DFT+U Hubbard parameters for Ti and V on anatase supercells

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Introduction

In general, it is well known that the DFT-LDA and DFT-GGA methods underestimates the values of interval between the valence and conduction bands, i.e., gap values obtained by these methods present lower values than the experimental.^{1,2,3}

The LSDA+U, LDA+U approximate methods are alternative to correct the failures of LSDA and LDA methods, in inadequately describing the high correlation and Coulomb electronic interaction between electrons of d and f orbitals in transition metals.

Methodology

All calculations were performed using VASP software (Vienna Ab initio Simulation Package) with version 5.4.1. The DFT method was applied using the Generalized Gradient Approximation (GGA) with the Perdew-Burke-Ernzerhof functional (PBE). This method was corrected with the Hubbard theory (DFT-GGA-PBE+U). The cutoff energy value was 300 eV and the K-points used was 3x3x1. For determination of values of U for titanium and vanadium atoms, we have used the unit cells of titanium dioxide crystal, in the anatase phase, containing 12 atoms. The vanadium (II) pentoxide crystal contains 7 atoms. The calibration range of U term (electronic correlation parameter) used for Ti atom was 0 to 15 eV. For vanadium atom the range was 0 to 9 eV. For the J term (ionic change parameter) it was used the value of J = 0 eV, for all calculations.

Results and Discussion

The results of gap and energy value of bulk for titanium and vanadium atoms in function of U value are described in Figure 1:

Figure 1 – Results of gap and energy of unit cell of crystals TiO₂ and V₂O₅

The value of the gap for $U = 3.2$ eV for the vanadium atom and the value of $U = 13.8$ eV for the titanium atom, reproduced the value of the experimental gap. These values are consistent with other works of the literature that use the Hubbard parameter.

Final Remarks

The calibration of the electron-electron interaction parameter (U , Hubbard parameter) for the Ti and V atoms, using the GGA + U methodology, allowed the correction of the theoretical values of the range of the valence band and the conduction band to values close to those found experimentally. The experimental bulk gap values were used as the benchmarks for the determination of this parameters.

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