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Electronic structure of NiO with DFT+U

Version: 2017

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ATK Reference Manual
Basic QuantumATK Tutorial

By tuning the empirical Hubbard parameter U, one can sometimes obtain the correct band gap for semiconductors even with LDA or GGA. This tutorial shows how to approach this type of calculations by taking NiO as an example, and at the same time it also introduces the density of states (DOS) functionality in QuantumATK.

Introduction

The self-interaction error is probably the most serious drawback of the LDA and GGA approximations to the exchange-correlation energy. This self-interaction can be described as the spurious interaction of an electron with itself. It has two main consequences:

- Electrons are over-delocalized;
- Band gaps in semiconductors and insulators are predicted to be much lower than their real counterpart.

The mean-field Hubbard correction, popularly called DFT+U, is a semi-empirical correction which tries to improve on these deficiencies.

In the DFT+U an additional energy term,

$$E_U = \frac{1}{2} \sum_{\mu} U_{\mu} \left(n_{\mu} - n_{\mu}^2 \right) ,$$

is added to the Exchange-correlation energy [1]. In this equation,
n_{μ} is the projection onto an atomic shell and
U_{μ} is the value of the "*Hubbard U*" for that shell. The
E_U energy term is zero for a fully occupied or unoccupied shell, while positive for a fractionally occupied shell.

The energy is thereby lowered if states become fully occupied. This may happen if the energy levels move away from the Fermi Level, i.e. increasing the band gap, or if the broadening of the states is decreased, i.e. the electrons are localized. In this way, the Hubbard U improves on the deficiencies of LDA and GGA.

The NiO crystal has a too low band gap in LDA and GGA and is one of the standard examples of how the DFT+U approximation can be used to improve the description of the electronic structure of solids [2]. In this tutorial you will compare the DFT and DFT+U models for this system using the GGA.

Further details of the Hubbard U implementation in QuantumATK can be found in the ATK Reference Manual, particularly the section XC+U mean-field Hubbard term.

The electronic structure of NiO calculated with DFT

NiO has a fcc crystal structure with two atoms in the unit cell. The Ni atoms have a net magnetic moment and form an anti-ferromagnetic arrangement in the (111) direction of the fcc cell. The structure can be described by a rhombohedral unit cell with 4 atoms in the basis [1]. The structure is given below in the QuantumATK ATK-Python format:

```
# Set up lattice
lattice = Rhombohedral(5.138*Angstrom, 33.5573*Degrees)

# Define elements
elements = [Nickel, Oxygen, Nickel, Oxygen]

# Define coordinates
fractional_coordinates = [[ 0.  ,  0.  ,  0.  ],
                          [ 0.25,  0.25,  0.25],
                          [ 0.5 ,  0.5 ,  0.5 ],
                          [ 0.75,  0.75,  0.75]]

# Set up configuration
bulk_configuration = BulkConfiguration(
    bravais_lattice=lattice,
    elements=elements,
    fractional_coordinates=fractional_coordinates
    )
```

Copy the script and save it as `NiO.py`, or download it directly: NiO.py.

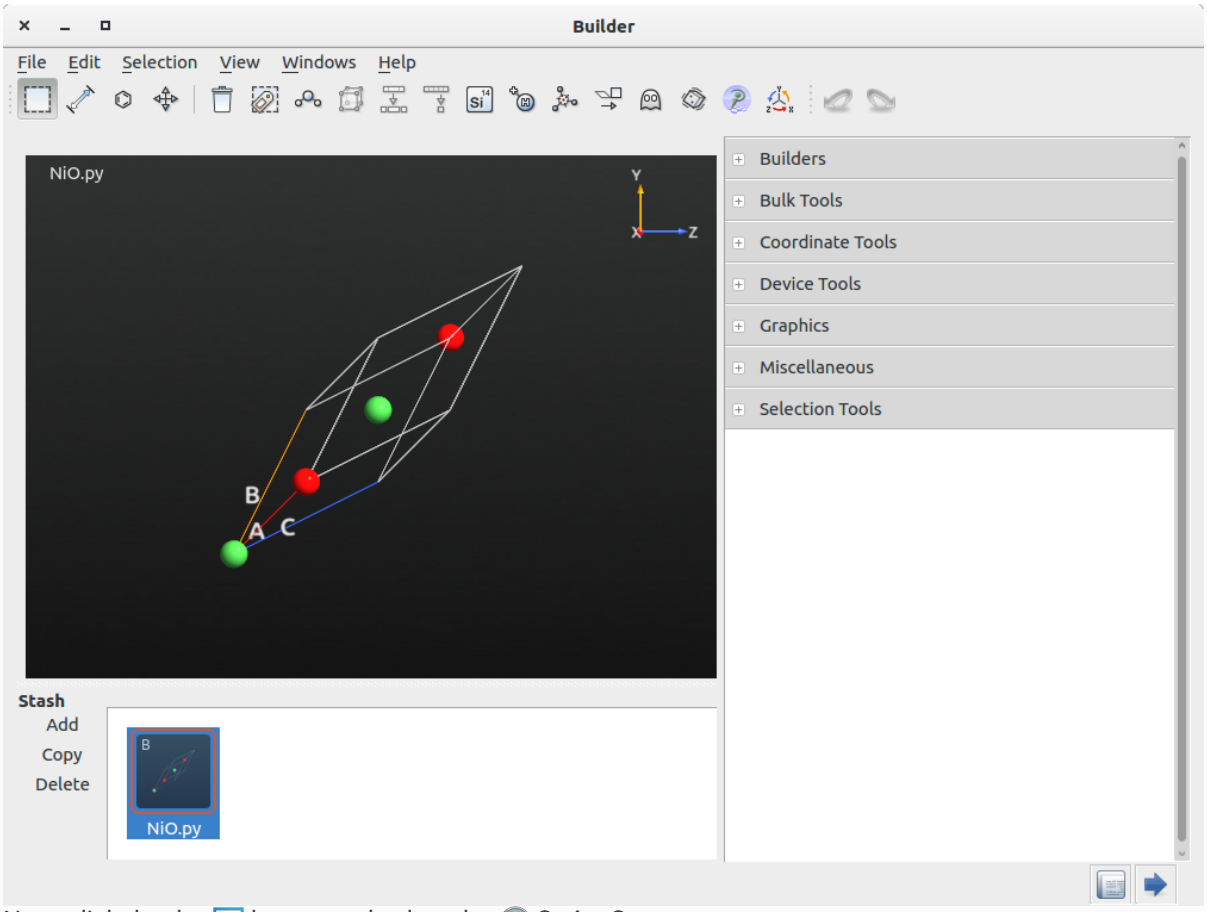
Note

The rhombohedral unit cell vectors are given as
$(1, \frac{1}{2}, \frac{1}{2})a$, where
a is the fcc lattice constant. The length of the rhombohedral unit cell vectors are therefore given by $\sqrt{\frac{3}{2}}a$, and are in accordance with the experimental fcc lattice constant of 4.19 Å.

Setting up the calculation

You will in this section set up a spin-polarized DFT calculation using the spin-polarized version of the generalized gradient approximation (SGGA) for the NiO electronic structure and calculate the Mulliken population and density of states. If you are not familiar with the workflow of QuantumATK you are recommended to first go through the Basic QuantumATK Tutorial.

Start up QuantumATK and drag the script NiO.py onto the **Builder**. The NiO crystal will be added to the Stash.



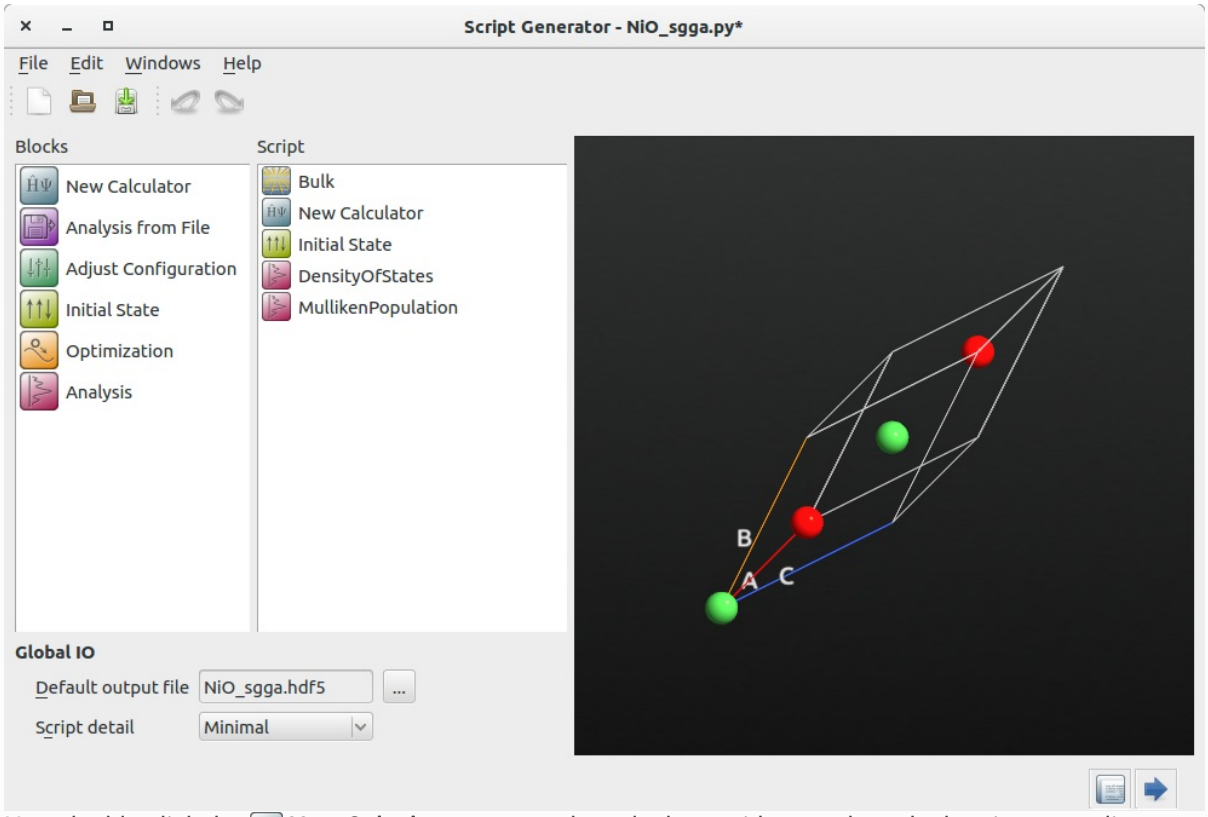
Next, click the the button and select the **Script Generator**.

Tip

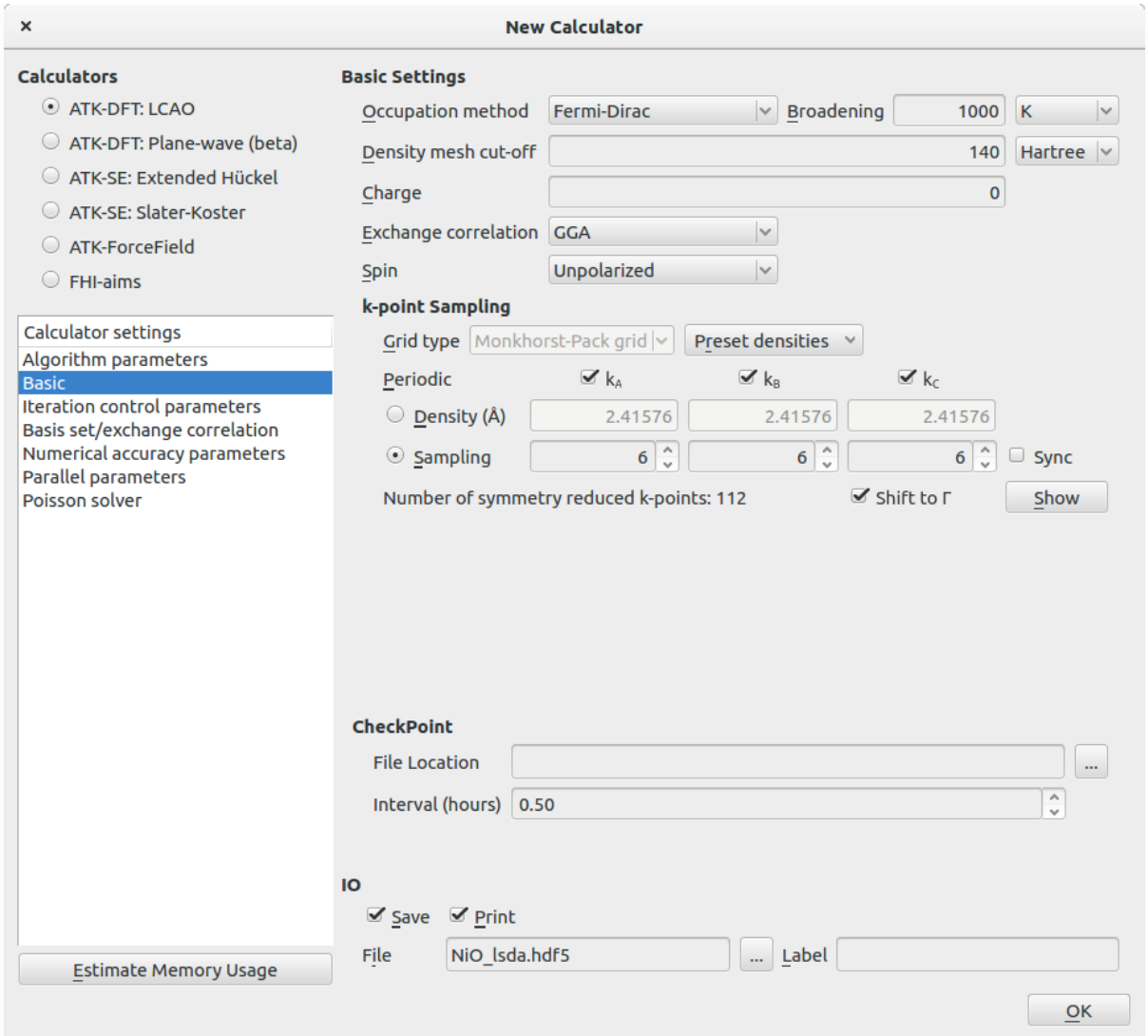
Alternatively you can drag the script NiO.py directly onto the **Scripter** from the QuantumATK Project Files list.

Change the default output file name to `NiO_sgga.hdf5` and add the following blocks to the script:

- New Calculator
- Initial State
- Analysis ▸ DensityOfStates
- Analysis ▸ MullikenPopulation



Now double-click the **New Calculator** to open the calculator widget, and set the k-points sampling to 6x6x6.

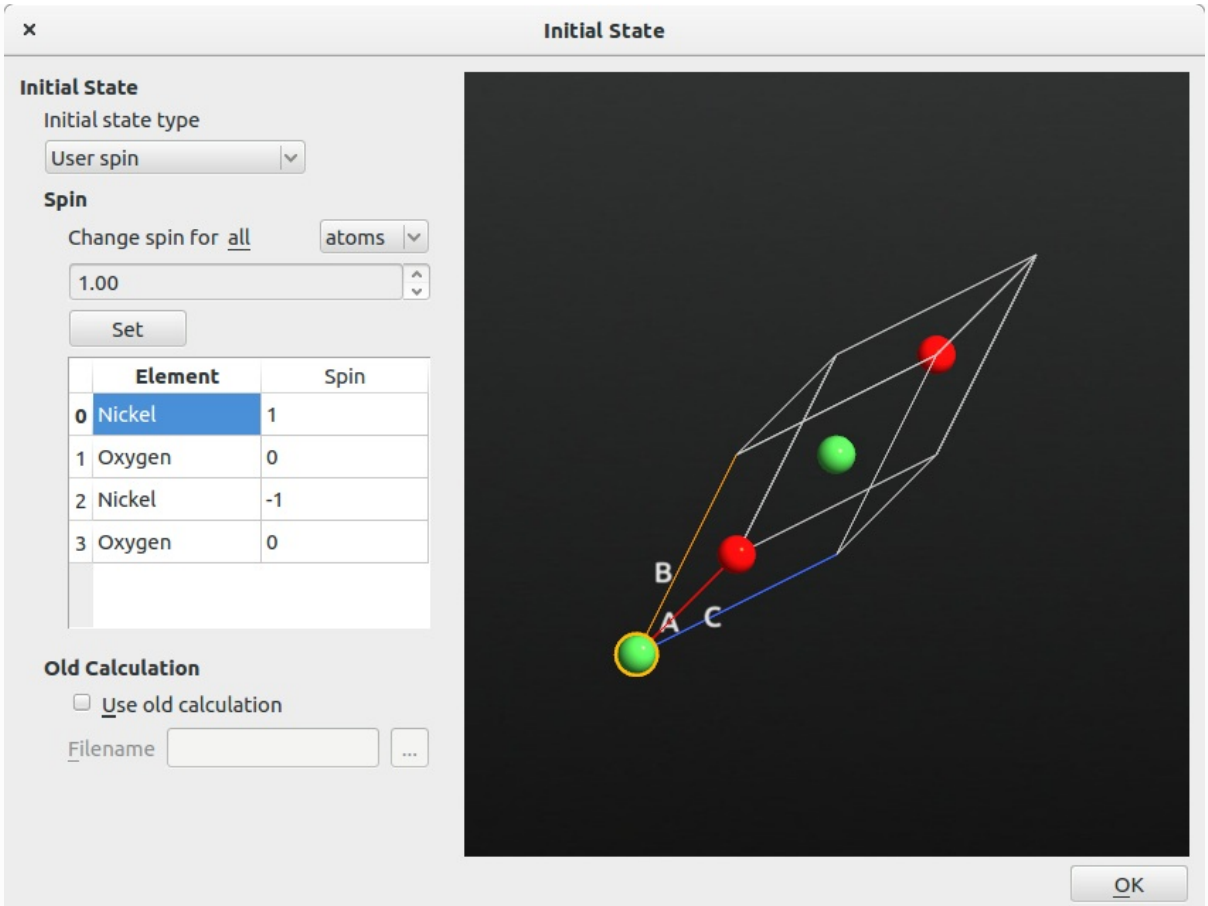


Note

When an even sampling grid is used, the grid is automatically shifted to make sure that the Γ-point is included. The automatic shift can be avoided by unticking the option "*Shift to Γ*".

The next step is to set up the anti-ferromagnetic NiO spin arrangement. For this purpose, open the **Initial State** block.

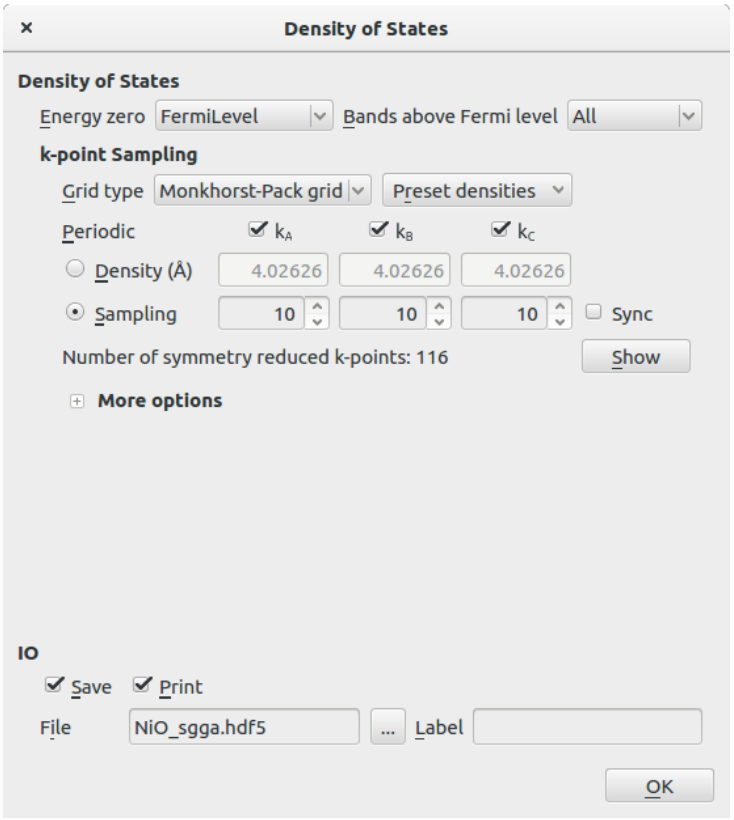
Select *User spin* – this will allow you to individually set the spin on each atom. Set opposite spins on the two nickel atoms and no spin on the oxygen atoms as illustrated below.



Important

The initial spin on each atom is given relative to the atomic spin of the element as obtained by Hund's rule. For nickel the electronic configuration of the atom is $[Ar]3d^8 4s^2$ (see periodic table in the ATK Reference Manual.). The 3d shell is fractionally occupied, and only this shell will contribute to the spin of the atom. According to Hund's rule the 3d shell has 5 electrons in the up direction and 3 electrons in the down direction, giving a total atomic spin of 2 μ_B for nickel.

Finally, open the **DensityOfStates** block and set the k-points sampling to 10x10x10. In general, one should choose a quite dense k-points grid for DOS analyses, in order to capture possible sharp features in the density of states.



Save the script as `NiO_sgga.py`, but do not close the Scripter window – you will need it again later.

Performing the calculation

To start the calculations, send the script to the **Job Manager** by using the button.

Choose a *Local* machine for executing the job and click start. The job will finish after 1-2 minutes and you can inspect the results.

Analysing the results

Mulliken Population

To inspect the Mulliken population reported in the calculation log file, scroll down to the end of the log file and you will find a report as shown below.

```
+-------------------------------------------------------------------------+
|                                                                         |
| Mulliken Population Report                                              |
|                                                                         |
| ----------------------------------------------------------------------- |
|                       |                                                 |
| Element   Total  Shell | Orbitals                                       |
|                       |                                                 |
|                       |      s                                          |
|   0  Ni   9.244  0.994 |  0.994                                         |
|           7.892  0.994 |  0.994                                         |
|                       |      y      z      x                            |
|                 2.997 |  0.999  0.999  0.999                           |
|                 2.996 |  0.999  0.999  0.999                           |
|                       |      s                                          |
|                 0.127 |  0.127                                         |
|                 0.127 |  0.127                                         |
|                       |     xy     zy  zz-rr     zx  xx-yy             |
|                 4.887 |  0.986  0.986  0.964  0.986  0.964             |
|                 3.533 |  0.980  0.980  0.297  0.980  0.297             |
|                       |      y      z      x                            |
|                 0.042 |  0.014  0.014  0.014                           |
|                 0.044 |  0.015  0.015  0.015                           |
|                       |     xy     zy  zz-rr     zx  xx-yy             |
|                 0.056 |  0.007  0.007  0.018  0.007  0.018             |
|                 0.053 |  0.007  0.007  0.016  0.007  0.016             |
|                       |      y      z      x                            |
|                 0.140 |  0.047  0.047  0.047                           |
|                 0.145 |  0.048  0.048  0.048                           |
|                       | ----------------------------------------------- |
```

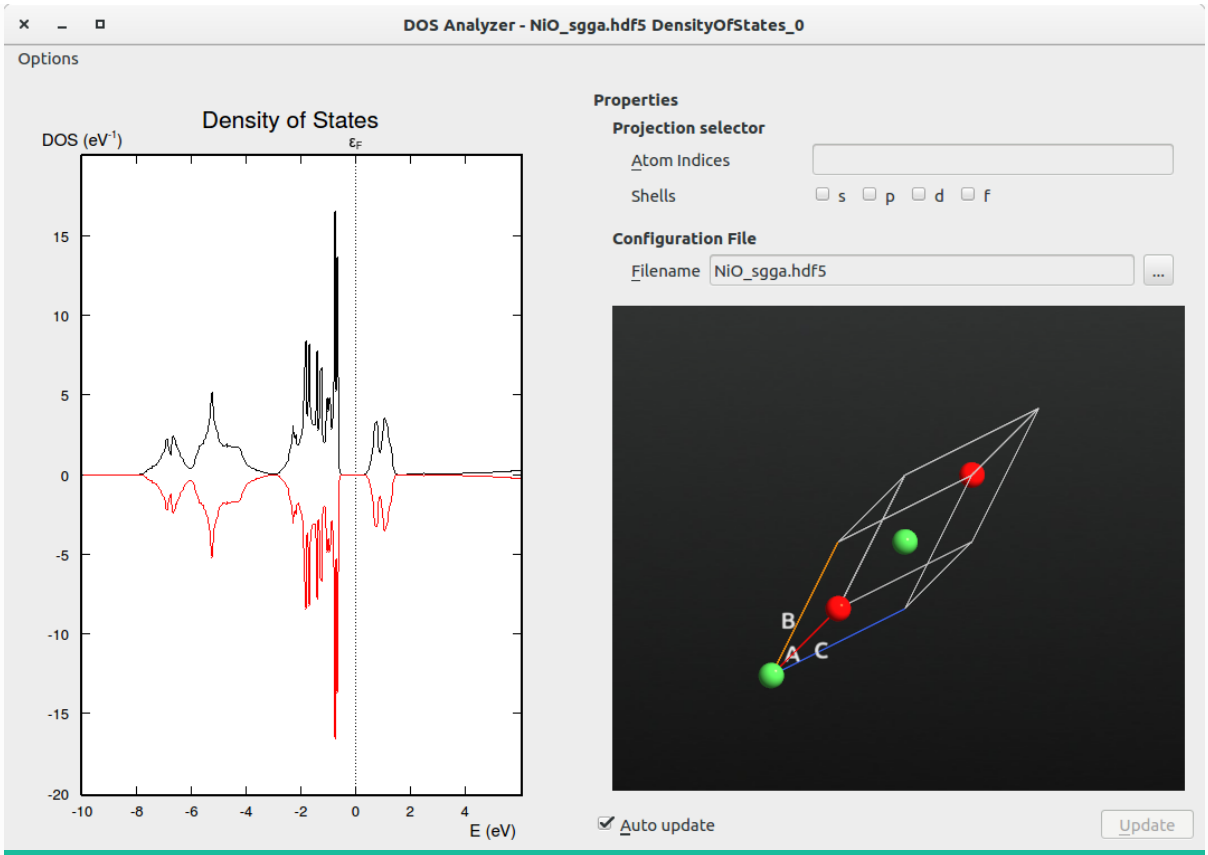
Tip

The Mulliken population can also be inspected by selecting the $\mathrm{Tr}(\rho\mathbf{S})$ Mulliken Population item on the QuantumATK LabFloor. Use the **Text Representation** tool in the right-hand panel to see the results.

The Mulliken population reports the numbers of electrons per spin and orbital, as well as the orbital sum for each atom. Note that oxygen atoms are not polarized while the two nickel atoms are polarized in opposite directions, thus forming an anti-ferromagnetic arrangement. The polarization can be calculated from the difference between the number of electrons in the spin-up channel (9.244) and that in the spin-down channel (7.892). The resulting value of 1.35 μ_B is in good agreement with other DFT calculations [1].

Projected density of states

To investigate the NiO density of states (PDOS), select the $D(\epsilon)$ **DensityOfStates** item on the LabFloor, click the **2D Plot** tool in the right-hand panel. You may need to zoom in a little on the plot; use the left mouse button for this.

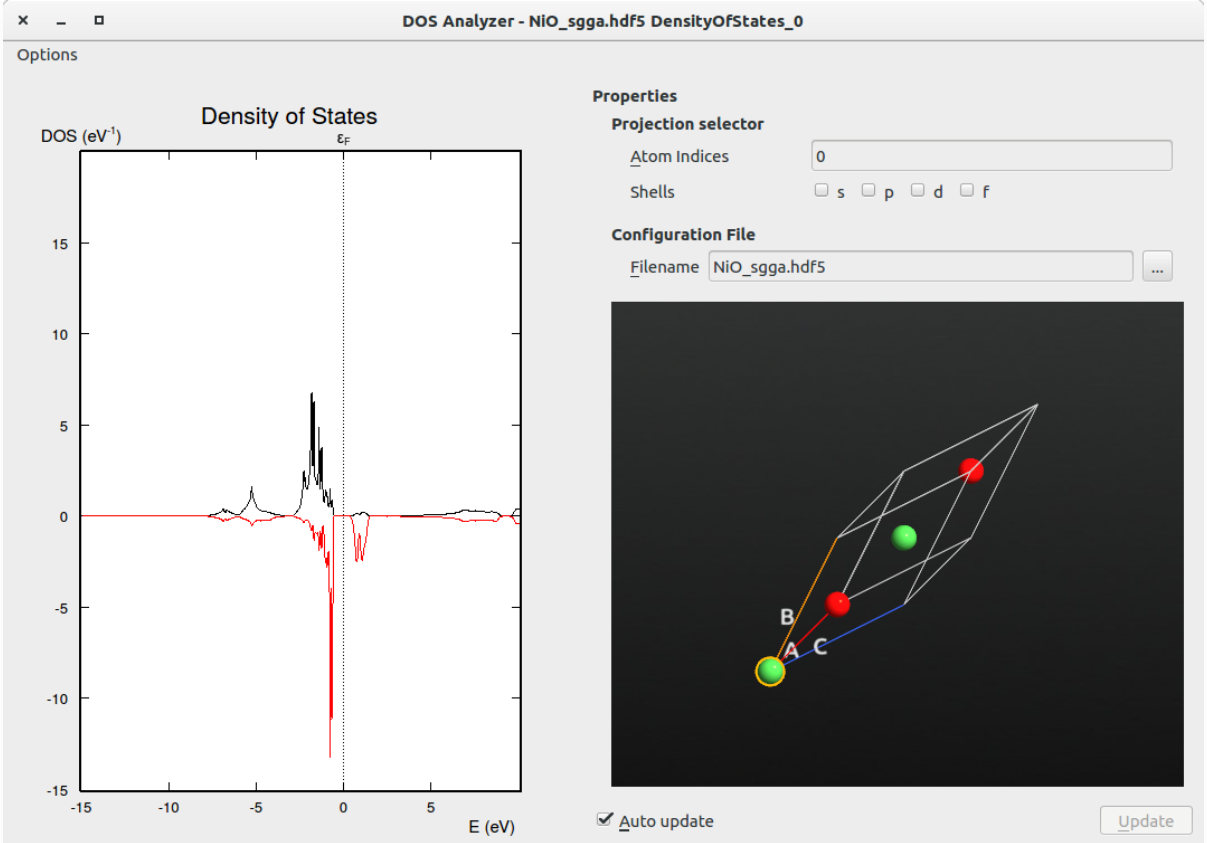


Tip

The plot shows the total density of states of the spin-up channel with a black line and minus the result for the spin-down channel with a red line. If you de-select Flip spin-down in the Options menu, the density of states of the spin-down channel will also be plotted on the positive axis.

The total DOS shows no difference between the two spin channels. However, you saw from the Mulliken population that the nickel atoms are spin polarized!

To inspect the projected DOS corresponding to just one nickel atom, select a nickel atom with the left-hand button of the mouse, as illustrated below.



The PDOS is simply the total DOS projected onto the selected nickel atom. The expected difference between the spin-up and spin-down DOS channels is now apparent.

Tip

You can also create combined projections by selecting multiple atoms (use the left-hand button of the mouse while holding `Ctrl`) and more than one shell.

The calculation predicts a band gap of ~0.8 eV, which is much smaller than the experimental value of 4.0 eV [3]. In the next chapter you will see how the description of the band gap is improved with the DFT+U approximation.

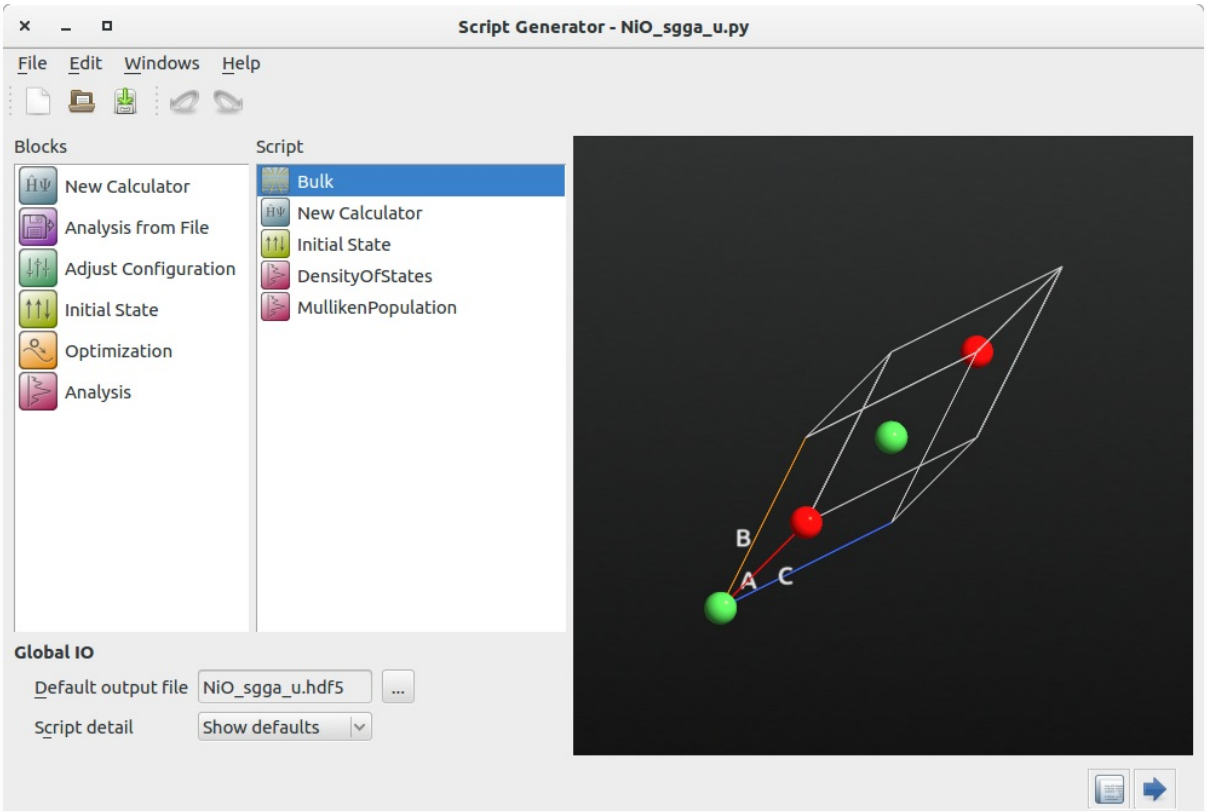
DFT+U calculation for the NiO crystal

You will now perform a DFT+U calculation of the NiO crystal, using U = 4.6 eV for the nickel *d*-states, as proposed in [1].

Calculations

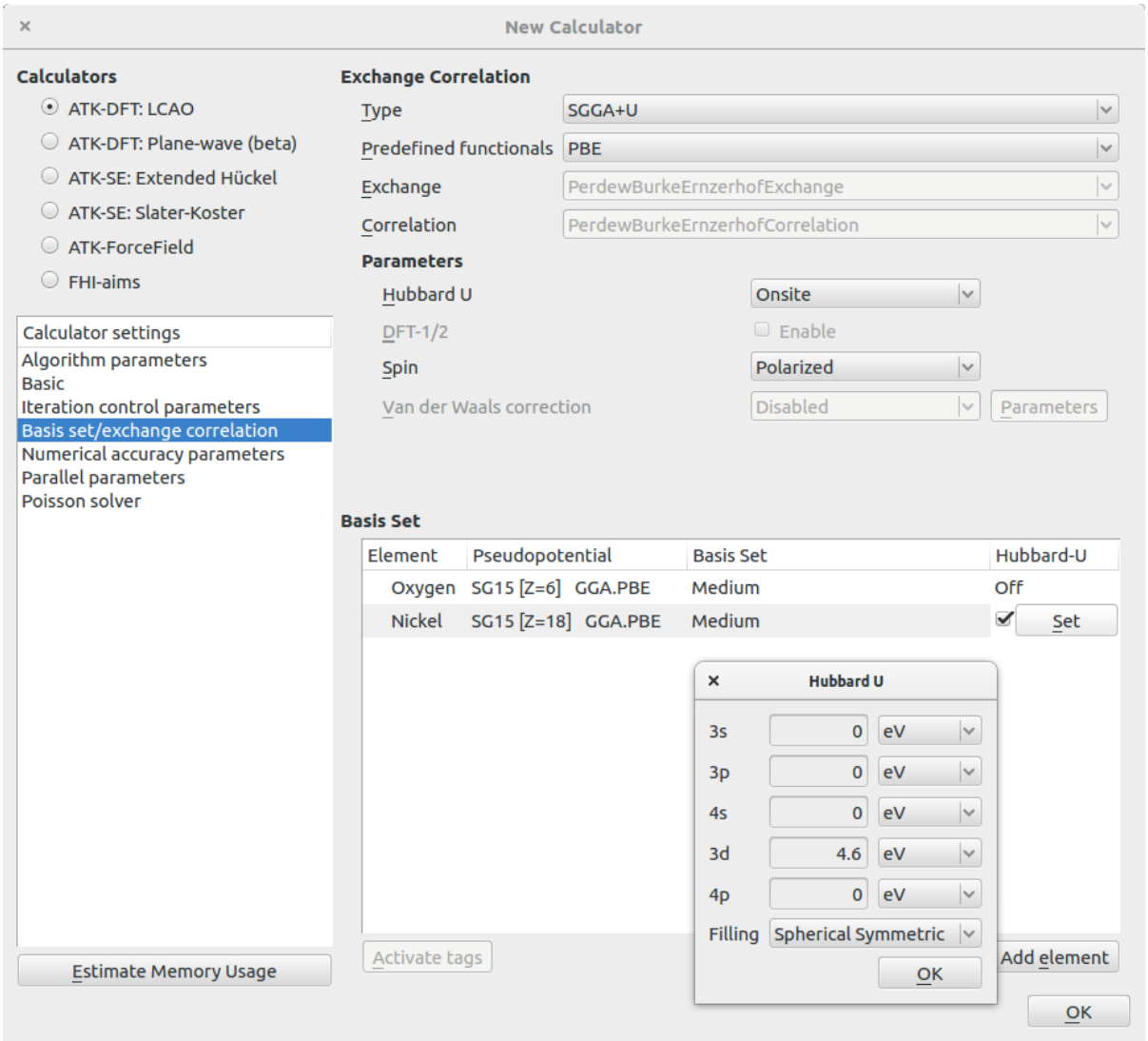
You will need to modify the script generated above for the SGGA calculation. Open the **Scripter** used in the previous chapter and make the following modifications:

- Change the default output file name to `NiO_sgga_u.nc`.
- Change the **Script detail** to *Show defaults*.



Open the **New Calculator**:

- Switch to the **Basis set/exchange correlation** tab.
- Change the option **Hubbard U** from *Disabled* to *Onsite*.
- In the **Basis set** section, click **Set** in the column on the right-hand side on the row corresponding to nickel, and set the Hubbard U parameter for the 3d orbital to 4.6 eV.



Next transfer the script to the **Editor** using the send to button, in order to check that all the parameters are properly set.

In the editor locate the line where the nickel basis is defined and check that the hubbard U parameter is set to 4.6 eV for the `nickel_3d` and `nickel_3d_0` orbitals.

```
190 NickelBasis = BasisSet(
191     element=PeriodicTable.Nickel,
192     orbitals=[nickel_3s, nickel_3p, nickel_4s, nickel_3d, nickel_3p_0, nickel_3d_0, nickel_4p],
193     occupations=[2.0, 6.0, 0.0, 8.0, 1.0, 1.0, 0.0],
194     hubbard_u=[0.0, 0.0, 0.0, 4.6, 0.0, 4.6, 0.0]*eV,
195     dft_half_parameters=Automatic,
196     filling_method=SphericalSymmetric,
197     onsite_spin_orbit_split=[0.0, 0.0, 0.0, 0.0, 0.0, 0.0, 0.0]*eV,
198     pseudopotential=NormConservingPseudoPotential("normconserving/sg15/gga/28_Ni.upf"),
199     )
```

Now save the script as `NiO_sgga_u.py` and execute the job using the **Job Manager**.

Analyzing the results

First inspect the Mulliken population in the log file. You should find a magnetic moment of 1.80 μ_B on a nickel atom, which is in good agreement with the experimental result of 1.64 – 1.9 μ_B [3].

To determine the band gap, inspect the printed density of states in the log file. You should find that the

DOS is zero in the range -1.69 to 1.69 eV, corresponding to a band gap of 3.38 eV. This is much higher than the SGGA value of 0.8 eV, and in better agreement with the experimental value of 4.0 eV [3].

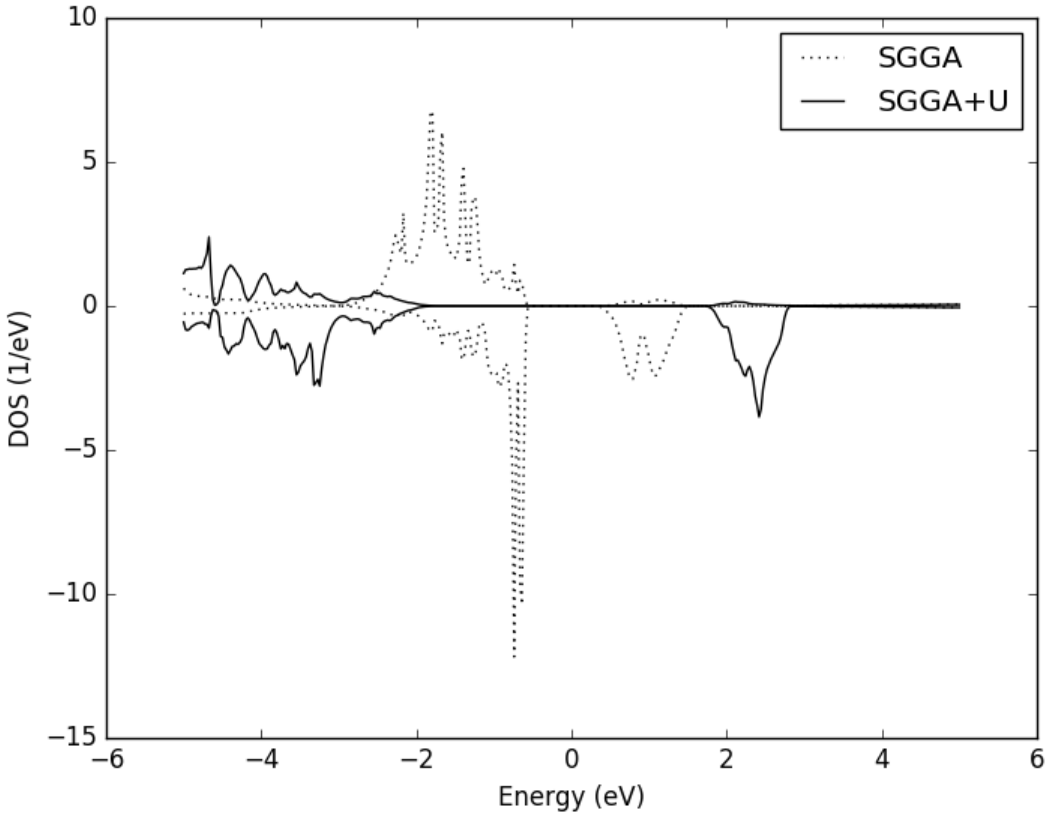
Comparing the DFT and DFT+U projected DOS

The final step is to compare the nickel PDOS obtained with DFT and DFT+U. You will here use Python scripting to perform the analysis.

The script dos-comparision.py performs the analysis. It is shown below:

```
#read in the dos object
dos = nlread('NiO_sgga.hdf5',DensityOfStates)[0]
#generate some energies
energies = numpy.linspace(-5,5,400)*eV
#calculate the spectrum
n0_up = dos.tetrahedronSpectrum(energies=energies,
                                spin=Spin.Up,
                                projection_list = ProjectionList([0]))

n0_down = dos.tetrahedronSpectrum(energies=energies,
                                  spin=Spin.Down,
                                  projection_list = ProjectionList([0]))
e = dos.energies()

#do the same for GGA+U
dos_u = nlread('NiO_sgga_u.hdf5',DensityOfStates)[0]
n0_up_u = dos_u.tetrahedronSpectrum(energies=energies,
                                    spin=Spin.Up,
                                    projection_list = ProjectionList([0]))

n0_down_u = dos_u.tetrahedronSpectrum(energies=energies,
                                      spin=Spin.Down,
                                    projection_list = ProjectionList([0]))

#plot the spectrum using pylab
import pylab
#first plot the up component with dots
pylab.plot(e.inUnitsOf(eV), n0_up.inUnitsOf(eV**-1), 'k:',label = 'SGGA')
#now plot the down component with negative values and dots
pylab.plot(e.inUnitsOf(eV), -1.*n0_down.inUnitsOf(eV**-1), 'k:')
#now plot the GGA+U up  components with solid
pylab.plot(e.inUnitsOf(eV), n0_up_u.inUnitsOf(eV**-1),'k',label = 'SGGA+U')
#now plot the  GGA+U down component with negative values and solid
pylab.plot(e.inUnitsOf(eV), -1.*n0_down_u.inUnitsOf(eV**-1),'k')
#show legends
pylab.legend()
pylab.xlabel("Energy (eV)")
pylab.ylabel("DOS (1/eV)")
pylab.show()
```

Download the script and execute it using the **Job Manager**. The following plot is produced, illustrating the projected DOS for the nickel atom obtained using SGGA and SGGA+U. Notice the large difference in band gap between the two calculations (region of zero DOS around the Fermi level, at 0 eV energy).



Note

The plotting is based on the matplotlib package which is part of QuantumATK, see Plotting using pylab for more information.

References

[1] (1,2,3,4)
M. Cococcioni and S. de Gironcoli. Linear response approach to the calculation of the effective interaction parameters in the LDA+U method. *Phys. Rev. B*, 71:035105, Jan 2005. doi:10.1103/PhysRevB.71.035105.

[2]
A. B. Shick, A. I. Liechtenstein, and W. E. Pickett. Implementation of the LDA+U method using the full-potential linearized augmented plane-wave basis. *Phys. Rev. B*, 60:10763–10769, Oct 1999. doi:10.1103/PhysRevB.60.10763.

[3] (1,2,3)
Vladimir I Anisimov, F Aryasetiawan, and A I Lichtenstein. First-principles calculations of the electronic structure and spectra of strongly correlated systems: the lda + u method. *Journal of Physics: Condensed Matter*, 9(4):767, 1997. doi:10.1088/0953-8984/9/4/002.

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