its optical properties, has been calculated. It was observed that the application of the GGA + U approximation has very simple consequence for the simplicity of the band structure of alkali hydrides.

Conflicts of Interest

The authors declare no conflicts of interest.

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