

Original Article

# Electronic Properties of Uranium Oxide: A Standard DFT and DFT+U Investigation

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**Abstract** - This paper uses the first principle approach to investigate the electronic properties of uranium oxide. First, the structure was optimized, and the converged parameters were used for the rest of the calculations. For this article, the density functional theory as implemented on the quantum espresso code was, the ultrasoft Perdew Burke Erzhendorf (PBE) pseudo potential was used, and the 4.0 eV Hubbard parameter was applied to the 5f orbital of the uranium atom in the bulk uranium oxide. The results show that the Hubbard correction applied to the 5f orbital of uranium accounting for the effect of strong electron-electron correlation has improved the electronic properties of uranium oxide by shifting the 5f of uranium orbital away from the Fermi level and increasing the probability of electronic transition from the valence to the conduction band. Finally, the result suggested that Hubbard corrected uranium oxide, which is the best system to use for future calculations, particularly in applications relating to nuclear fuel.

**Keywords** - Band structure, Density functional theory, Density of state, Hubbard parameter, Quantum espresso.

## 1. Introduction

Uranium oxide (UO<sub>2</sub>) has long been a subject of extensive research due to its critical role in nuclear energy applications [1,2]. Understanding its electronic properties is essential for improving reactor performance, safety, and efficiency [3]. The electronic structure of uranium oxide presents a unique challenge due to the strong electron-electron interactions in its 5f orbitals. Traditional computational methods like Density Functional Theory (DFT) often struggle to accurately describe these interactions, leading to discrepancies between theoretical predictions and experimental observations [4,5]. In recent years, the DFT + U method has emerged as a powerful tool to address the limitations of standard DFT by incorporating a Hubbard U correction [6]. This approach improves the treatment of localized electrons, providing a more accurate description of the electronic structure and properties of materials with strong electron correlation effects, such as uranium oxide. Over the years, researchers have attempted to design better reactor fuel with the aim of improving reactor safety and minimizing fuel meltdown. This has become necessary due to heat generated within the core during the fission reaction. Actually, this work aims to accurately define the electronic properties of this fuel material to avert the effect of fuel meltdown [2,4]. A reactor in a safe working condition must have a fuel material like uranium

oxide that is capable of removing heat generated in the ore to the coolant, and it is, therefore, necessary to use this approach to understand the correct electronic properties for fuel design and optimization of materials like the uranium oxide. Since the effect of the 5f orbital of the uranium is not accounted for in the standard DFT, it is difficult to say that the standard DFT can give reliable results in any calculation involving this material, hence the need for the correction of this effect by incorporating the Hubbard energy in uranium atom.

## 2. Computational Details Methods

This study employed the Quantum ESPRESSO package [7] to investigate the electronic properties of uranium oxide (UO<sub>2</sub>). Density Functional Theory (DFT) calculations were performed utilizing the Perdew-Burke-Ernzerhof (PBE) functional within the Generalized Gradient Approximation (GGA). To account for the strong correlation of uranium's 5f electrons, a limitation of standard DFT, the DFT+U method by Dudarev [8] was applied with a Hubbard U correction of 4.0eV. The material's structure was optimized, and the lowest-energy configuration was selected for subsequent calculations.

## 3. Results and Discussion

The Hubbard U parameter is a critical correction within Density Functional Theory (DFT) for accurately modeling



transition metal-based materials. Standard DFT often underestimates the strong electron-electron interactions in these systems, leading to inaccurate predictions of material properties. By incorporating the Hubbard U, the DFT+U method effectively addresses this limitation [9]. Crucially, the Hubbard U correction significantly impacts the calculated band structure. For instance, it rectifies the tendency of standard DFT to underestimate band gaps, especially in materials with localized d or f electrons. This improvement is essential for accurately predicting insulating or semiconducting behavior, particularly in transition metal oxides where the band gap governs electronic and optical properties [10,11]. Furthermore, the Hubbard U parameter refines the electronic density of states (DOS) by shifting d or f states away from the Fermi level. This correction is crucial for correctly predicting a material's conductive or insulating nature, as standard DFT often misplaces these states [11].

The Hubbard U correction can significantly enhance the accuracy of a material's electronic structure representation, particularly regarding the presence or absence of states at the Fermi level, which is crucial for determining metallic or insulating behavior. The calculations for both standard and Hubbard-corrected uranium oxide indicate a metallic nature, and the correction plays a pivotal role in increasing the probability of electron transitions from the valence to the conduction band. This is evident in the increased Fermi energy from 15.823 eV to 16.345 eV when comparing the standard and Hubbard-corrected systems. This observation aligns with previous findings that standard DFT often underestimates band gaps [12-15]. In the case of uranium dioxide, the Hubbard correction specifically targets the uranium 5f orbitals. The impact of this correction is clearly demonstrated in the Projected Density of States (PDOS) plots (Figures 5 and 6), which reveal a distinct shift of the uranium 5f orbitals away from the Fermi level. Although this shift is less apparent in the total density of states (Figures 3 and 4) due to orbital contributions, the PDOS provides a more accurate depiction of the Hubbard U correction's influence on the electronic structure.

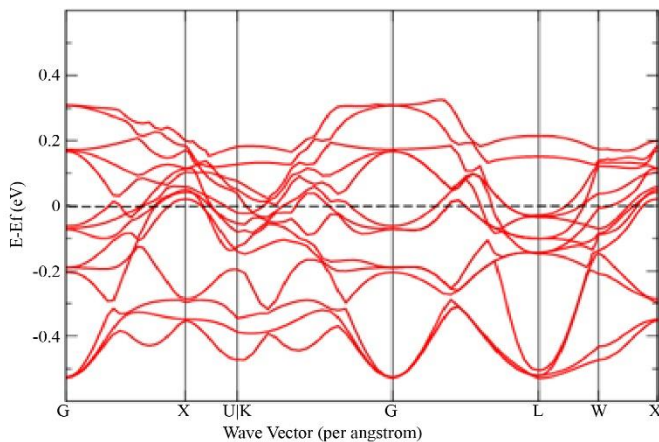


Fig. 1 Band structure for standard DFT

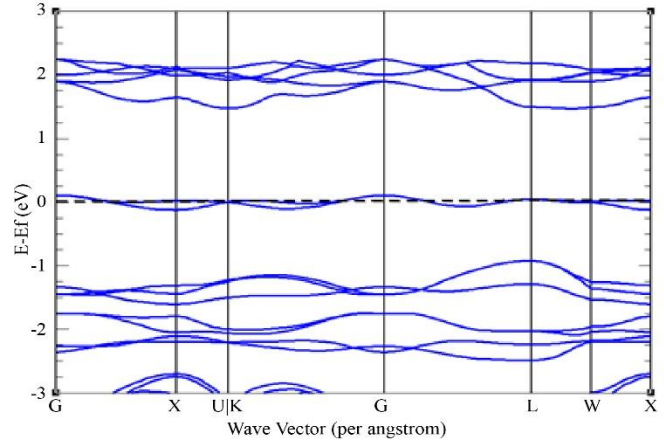


Fig. 2 Band structure for DFT+U

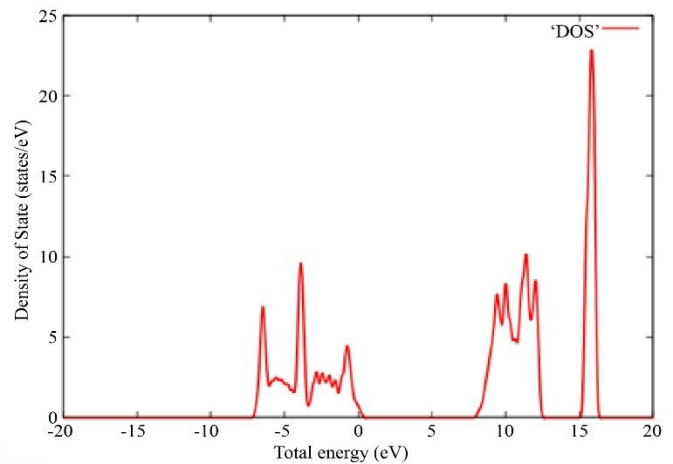


Fig. 3 Density of States for standard DFT

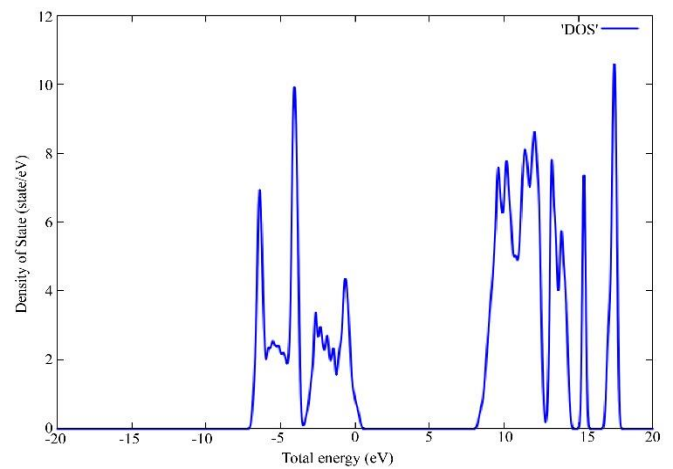


Fig. 4 Density of state for DFT+U

The consequence of this investigation is to clearly identify which of the two methods gives an accurate description of the electronic properties of uranium oxide. It is not a hidden fact that UO<sub>2</sub> is a fuel material in a nuclear reactor. If the proper material is not selected for its optimization, the risk of nuclear accidents may not be avoided.

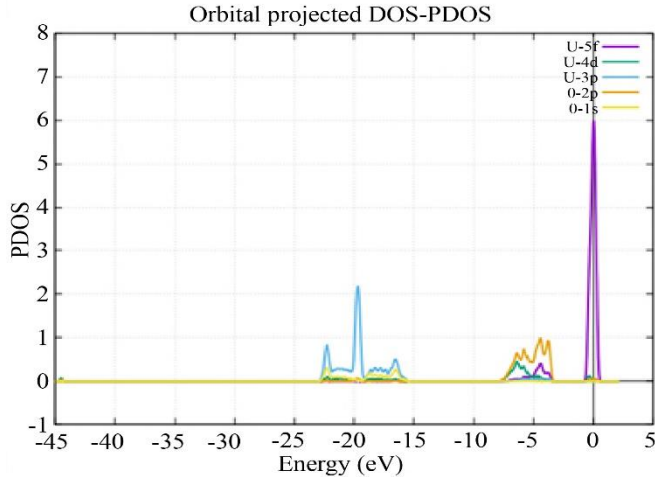


Fig. 5 Projected density of state for standard DFT

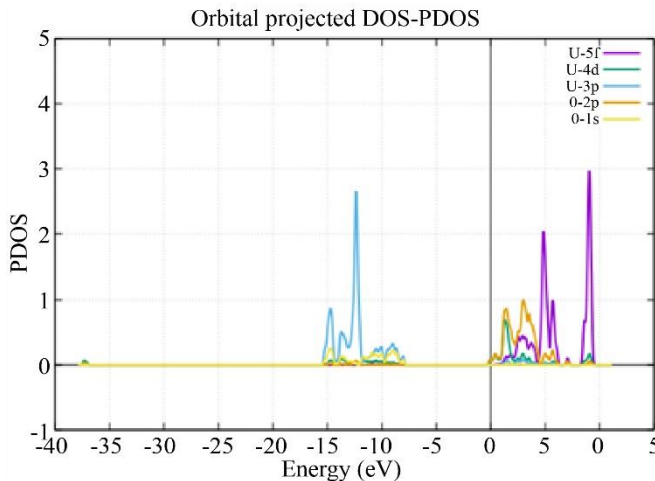


Fig. 6 Projected density of state for DFT+U

Many researchers have focused on optimizing the  $\text{UO}_2$  fuel material through alloying and other means. They used the Hubbard corrected parameter for their results to be consistent with the experiment [16-18], even though their work was too explicit about the electronic properties. However, this present work gives insight into the effect of the Hubbard-corrected parameter on the electronic properties of this fuel material, which may be the reason why a selection of Hubbard-

corrected  $\text{UO}_2$  is essential for fuel materials and thermoelectric applications[19,20].

#### 4. Conclusion

In this study, Density Functional Theory (DFT), as implemented in the Quantum ESPRESSO package, was employed to investigate the electronic properties of uranium oxide ( $\text{UO}_2$ ). This calculation was conducted using both standard DFT and the DFT+U method to account for the strongly correlated nature of the 5f electrons in uranium. The results indicate that the standard DFT approach underestimates the band gap of  $\text{UO}_2$  (though, in this case, the band gaps are zeroes, but the Fermi level shift justifies this argument), leading to inaccuracies in the predicted electronic structure. Conversely, the DFT+U method, with an appropriately chosen Hubbard U parameter, provides a much better approximation of the electronic properties, yielding results that are in closer agreement with experimental data and other theoretical studies.

The improved accuracy of the DFT+U method underscores the importance of including strong correlation effects when studying materials with localized f-electron states, such as uranium oxide. Given the significant role of  $\text{UO}_2$  in nuclear fuel applications, accurately modeling its electronic properties is crucial for understanding its performance and safety under various operating conditions. This study recommends the adoption of the DFT+U approach in future computational studies involving uranium oxide to achieve more reliable predictions of its electronic properties. The incorporation of the U parameter not only enhances the fidelity of electronic structure calculations but also contributes to a better understanding of the material's behavior in nuclear reactors. This improved theoretical framework will aid in the design and optimization of nuclear fuels, ultimately contributing to the development of safer and more efficient nuclear energy technologies.

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