DFT+U Study of Simple 3d Transition Metal Oxides to Predict Ground-State Electronic Structure Properties

PH4100

Irfan Khan

Professor K. Refson

1. Motivation

- Density functional theory (DFT) is used to predict a specific material's ground-state properties.

- Experimentally, the simple 3d transition metal oxides are found to be antiferromagnetic insulators at low temperatures.

- DFT within an ansatz (LDA or GGA), fails to predict these metal oxides as a insulating antiferromagnet, but rather as a metallic antiferromagnet.

- DFT+U contains a correction to allow the prediction of the ground-state to be in better agreement with experiment.

Aim 1: Make DFT and DFT+U calculations, as provided by Castep, to make predictions for MnO, FeO, NiO and CuO.

Aim 2: Compare with results from experimental observations and similar first principle studies.

2. Kohn-Sham Approach

The Kohn-Sham formulation of density functional theory solves N one-electron Schrodinger equations self-consistently to find the ground-state density,

$$\sum_i \left\{ -\frac{1}{2}\nabla^2 + V_{eff} \right\} \phi_i = \sum_i \phi_i .$$

The Kohn-Sham states are denoted ϕ_i In Castep, the Kohn-Sham states are projected onto a plane wave basis. The electron density $n(r)$ has the form,

$$n(\mathbf{r}) = \sum_i |\phi(\mathbf{r})|^2 .$$

The equations are found by considering the Kohn-Sham energy functional $E[n]$. The energy functional $E[n]$ consists of functionals corresponding to the Independent kinetic energy term, electron-electron interaction energy, an external potential felt by the electrons and an exchange-correlation energy term.

3. DFT+U Method

The form of the exchange-correlation energy functional is not known, therefore approximations are used. We use the approximations known as LDA (Local Density Approximation) and GGA (Generalised Gradient Approximation). GGA has different implementations known as flavours.

Using LDA or GGA in a DFT calculation for the simple 3d transition metal oxides, underestimates the 3d electron-electron interaction. The corrective Hubbard functional used is based on simplified rotationally invariant LDA+U method [1,2]. It is applied to the d-shell orbital to correct the underestimated Coulomb interaction.

Associated with each Kohn-Sham orbital is an orbital occupation. The orbital occupation matrix is a projection of Kohn-Sham states onto a particular orthonormal atomic basis. The orbital occupancy matrices are defined

$$n_{mm'}^{\sigma} = \sum_i \langle \phi_i^{\sigma} | P_{mm'} | \phi_i^{\sigma} \rangle$$

where the σ is the spin, m is the orbital in the 3d-shell and ϕ_i is i^{th} Kohn-Sham orbital. $P_{mm'}$ is the projector onto an orthonormal atomic basis [2].

The DFT+U energy functional has the form,

$$E_{DFT+U}[\rho] = E_{DFT}[\rho] + \frac{U}{2}\sum_{I,\sigma} \mathbf{Tr}[n^{I\sigma}(1-n^{I\sigma})] .$$

where the second term is the correction applied. The term $n^{I\sigma}$ is the total orbital occupancy of the d shell with spin σ. I denotes the lattice site and ρ is now the ground-state electron density.

The correction is a penalty function:

- If the d orbital occupancy is fractional, the Hubbard correction is used.
- If the d orbital occupancy is 0 or 1, no correction is applied.

4. Anti-Ferromagnetic Type-II Ordering

The simple 3d transition metal oxides below the neel temperature have a rock-salt unit cell with antiferromagnetic (AFM) ordering of type-II. AFM type-II ordering are [111] planes containing ions with parallel spin, and nearest neighbouring [111] planes containing ions with anti-parallel spins, as shown in Figure 1a.
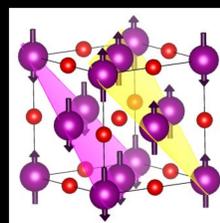

Figure 1a: Rock-Salt unit cell with AFM type-II order. Purple spheres are Ni ions and red spheres are O ions. Arrows represent direction of spin [3].
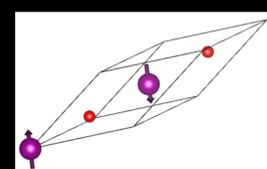

Figure 1b: Antiferromagnetic unit cell obtained from figure 1a by defining lattice vectors from one Mn ion on a ferromagnetic plane to Mn ions on the next ferromagnetic plane [3].

Figure 1b shows the rhombohedral antiferromagnetic unit cell obtained from figure 1a, which preserves discrete translational symmetry. The new unit cell has space group $r3/m$.
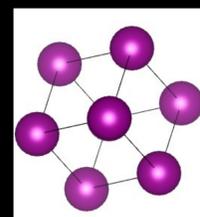

Figure 1c: The 3-fold rotation axis of the rhombohedral unit cell shown in figure 1b. The [111] direction goes into the page [3].
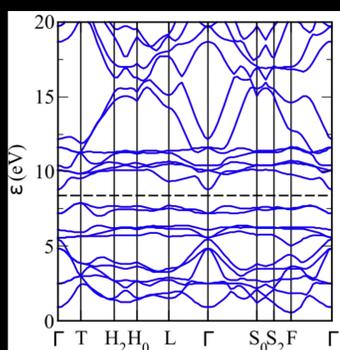
5. DFT Study of MnO

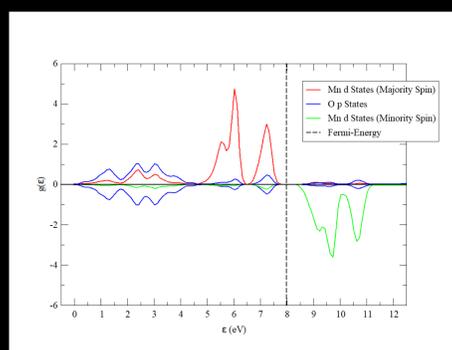Figure 2a: Band-structure plot calculated and visualised using Castep.

Figure 2b: Projected density of states calculated and visualised using Castep and Optados.

For our DFT calculations, the PBE flavour of GGA is used as the exchange-correlation functional. Initially, the unit cell is geometry optimized,. We then perform band-structure calculations on the optimized unit cell. The MnO crystal is predicted to be antiferromagnetic, and the Mn ion has a magnetic moment of $4.67\mu_b$, compared to the experimental value of $4.58\mu_b$. Figures 2a and 2b show that there is a small band-gap of width 0.5eV approximately. The experimentally observed band-gap is 3.6eV — 3.9eV.

The Mn 3d shell is spin-polarized and contains 5 electrons. The projected density of states, in figure 2b, shows the greatest contribution to the valence band are from occupied d states lying below the Fermi-Energy,. The unoccupied d states lie above the Fermi energy. The small band-gap is due to d-d electron interaction.
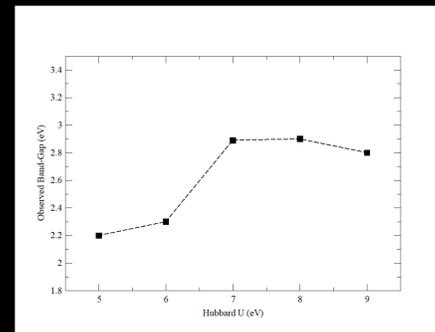
6. DFT+U Study of MnO

Figure 3a: A graph showing the effect of changing the value of the Hubbard U in the width of the observed band-gap in a density of states plot.

The value of Hubbard U parameter determines the width of the band-gap that opens in the DFT+U density of states plot. We vary the Hubbard U by integer increments to find the band-gap closest to the experimental value. Figure 3a shows the observed band-gap width in a projected density of states plot for a particular value of U.
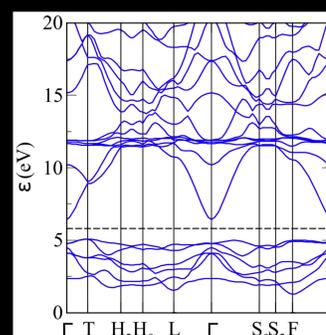

Figure 3b: DFT+U band-structure plot for MnO calculated and visualized using Castep.
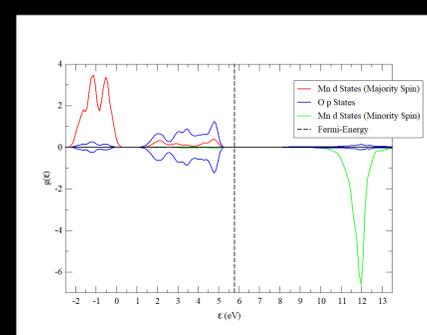

Figure 3c: DFT+U projected density of states plot for MnO calculated and visualized using Castep and Optados.

Again the PBE flavour of GGA is used for exchange-correlation functional. The application of the Hubbard U functional now opens a band gap of width 2.9 eV for U=8eV. The DFT+U projected density of states, in figure 3c, now shows the valence band contains O p states and Mn $3d$ states. Compared to figure 2b, the occupied majority-spin d states have decreased in energy and the unoccupied minority-spin d states have increased in energy. Within the region 1eV to 5eV, there is some mixing between the O p states and Mn d states. The DFT+U band-structure plot shows some overlap between the dispersive bands containing the O p states and the Mn bands containing the d states. The DFT+U calculated band-structure is characteristic of a charge-transfer type insulator.

7. Conclusion

- The DFT+U method was able to increase the band-gap in MnO, FeO, and NiO to values close to the experimental value. However, for MnO and NiO, the value was still underestimated.

- The elongation of the FeO^6 octahedral complex was eledicted for a monoclinic unit cell.

- The band-gap could not be opened for CuO with a rhombohedral unit cell when using DFT+U. CuO does not have a rhombohedral unit cell, but rather a monoclinic unit cell at low temperatures, and this may be a possible reason for the DFT+U method failing.

[1] S. L. Dudarev, G. A. Botton, S. Y. Savrasov, C. J. Humphreys, and A. P. Sutton, Phys. Rev. B 57, 1505 (1998).

[2] M. Cococcioni and S. de Gironcoli, Phys. Rev. B 71, 035105 (2005).

[3] Diagrams produced using Vesta.