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Relativistic effects in bulk gold

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Gold is one of the more heavy transition metals, and the electronic structure of bulk gold is therefore significantly affected by relativistic effects, including spin-orbit coupling (SOC).

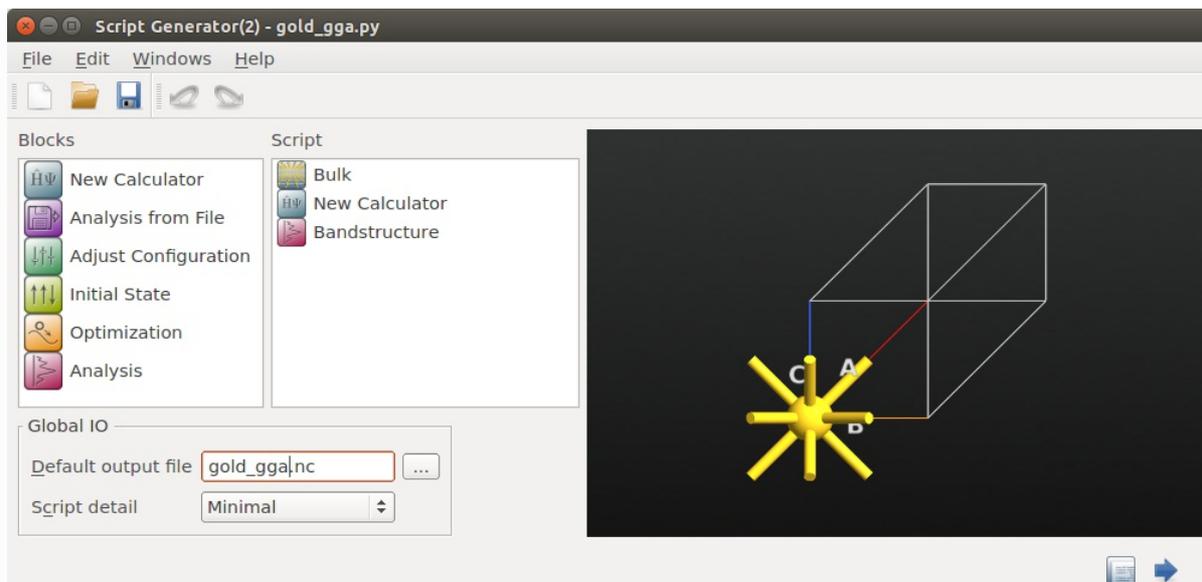
Relativistic *ab initio* band structure calculations for gold were first reported in the early 1970s, see e.g. Refs. [Ram70], [CS71], and [Chr76]. Those studies, and later ones, found that relativistic effects cause a significant reorganization of the electronic energy bands in gold. In particular, inclusion of relativistic effects removes a large part of the band crossings in the deeper valence bands found in standard calculations. In this tutorial, you will demonstrate this using ATK-DFT for standard scalar-relativistic (GGA) and relativistic (SOGGA) calculations of the gold band structure.

GGA band structure

Use the QuantumATK Builder  to create the gold bulk configuration. This is most easily done using the Add ▶ From Database tool. Keep the gold lattice constant at the experimental value (4.078 Å).

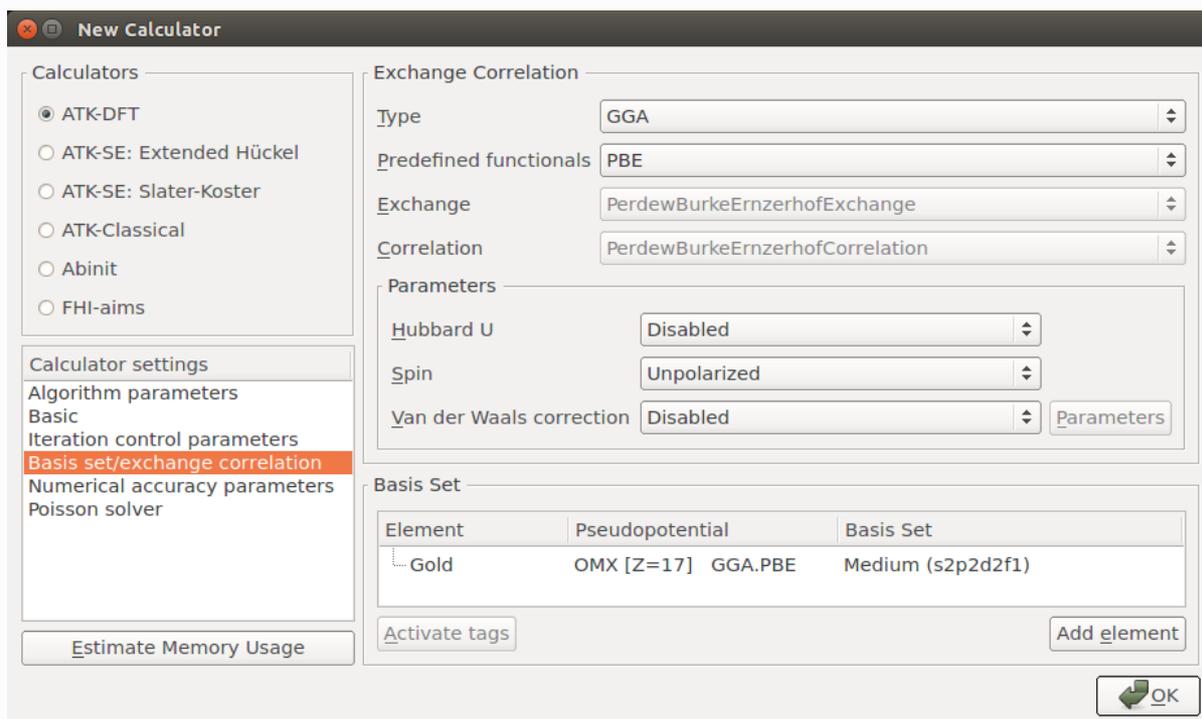
Then transfer the configuration to the Script Generator  and set up a standard GGA-PBE band structure calculation using an OMX pseudopotential.

First, add a New Calculator  block and a Bandstructure  analysis block, and set `gold_gga.nc` as the output file.

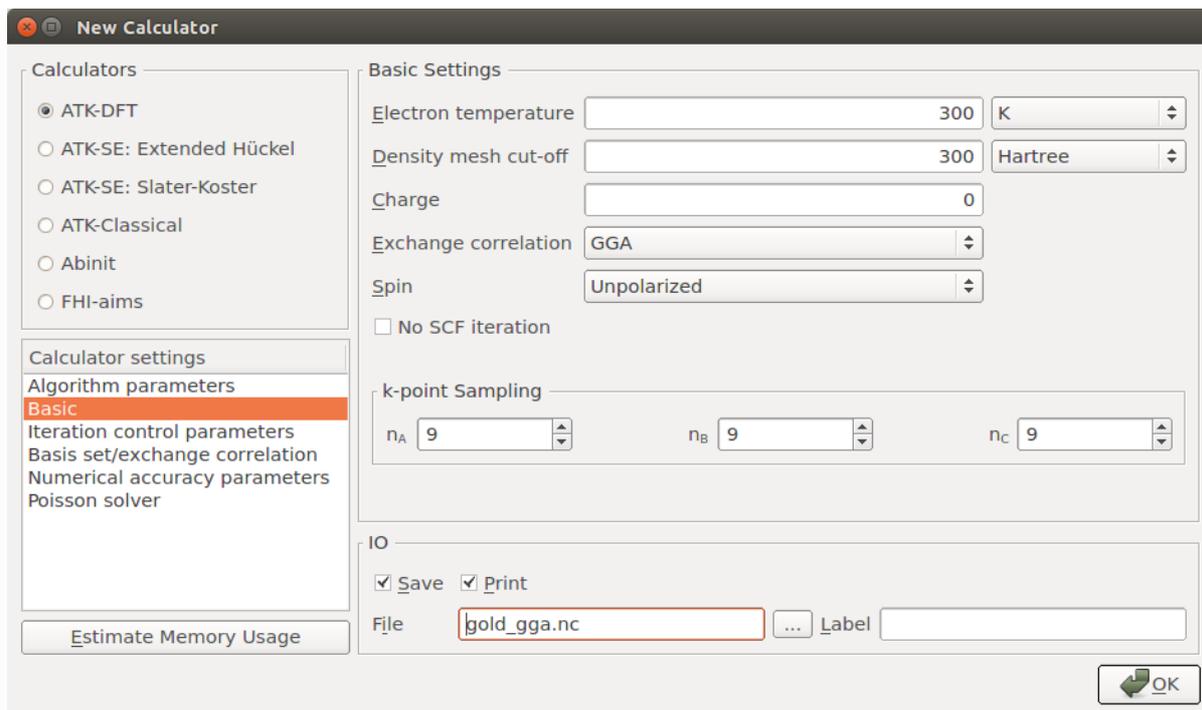


Edit the New Calculator settings:

- In the **Basis set/exchange correlation** panel, choose the GGA-PBE exchange-correlation functional and the OMX pseudopotential with a *Medium* accuracy basis set.

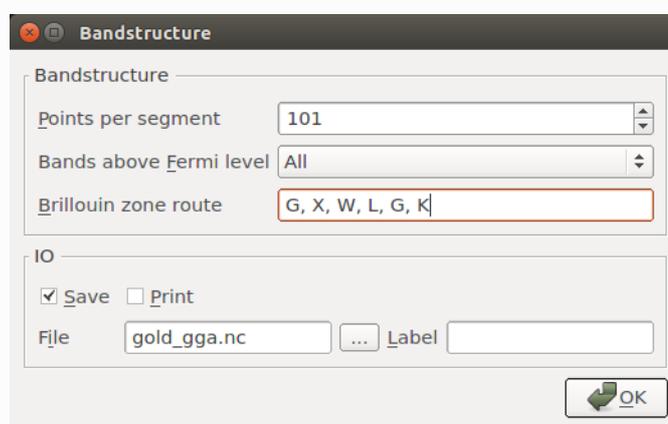


- In the **Basic** panel, set the *Density mesh-cutoff* to 300 Hartree and increase the *k-point Sampling* to 9x9x9.



Open the Bandstructure block and edit it:

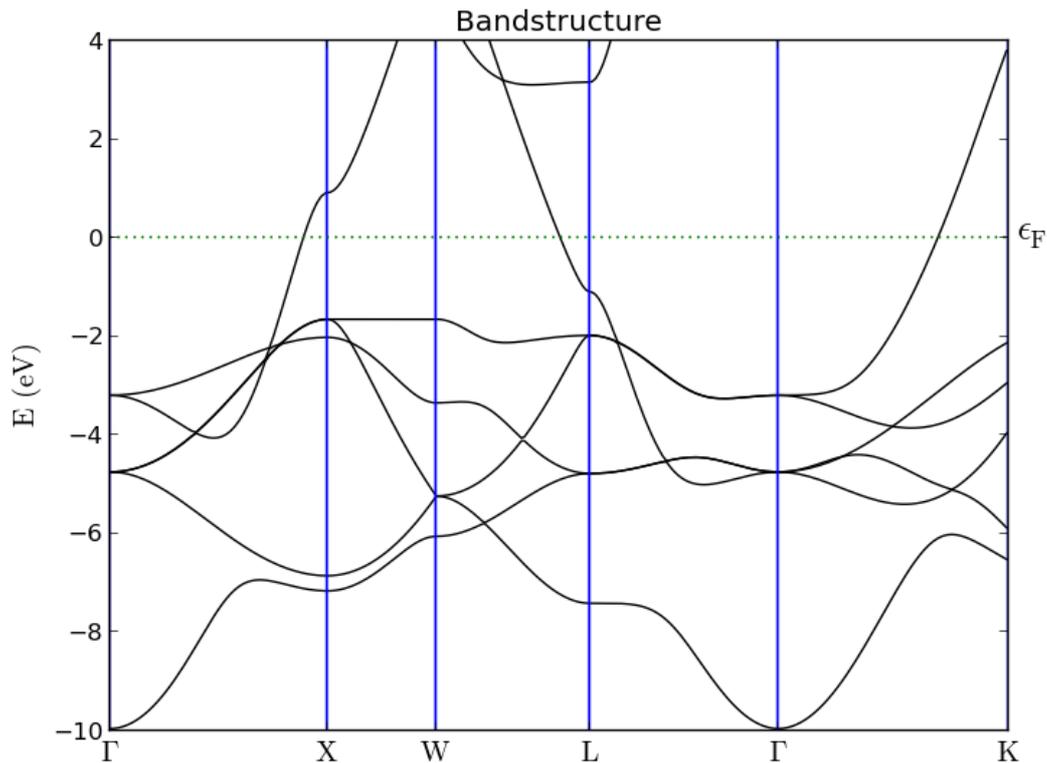
- Increase *Points per segment* to 101 in order to finely sample the band structure between each high-symmetry point, and trim the default *Brillouin zone route* such that it reads "G, X, W, L, G, K".



Save the script as `gold_gga.py` and run it. You can use the Job Manager  for this. It should take around a minute if executed on a single processor.

Results

Find the Bandstructure object in the output file on the QuantumATK LabFloor and use the **Bandstructure Analyzer** to plot it. The results are shown below and are very similar to those reported in Refs. [CS71] and [Chr76]. Gold is clearly not an insulator, since there are plenty of bands crossing the Fermi level. Also note the frequent band crossing in the deeper valence bands, from ca. -2 to -5 eV below the Fermi energy. As we shall see, most of these crossings disappear in a relativistic calculation including SO interactions.



Spin-orbit GGA band structure

You will here set up and execute a GGA calculation that includes the SOC. This must be done in a noncollinear representation of electron spin, which is computationally more expensive than the GGA calculation and can exhibit poor SCF convergence. You should therefore apply two tricks: a) start the noncollinear calculation from a converged spin-polarized state (SGGA), and b) use a special electron density mixing scheme.

Note

We know that gold is not magnetic, so it may seem a bit silly to do a spin-polarized calculation for gold. After all, the results should not differ from those found in the collinear spin-compensated calculation done in the previous section.

Indeed, they do not, but the converged spin-polarized state offers a much better initial guess for the self-consistent noncollinear+SO state than the spin-compensated state does: Fewer noncollinear SCF steps are required if starting from the spin-polarized state, and computational time is therefore saved.

SGGA initial state

You have two options for setting up a script for the SGGA calculation:

- Use the **Scripter**: Set up the script exactly like in the previous section, but choose "Polarized" for the *Spin* parameter, remove the Bandstructure analysis object, set the output file to `gold_sgga.nc`, and save the new script as `gold_sgga.py`.
- Use the **Editor**: Copy `gold_gga.py` to `gold_sgga.py` and open the new script in the Editor  and edit it a bit. Set the exchange-correlation to `SGGA.PBE`, remove the bottom lines that execute the bandstructure calculation, and rename the output file to `gold_sgga.nc`.

In any case, the script should look like this:

```
# -----  
# Bulk Configuration  
# -----  
  
# Set up lattice  
lattice = FaceCenteredCubic(4.07825*Angstrom)  
  
# Define elements  
elements = [Gold]  
  
# Define coordinates  
fractional_coordinates = [[ 0., 0., 0.]]  
  
# Set up configuration  
bulk_configuration = BulkConfiguration(  
    bravais_lattice=lattice,  
    elements=elements,  
    fractional_coordinates=fractional_coordinates  
)  
  
# -----  
# Calculator  
# -----  
#-----  
# Basis Set  
#-----  
  
GoldBasis = OpenMXBasisSet(  
    element=PeriodicTable.Gold,  
    filename="openmx/pao/Au7.0.pao.zip",  
    atomic_species="s2p2d2f1",  
    pseudopotential=NormConservingPseudoPotential("normconserving/upf2/Au_PBE13.upf.zip"),  
)  
  
basis_set = [  
    GoldBasis,  
]  
  
#-----  
# Exchange-Correlation  
#-----  
exchange_correlation = SGGA.PBE  
  
numerical_accuracy_parameters = NumericalAccuracyParameters(  
    k_point_sampling=(9, 9, 9),  
    density_mesh_cutoff=300.0*Hartree,  
)  
  
calculator = LCAOCalculator(  
    basis_set=basis_set,  
    exchange_correlation=exchange_correlation,  
    numerical_accuracy_parameters=numerical_accuracy_parameters,  
)  
  
bulk_configuration.setCalculator(calculator)  
nlprint(bulk_configuration)  
bulk_configuration.update()  
nlsave('gold_sggga.nc', bulk_configuration)
```

Run the script, it should be very fast. Note that the output file `gold_sggga.nc` is generated and that it contains only a single object;  the gold bulk configuration including the self-consistent SGGA electronic

state, which will be used in the next step.

SOGGA band structure

Use the script below to perform the following work-flow:

1. Read the `bulk_configuration` from the file `gold_sgga.nc`.
2. Get the `calculator` used in the SGGA calculation and modify it slightly; use the SOGGA exchange-correlation and a special mixing scheme for noncollinear calculations.
3. Use the converged SGGA state as initial guess for the SOGGA electron density.
4. Do the SOGGA ground state calculation followed by band structure analysis.

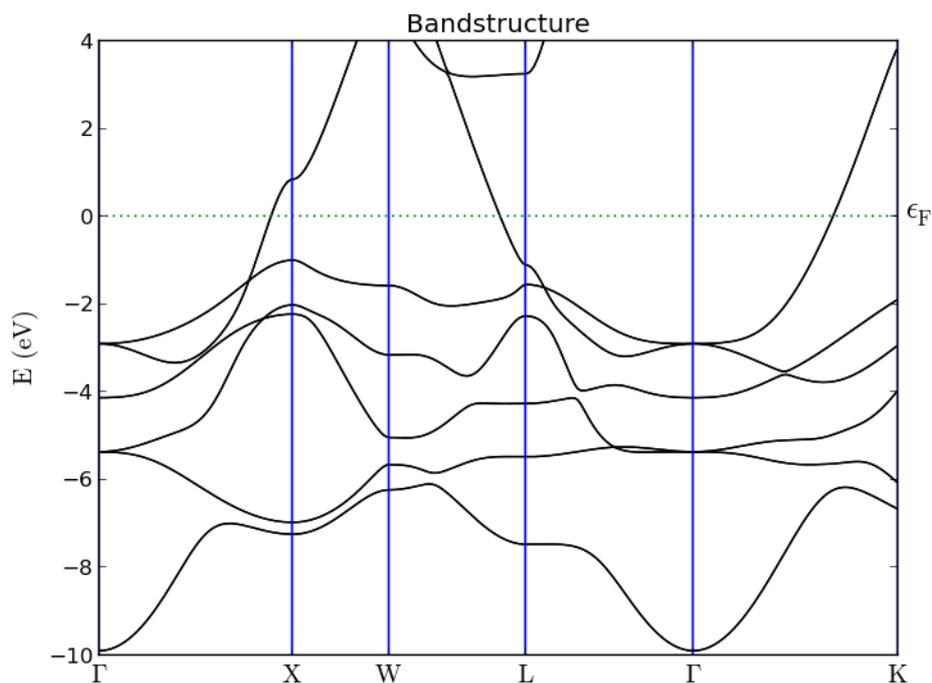
```
# -----  
# Bulk Configuration  
# -----  
bulk_configuration = nload('gold_sgga.nc', BulkConfiguration)[0]  
  
# -----  
# Calculator  
# -----  
  
# Use the special noncollinear mixing scheme  
iteration_control_parameters = IterationControlParameters(  
    algorithm=PulayMixer(noncollinear_mixing=True)  
)  
  
# Get the calculator and modify it for spin-orbit GGA  
calculator = bulk_configuration.calculator()  
calculator = calculator(  
    exchange_correlation = SOGGA.PBE,  
    iteration_control_parameters = iteration_control_parameters  
)  
  
# Setup the initial state from the GGA calculation  
bulk_configuration.setCalculator(  
    calculator,  
    initial_state = bulk_configuration  
)  
nload(bulk_configuration)  
bulk_configuration.update()  
nload('gold_sogga.nc', bulk_configuration)  
  
# -----  
# Bandstructure  
# -----  
bandstructure = Bandstructure(  
    configuration=bulk_configuration,  
    route=['G', 'X', 'W', 'L', 'G', 'K'],  
    points_per_segment=101,  
    bands_above_fermi_level=All  
)  
nload('gold_sogga.nc', bandstructure)
```

Save the script as `gold_sogga.py` and run the calculation. It should take roughly 6 minutes to finish if executed in parallel on 4 CPUs.

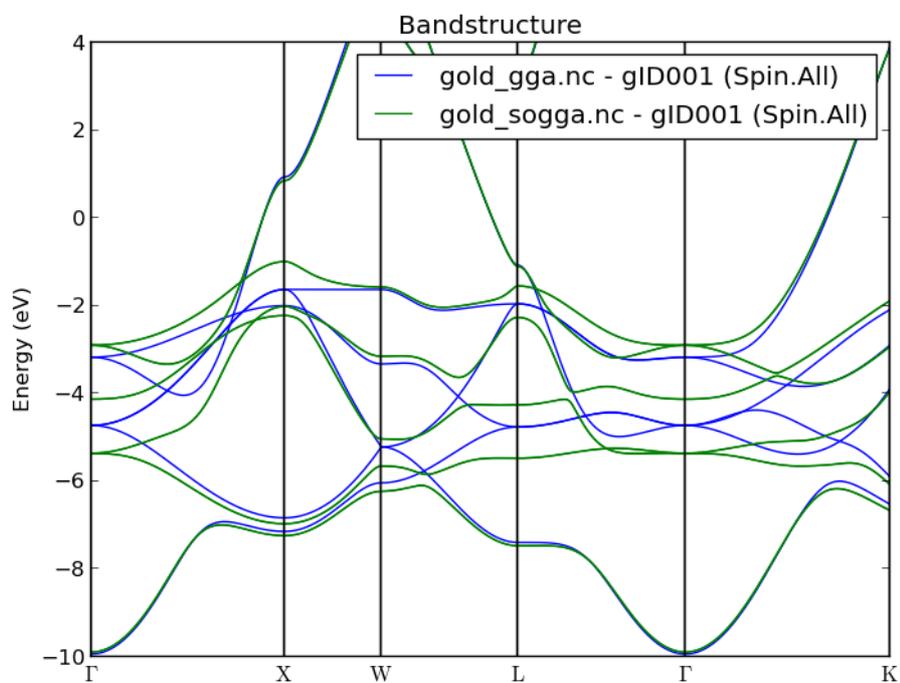
Results

The plot below shows the band structure obtained from the SOGGA calculation. It follows very closely the literature results in Refs. [CS71] and [Chr76] and is virtually identical to the SOGGA band structure of gold recently published in Ref. [RKT+12]. Note how most of the valence band crossings found in the standard

GGA calculation have now been lifted.



You can also use the **Compare Data** plugin for a more direct comparison of the two band structures, as illustrated below. Simply highlight both the GGA and the SOGGA bandstructure objects, and click the plugin. It is quite clear that relativistic effects have a significant impact on the gold valence bands. The data illustrated below is essentially identical to that in Figure 6 of Ref. [RKT+12].



References

- [CS71] (1, 2, 3) N. Egede Christensen and B. O. Seraphin. Relativistic band calculation and the optical properties of gold. *Phys. Rev. B*, 4:3321–3344, Nov 1971. doi:10.1103/PhysRevB.4.3321.
- [Chr76] (1, 2, 3) N. Egede Christensen. High-energy band structure of gold. *Phys. Rev. B*, 13(6):2698–2701, 1976. doi:10.1103/PhysRevB.13.2698.
- [Ram70] M. G. Ramchandani. Energy band structure of gold. *Journal of Physics C: Solid State Physics* 3(1S):S1, 1970. URL: <http://stacks.iop.org/0022-3719/3/i=1S/a=301>.
- [RKT+12] (1, 2) T. Rangel, D. Kecik, P. E. Trevisanutto, G.-M. Rignanese, H. Van Swygenhoven, and V. Olevano. Band structure of gold from many-body perturbation theory. *Phys. Rev. B*, 86:125125, Sep 2012. doi:10.1103/PhysRevB.86.125125.

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