

Optical Properties of Silicon

Tutorial on using meta-GGA and computing optical response functions

Optical Properties of Silicon: Tutorial on using meta-GGA and computing optical response functions

Version 12.2.0

Copyright © 2008–2012 QuantumWise A/S

Atomistix ToolKit Copyright Notice

All rights reserved.

This publication may be freely redistributed in its full, unmodified form. No part of this publication may be incorporated or used in other publications without prior written permission from the publisher.

TABLE OF CONTENTS

1. Introduction	1
2. Electronic structure and optical properties of silicon	2
Setting up the calculation	2
Running and analyzing the calculation	4
Bibliography	7

CHAPTER 1. INTRODUCTION

The purpose of this tutorial is to show how ATK can be used to compute accurate electronic structure, optical, and dielectric properties of semiconductors from DFT combined with the meta-GGA functional by Tran and Blaha [1] (TB09). TB09 is a semi-empirical functional that is fitted to give a good description of the band gaps in non-metals. The results obtained with the method are often comparable with very advanced many-body calculations, however with a computational expense comparable with LDA, i.e. several order of magnitudes faster. Thus, the meta-GGA functional is a very practical tool for obtaining a good description of the electronic structure of insulators and semiconductors.

It is important to note that the TB09 functional does not provide accurate total energies [1], and it can therefore only be used for calculating the electronic structure of the materials, while the GGA-PBE functional should be used for computing total energies and atomic geometries. Furthermore, TB09 does not give a good description of the band structure of metals, and caution must be taken if material combinations including metals are modelled with meta-GGA functionals. For such systems an alternative is to use the Hubbard +U correction, which is also implemented in ATK, to improve the description of the electronic structure of the insulator.

It is assumed that you are familiar with the general workflow of VNL, as described in [the basic ATK Tutorial](#).

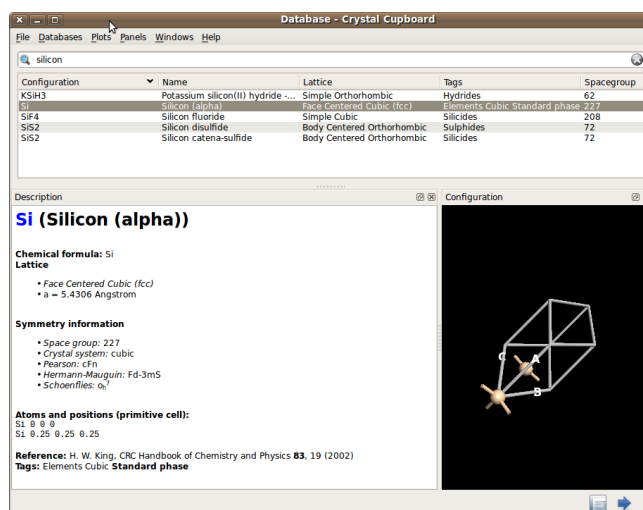
This tutorial uses silicon as an example. As for most semiconductors, GGA/LDA both severely underestimate the Si band gap (between 0.5 and 0.6 eV), while the experimental band gap of 1.18 eV is reproduced almost exactly by TB09. The experimental dielectric constant is also reproduced by the optical properties module in ATK to within a few percent.


CHAPTER 2. ELECTRONIC STRUCTURE AND OPTICAL PROPERTIES OF SILICON

SETTING UP THE CALCULATION

Launch the Database  via the **Tools** menu in the VNL main window.

Type “silicon” in the search field, and select the silicon standard phase in the list of matches. Information about the lattice, including its symmetries (e.g. that the selected crystal is face centered cubic), can be seen in the lower panel.

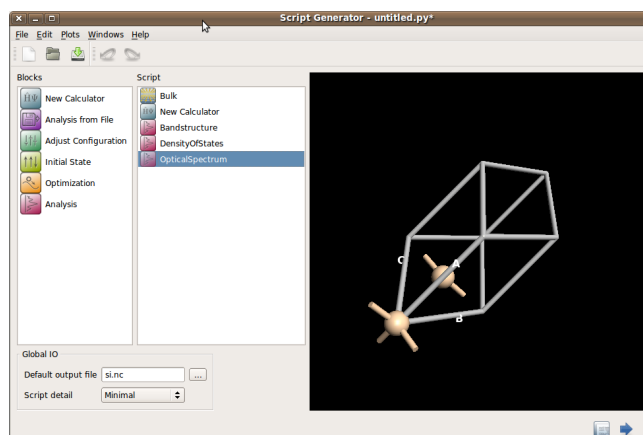


Transfer the crystal to the Script Generator via the "Send to" icon  in the lower right-hand corner of the Database window.


In the Script Generator perform the following steps to set up the calculation.

1. Add a **New Calculator** to the script by double-clicking on the corresponding icon in the **Blocks** panel.
2. To calculate the band structure of the crystal, double-click on **Analysis** and select **Band-structure** from the pop-up menu.
3. Insert **DensityOfStates** and **OpticalSpectrum** blocks, which are also available under **Analysis**.

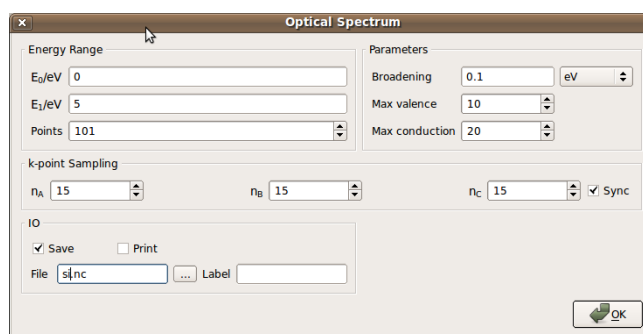
4. Finally, enter `si.nc`, as the file name where the results will be saved, in the box **Default output file**. If you do not specify a directory, but only a file name, the NetCDF file will be saved in the directory where you started VNL.




The next step is to adjust the parameters of each block.

Open the New Calculator  block, and

- select the ATK-DFT calculator (selected by default),
- set the k-points to (4,4,4),
- select the MGGGA exchange-correlation functional,
- and finally under "LCAO basis set", select the **DoubleZetaDoublePolarized** basis set for Si.
- Next open the DensityOfStates block and select 15 x 15 x 15 kpoints.
- Finally open the OpticalSpectrum block and again select 15 x 15 x 15 kpoints, and use 10 bands below and 20 above the Fermi level (this controls how many bands are included in the calculation of the optical matrix elements).



For this calculation you will use the Hartwigsen, Goedecker, Hutter (HGH) pseudopotentials [2] introduced in ATK 11.8, combined with new basis sets that have been optimized for ATK 12.2. For this purpose, transfer the script to the **Editor** using the "Send To"  button.

Locate the line

```
basis_set = LDABasis.DoubleZetaDoublePolarized
```

and change this to

```
basis_set = BasisGGAPBEHGH.Silicon_4_Tier_3
```

Note

The calculation of optical properties requires a good description of virtual states far above the Fermi level. The "Tier 3" basis set for Si consists of optimized 3s, 3p (2 orbitals), 3d, 4s orbitals. Going higher to "Tier 4" would add another 3s orbital, and so on, but this appears to have no significant influence on the band gap (just taking longer time). With a smaller basis set, however, the band gap comes out incorrectly even with MGGA.

Tip

To print a list of the orbitals in a basis set, use these lines of code:

```
basis_set = BasisGGAPBEHGH.Silicon_4_Tier_3
for o in basis_set.orbitals():
    print "%i%s" % (o.principalQuantumNumber(), 'spdf'[o.angularMomentum()]),
```

Save the script from the Editor, for future reference.

RUNNING AND ANALYZING THE CALCULATION

Transfer the script to the **Job Manager** and start the calculation.

After a few minutes the job will finish. Locate the result file `si.nc` to plot the data.

DOS OF SILICON

From the density of states it is possible to determine the band gap of silicon.

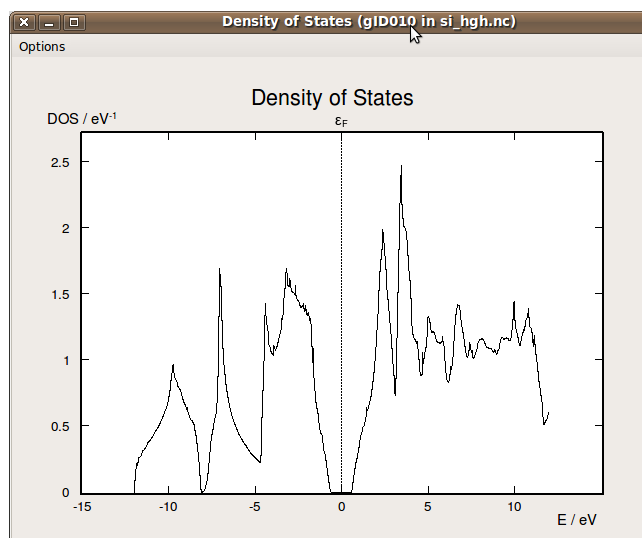


Figure 2.1: Density of states (DOS) of Si, computed with meta-GGA.

To read off the band gap, you may zoom the plot or export the DOS data to a file. The band edges are located around -0.59 eV and 0.57 eV, resulting in a band gap of 1.16 eV. This is in excellent agreement with the experimental band gap of 1.17 eV (at 0 Kelvin), in contrast to the LDA band gap of 0.55 eV.

OPTICAL SPECTRUM

Next plot the optical spectrum from the output file `si.nc`. The plot is shown below.

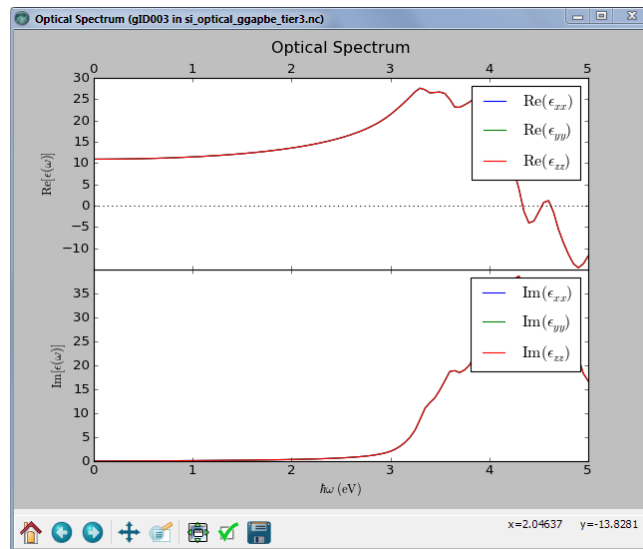


Figure 2.2: Real and imaginary parts of the diagonal components of the dielectric constant. Since silicon has cubic symmetry the dielectric constant is isotropic, i.e. $\epsilon_{xx} = \epsilon_{yy} = \epsilon_{zz}$.

By zooming in, in the figure, you can determine the static dielectric constant, $\text{Re}[\epsilon(\omega = 0)] = 10.9$, in qualitative agreement with the experimental value of 11.9 (with a bit larger basis set we can get values around 12.2, but also note that we did not optimize the k-point sampling).

The absorption coefficient and refractive index are related to the dielectric constant, see for instance the [ATK reference manual](#).

The script below calculates the absorption coefficient and refractive index from the dielectric constant and plots it as a function of the wavelength.

```
# Load the optical spectrum
spectrum = nload('si.nc', OpticalSpectrum)[-1]

# Get the energies range
energies = spectrum.energies()

# get the real and imaginary part of the e_xx component of the dielectric tensor
d_r = spectrum.evaluateDielectricConstant()[0,0,:]
d_i = spectrum.evaluateImaginaryDielectricConstant()[0,0,:]

# Calculate the wavelength
l = (speed_of_light*planck_constant/energies).inUnitsOf(nanoMeter)

# Calculate real and complex part of the refractive index
n = numpy.sqrt(0.5*(numpy.sqrt(d_r**2+d_i**2)+d_r))
k = numpy.sqrt(0.5*(numpy.sqrt(d_r**2+d_i**2)-d_r))

# Calculate the adsorption coefficient
```

```

alpha = (2*energies/hbar/speed_of_light*k).inUnitsOf(nanoMeter**-1)

# Plot the data
import pylab
pylab.figure()
pylab.subplots_adjust(hspace=0.0)
ax = pylab.subplot(211)
ax.plot(l,n,'b', label='refractive index')
ax.axis([180,1000,2.2,6.4])
ax.set_ylabel(r"$n$", size=16)
ax.tick_params(axis='x', labelbottom=False, labeltop=True)
ax = pylab.subplot(212)
ax.plot(l,alpha,'r')
ax.axis([180,1000,0,0.24])
ax.set_xlabel(r"$\lambda$ (nm)", size=16)
ax.set_ylabel(r"$\alpha$ (1/nm)", size=16)
pylab.show()

```

Save the script onto your computer and execute the script by dropping it onto the **Job Manager**.

The script will generate the figure below.

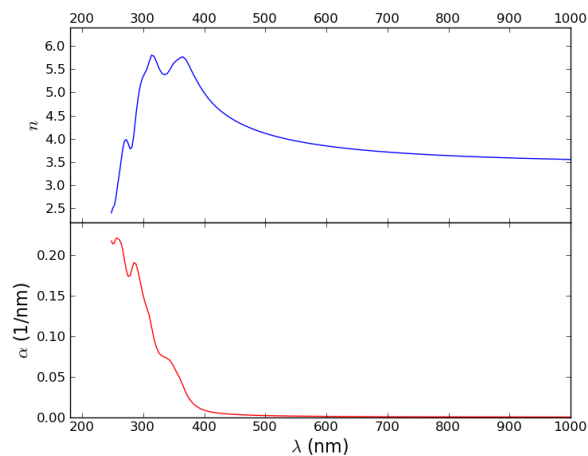


Figure 2.3: Refractive index (blue) and adsorption coefficient (red) of silicon as function of the wavelength of the incoming light.

BIBLIOGRAPHY

- [1] F. Tran, P. Blaha , *Phys. Rev. Lett.*, **102**, 226401, 2009.
- [2] C. Hartwigsen, S. Goedecker, J. Hutter. *Phys. Rev. B*, **58**, 3641, 1998.