

Electronic structure of NiO with LDA+U

Tutorial on how to use LDA+U for bulk systems

Version 12.2.0

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CHAPTER 1. INTRODUCTION

The LDA and GGA approximations to the exchange-correlation energy has a number of shortcomings, where the most important are

- Self interaction, an electron interacts with itself and this prevents electrons from localizing.
- Poor approximation for excited states, band gaps are often too low.

The mean field Hubbard correction, popularly called LDA+U or XC+U, is a semi-empirical correction which tries to improve on these deficiencies of the LDA and GGA functionals.

In the XC+U an additional energy term,

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

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 "Hubbard U" for that shell. The E_U energy term is zero for a fully occupied or un-occupied shell, while positive for a fractional 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. Thus, the Hubbard U improves on the deficiencies of the exchange-correlation energies.

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

Further details of the Hubbard U implementation in ATK can be found in the [ATK reference manual](#).

CHAPTER 2. THE ELECTRONIC STRUCTURE OF NiO CALCULATED WITH LSDA

THE NiO CRYSTAL STRUCTURE

The NiO has a fcc crystal structure with two atoms in the unit cell. The Ni atoms spin polarize 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 in the ATK format below

```
# 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
)
```




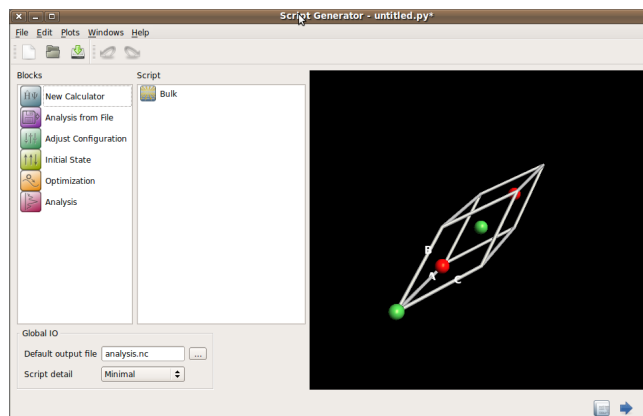
Note

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 setup a Spinpolarized DFT calculation using the Local Spin Density Approximation(LSDA) for the NiO crystal and calculate the Mulliken population and density of states. You will use VNL for the calculation, and it is recommended that you take the VNL tutorial to be familiar with the work flow of VNL.

Start up VNL and select the text in the `nio2.py` script above and drag it onto the Script-generator tool . The tool will interpret the script and open up with the imported geometry



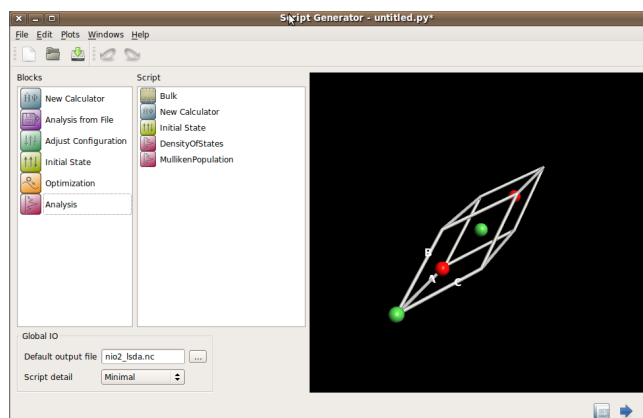
i Tip

Alternatively you can save the script to a file and drag and drop the file to the Script Generator from the VNL result browser

Next do the following steps:

- Change the Default output file to `nio2_1sda.nc`.
- **left** double-click **New Calculator**.
- **left** double-click **Initial State**.
- **left** double-click **Analysis** and select **DensityOfStates**.
- **left** double-click **Analysis** and select **MullikenPopulation**.

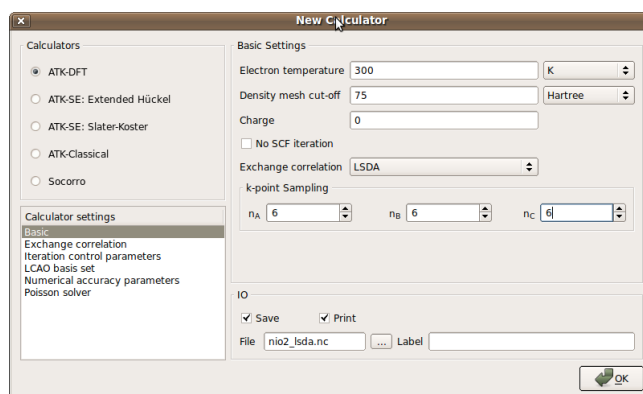
The Script-generator tool should now have the following settings



ADJUSTING THE SCRIPT COMPONENTS

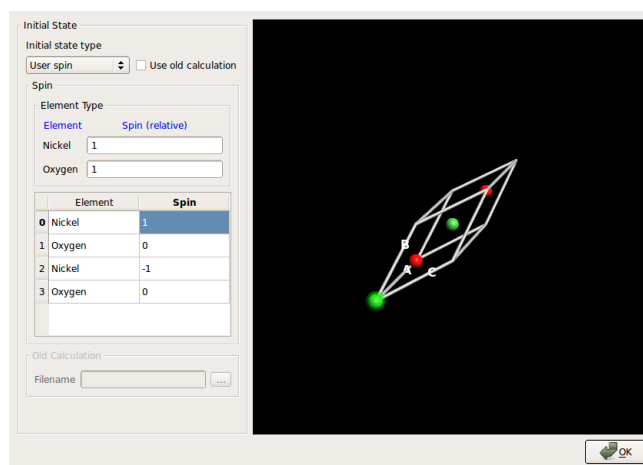
Now **left** double-click the “ New Calculator ” block to open the calculator widget.

Select a 6x6x6 k-point sampling and LSDA Exchange-correlation.



The next step is to set up the NiO lattice in an anti-ferromagnetic spin arrangement. For this purpose open the initial state block in the Script-generator Tool.

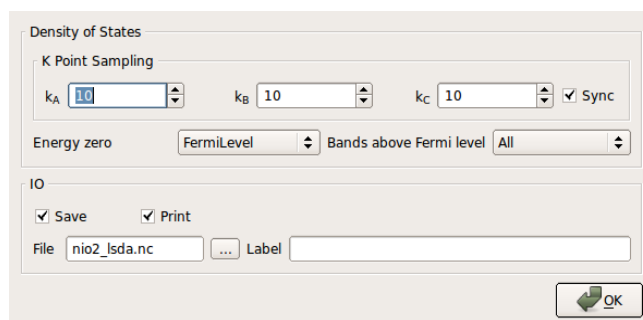
Select **User spin**, this will allow you to set the spin on each atom. Next set opposite spins on the two nickel atoms and no spin on the Oxygen's as illustrated below.




Note


The initial spin of 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 $[Ar]3d^84s^2$ (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 Hunds rule the 3d shell has 5 electrons in the up direction and 3 electrons in the down direction, giving a total atomic spin of $2 \mu_B$ for nickel.

Finally, open the Density of States block and set the k-point sampling to 10x10x10. It is a good idea to make the k-point sampling quite dense for this analysis because otherwise it will not capture the accurate variation of the density of states with energy.



You now finished the script setup, close the Density-of-States window, press the save button  and save the script in the file `nio2_ksda.py` .

PERFORMING THE CALCULATION

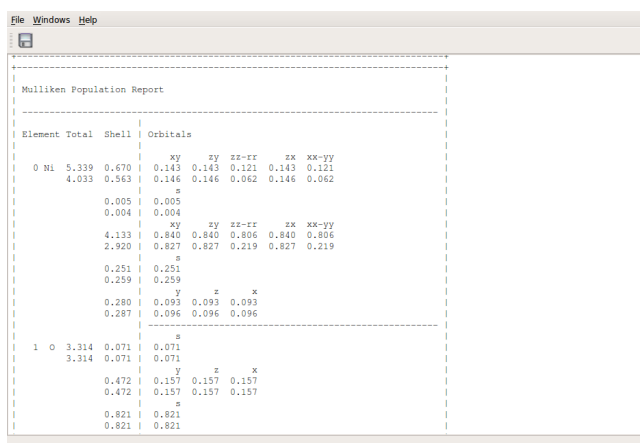
To start the calculation, **left**-click the  icon located in the lower-right of the script Generator tool and select Job Manager from the pop-up menu.

The job manager tool will now pop up, select the dropped scripted and press start. You should see the log window pop up with the output of the calculation. After 1-2 minutes, the calculation has finished and you can inspect the results.

ANALYSING THE RESULTS

MULLIKEN POPULATION

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



```
File Windows Help
-----
Mulliken Population Report
-----
Element Total Shell | Orbitals
-----
0 Ni 5.339 0.670 | xy sy zz-rr zx xx-yy
4.033 0.563 | 0.143 0.143 0.121 0.143 0.121
| 0.146 0.146 0.062 0.146 0.062
| s
| 0.005 | 0.005
| 0.004 | 0.004
| xy zy zz-rr zx xx-yy
| 4.133 | 0.840 0.840 0.806 0.840 0.806
2.920 | 0.827 0.827 0.219 0.827 0.219
| s
| 0.251 | 0.251
| 0.259 | 0.259
| y z x
| 0.280 | 0.093 0.093 0.093
0.287 | 0.096 0.096 0.096
-----
1 O 3.314 0.071 | 0.071
3.314 0.071 | 0.071
| y z x
| 0.472 | 0.157 0.157 0.157
0.472 | 0.157 0.157 0.157
| s
| 0.821 | 0.821
0.821 | 0.821
```

Tip

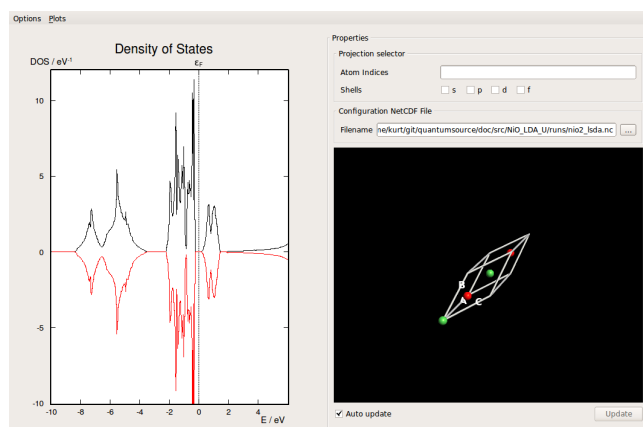
The Mulliken population can also be inspected by selecting the `nio2_ksda.nc` data file in the VNL result browser, selecting the Mulliken Population Object, and **left**-clicking Show plot.

The Mulliken population reports the numbers of electrons per spin and orbital, as well as the orbital sum for each atom. Note that oxygen is non-polarized while the two nickel atoms are polarized in different directions, thus forming an anti-ferromagnetic arrangement. The polarization can be read of as the difference between the number of electrons in each spin direction (5.339) and (4.033). The resulting value of $1.34 \mu_B$ is in good agreement with other LSDA calculations[2].

PARTIAL DENSITY OF STATES

To investigate the Partial Density of States (PDOS), select the `nio2_ksda.nc` data file in the VNL result browser, select the Density of States Object, and **left**-click the PDOS Show button.

You may zoom the plot, by selecting part of it with the left mouse button, and get the following plot.

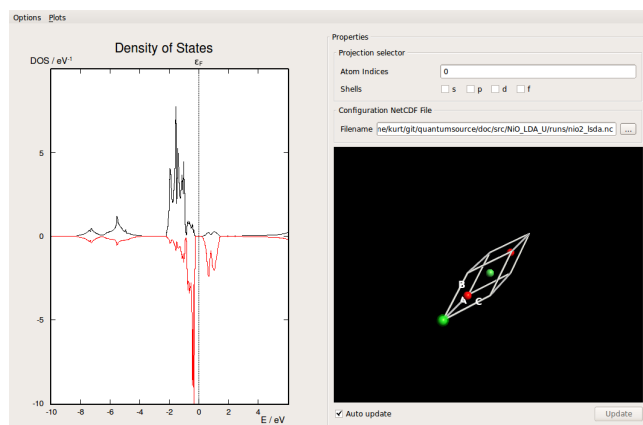


i Tip

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 you will obtain a positive axis for the spin down channel.

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 PDOS of the Nickel Atom, select the nickel with the left-mouse, as illustrated below



i Tip

By selecting multiple atoms (using Ctrl+left-mouse) and ticketing of several shells you can make combined projections.

The calculation predicts a band gap of ~ 0.4 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 LSDA+U approximation.

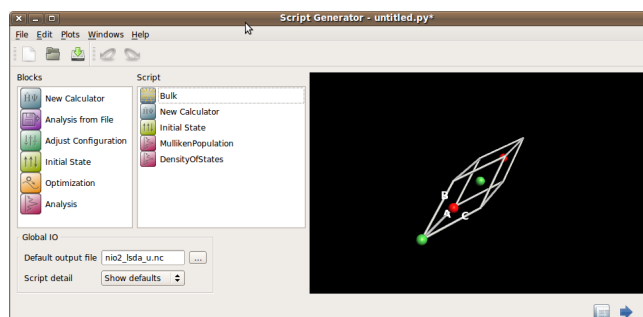
CHAPTER 3. LDA+U CALCULATION FOR THE NiO CRYSTAL

SETTING UP THE CALCULATION

You will in this chapter perform a LSDA+U calculation of the NiO crystal. For the U parameter you will use 4.6 eV for the Nickel d-states, as proposed in Ref. [1].

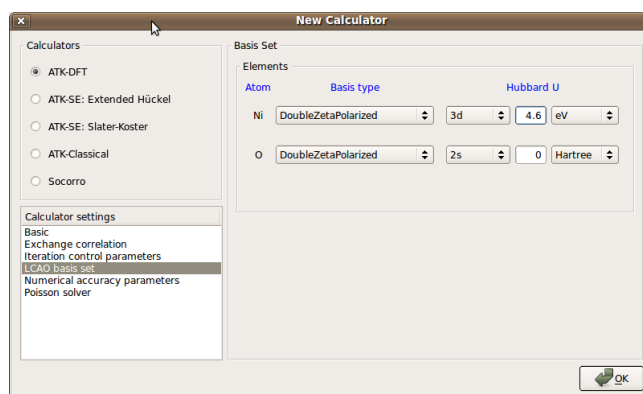
To set up the calculation you will need to modify the script generated for the LSDA calculation. Open the script generator tool used in the previous chapter (If you have closed it, redo the steps in the previous chapter).


- Change the Default output file to `nio2_ksda_u.nc`.
- Change the Script detail to **Show defaults**.



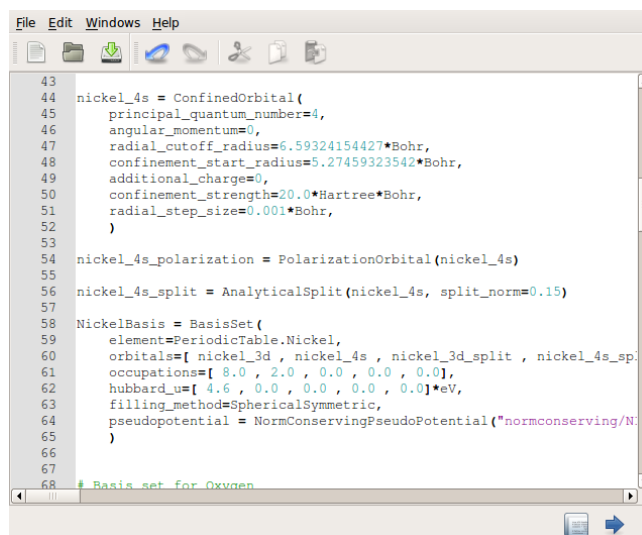
Open the New Calculator block.

- Select LSDA+U for the exchange-correlation.
- Switch to the LCAO basis set tab. Set the Hubbard U for the Ni-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 orbital.



```
43
44 nickel_4s = ConfinedOrbital(
45     principal_quantum_number=4,
46     angular_momentum=0,
47     radial_cutoff_radius=6.59324154427*Bohr,
48     confinement_start_radius=5.27459323542*Bohr,
49     additional_charge=0,
50     confinement_strength=20.0*Hartree*Bohr,
51     radial_step_size=0.001*Bohr,
52 )
53
54 nickel_4s_polarization = PolarizationOrbital(nickel_4s)
55
56 nickel_4s_split = AnalyticalSplit(nickel_4s, split_norm=0.15)
57
58 NickelBasis = BasisSet(
59     element=PeriodicTable.Nickel,
60     orbitals=[ nickel_3d , nickel_4s , nickel_3d_split , nickel_4s_sp
61     occupations=[ 8.0 , 2.0 , 0.0 , 0.0 , 0.0 ],
62     hubbard_u=[ 4.6 , 0.0 , 0.0 , 0.0 , 0.0 ]*eV,
63     filling_method=SphericalSymmetric,
64     pseudopotential = NormConservingPseudoPotential("normconserving/N
65 )
66
67
68 # Basis set for Oxygen
```

i Tip

Hubbard U calculations can have different self-consistent states, and the state that is obtained from the self consistent iteration may depend on the initial density matrix. For some systems you may need to change the filling_method from **SphericalSymmetric** to **Anisotropic** in order to end up in the ground state self-consistent state. Setting this parameter is currently not supported in the GUI and must be done by editing the script.

Next save the script into the file `nio2_ksda_u.py` and run the script by dropping the file onto the job manager.

ANALYZING THE RESULTS

First inspect the Mulliken population in the log file. You should find the magnetic moment of the nickel atom

$$M_s(\text{Ni}) = 1.72\mu_B,$$

which is in good agreement with the experimental result of 1.64-1.70 μ_B [3].

To determine the band gap, inspect the Density Of States in the log file. You may find that the Density of States is zero in the range [-0.67, 2.36] eV, corresponding to a band gap of 3.03 eV. This is much higher than the LSDA value of 0.4 eV, and in better agreement with the experimental value of 4.0 eV[3] and in accordance with Ref. [1].

USING SCRIPTING TO PLOT THE DENSITY OF STATES PROJECTED ONTO A NICKEL ATOM

The final step is to compare the LSDA and LSDA+U results for the Density of States projected onto the nickel atom. Instead of using the build in PDOS analyzer introduced in the previous

chapter, in this section you will use python scripting to perform the analysis. The scripting is based on the [matplotlib](#) package which is part of the atkpython.

The following script performs the analysis

```
#read in the dos object
dos = nload('nio2_ksda.nc',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]))

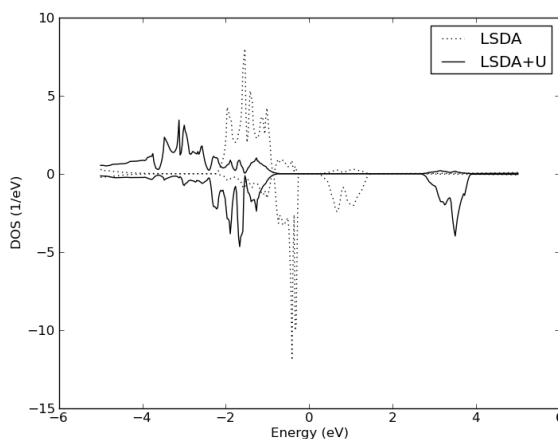
e = dos.energies()

#do the same for LSDA+U
dos_u = nload('nio2_ksda_u.nc',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 = 'LSDA')
#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 LSDA+U up components with solid
pylab.plot(e.inUnitsOf(eV), n0_up_u.inUnitsOf(eV**-1),'k',label = 'LSDA+U')
#now plot the LSDA+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()
```

Below is shown the output of the calculation for the projected density of states of the nickel atom



Notice the large difference in band gap between the two calculations.

BIBLIOGRAPHY

- [1] M. Cococcioni, S. de Gironcoli , *Phys. Rev. B*, **71**, 35105, 2005.
- [2] A. B. Shick, A. I. Liechtenstein, W. E. Pickett, *Phys. Rev. B* , **60**, 10763, 1999.
- [3] V. I. Anisimov, F. Aryasetiawan, A. I. Liechtenstein, *J. Phys. Cond. Matter* , **9**, 767, 1997.

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