Practical 8 – DOS and EELS with OptaDOS

There are 4 exercises here: DOS, projected DOS, EELS and JDOS. If you are already familiar with using `optados` then you may jump to whichever exercise is most relevant.

1. Density of States

This is a simple example of using `optados` for calculating electronic density of states of crystalline silicon in a 2 atom cell. It shows how `optados`'s adaptive broadening can be used to resolve fine spectral features that a fixed broadening scheme will obscure.

INSTRUCTIONS:
Perform a castep calculation on the bulk silicon using the `Si2.cell` and `Si2.param` input files. Examine the `optados` input file - `Si2.odi` – and then perform an `optados` calculation.

```
$ optados Si2
```

This generates 3 files:

1 `Si2.odo` -- optados general output file.
2 `Si2.adaptive.dat` -- The adaptive broadened DOS raw output data.
3 `Si2.adaptive.agr` -- The adaptive broadened DOS in a file suitable to be plotted by xmgrace.

Examine the `Si2.odo` file – you will see that `optados` has performed a Density of States calculation:

```
+---------------- Fermi Energy Analysis -------------------------+
| From Adaptive broadening                                       |
| Spin Component:1 occupation between 3.99961 and 4.00003 <-Oc |
| Spin Component:2 occupation between 3.99961 and 4.00003 <-Oc |
|       Fermi energy (Adaptive broadening) : 5.4109 eV  <- EfA |
+----------------------------------------------------------------+
```

It has used the integrated DOS to work out the Fermi level, and has suggested the error in the integration by indicating the number of electrons at the Fermi level. Since we had 4 up electrons and 4 down in the input file this analysis seems satisfactory:

```
+------------------------ Electronic Data ----------------------+
|  Number of Bands                              :       23       |
|  Grid size                                    :  10 x 10 x 10  |
|  Number of K-points                           :          110   |
|  Spin-Polarised Calculation                   :           True |
|  Number of up-spin electrons                  :         4.00   |
|  Number of down-spin electrons                :         4.00   |
+---------------------------------------------------------------+
```

Since we had **`efermi : optados`** then `optados` sets the internal value of the Fermi level to the one it has derived from the DOS. This is important for subsequent calculations. Other valid options are **`file`**, where `optados` uses the value calculated by the electronic structure code that generated the eigenvalues; **`insulator`**, where `optados` uses a value calculated from assuming the system is non-metallic; or a value set by the user.

`optados` now performs some analysis of the DOS at the Fermi level:

```
+-------------- DOS at Fermi Energy Analysis ----------------+
|                          Fermi energy used :   5.4109 eV   |
| From Adaptive broadening                                   |
| Spin Component:1 DOS at Fermi Energy:0.0011 eln/cell <-DEA |
| Spin Component:2 DOS at Fermi Energy:0.0011 eln/cell<- DEA |
+------------------------------------------------------------+
```

From this we may assume that there is a band gap.
Importantly, then `optados` calculates the band energy from the DOS it has calculated:

```
+------------------- Band Energy Analysis -------------------+
|     Band energy (Adaptive broadening) : 1.3609 eV   <- BEA |
|     Band energy (From CASTEP) :         1.3622 eV   <- BEC |
+------------------------------------------------------------+
```

As the quality of the `optados` calculation is increased these two values should converge to the same answer.
Finally `optados` shifts the Fermi level to 0eV, for the output files.

The DOS is written to Si2.adaptive.dat. This contains 5 columns as described in the header of the file:

```
################################################################
#
#                  O p t a D O S   o u t p u t   f i l e
#
#    Density of States using adaptive broadening
#  Generated on 12 Feb 2012 at 16:50:37
# Column         Data
#    1         Energy (eV)
#    2         Up-spin DOS (electrons per eV)
#    3         Down-spin DOS (electrons per eV)
#    4         Up-spin Integrated DOS (electrons)
#    5         Down-spin Integrated DOS (electrons)
#
################################################################
```

This file can be plotted by your favourite graph-plotting software. However, `optados` has made things easy and generated a `Si2.adaptive.agr` file which is directly plottable using xmgrace.

```
$ xmgrace Si2.adaptive.agr
```

We now try again with a better sampling of the DOS, by setting **`DOS_SPACING : 0.001`** and also analyse the band gap, by setting **`COMPUTE_BAND_GAP : true`**. You can set **`IPRINT : 2`** to see a progress report in `Si2.odo`.

In `Si2.odo` we now have a new section analysing the band gap in various ways.

```
+----------------------------- Bandgap Analysis ----------------+
|          Number of kpoints at       VBM       CBM             |
|                   Spin :   1  :      1         1              |
|                   Spin :   2  :      1         1              |
|               Thermal Bandgap :   0.6676272107  eV    <- TBg |
|            Between VBM kpoint :    0.05000    0.05000 0.05000|
|               and CBM kpoint:   -0.45000    -0.05000 -0.45000|
|             ==> Indirect Gap                                  |
+---------------------------------------------------------------+
|                             Optical Bandgap                   |
|                   Spin :   1  :     2.5542517447  eV  <- OBg |
|                   Spin :   2  :     2.5542463024  eV  <- OBg |
|          Number of kpoints with this gap                      |
|                   Spin :   1  :           1                   |
|                   Spin :   2  :           1                   |
+---------------------------------------------------------------+
|                             Average Bandgap                   |
|                   Spin :   1  :     3.8121372691  eV  <- ABg |
|                   Spin :   2  :     3.8121342659  eV  <- ABg |
|              Weighted Average :     3.8121357675  eV  <- wAB |
+---------------------------------------------------------------+
```

`optados` is very careful in its band gap analysis. It uses the bare eigenvalues (un-broadened) and works out the nature and size of the thermal gap, optical gap and the average gap over all of the Brillouin zone. In cases of multi-valleyed semiconductors `optados` will report the number of conduction band minima or valence band maxima with identical energies, but will not report the nature of the gap.

Increasing the number of integration points has improved the band energy of the adaptive smearing:

```
|      Band energy (Adaptive broadening) :  1.3623 eV   <- BEA |
```

We will now compare the DOS with the adaptive broadening scheme with simple Gaussian smearing. In the `optados` input file (`Si2.odi`) change the value of **`BROADENING`** to **`fixed`**

Plotting the fixed broadened DOS over the adaptive we see the advantages of the adaptive broadening,

```
$ xmgrace Si2.adaptive.agr Si2.fixed.agr
```

2. Projected Density of States

Outline

This is a simple example of using optados for calculating electronic density of states of 2 atoms of crystalline silicon projected onto LCAO basis states.

INSTRUCTIONS:

Examine the `optados` input file noting **`TASK : pdos`**. We choose to decompose the DOS into angular momentum channels **`PDOS : angular`** and as in the previous example we choose to recalculate the Fermi level using the calculated DOS, rather than use the Fermi level suggested by castep. Execute `optados` and examine the output in `Si2.pdos.dat`:

```
#################################################################
#
#                  O p t a D O S   o u t p u t   f i l e
#
#  Generated on 13 Feb 2012 at 10:15:10
#################################################################
#+--------------------------------------------------------------+
#|                    Partial Density of States -- Projectors   |
#+--------------------------------------------------------------+
#| Projector:    1 contains:                                    |
#|           Atom               AngM Channel                    |
#|          Si    1                 s                           |
#|          Si    2                 s                           |
#+--------------------------------------------------------------+
#| Projector:    2 contains:                                    |
#|           Atom               AngM Channel                    |
#|          Si    1                 p                           |
#|          Si    2                 p                           |
#+--------------------------------------------------------------+
#| Projector:    3 contains:                                    |
#|           Atom               AngM Channel                    |
#|          Si    1                 d                           |
#|          Si    2                 d                           |
#+--------------------------------------------------------------+
#| Projector:    4 contains:                                    |
#|           Atom               AngM Channel                    |
#|          Si    1                 f                           |
#|          Si    2                 f                           |
#+--------------------------------------------------------------+
```

The header shows that there are four projectors described below. The first containing the s-channels of both silicon atoms, the second the p-channels etc.

Setting **`DOS_SPACING : 0.001`** gives a high quality plot, which can be plotted using xmgrace as shown in Fig1

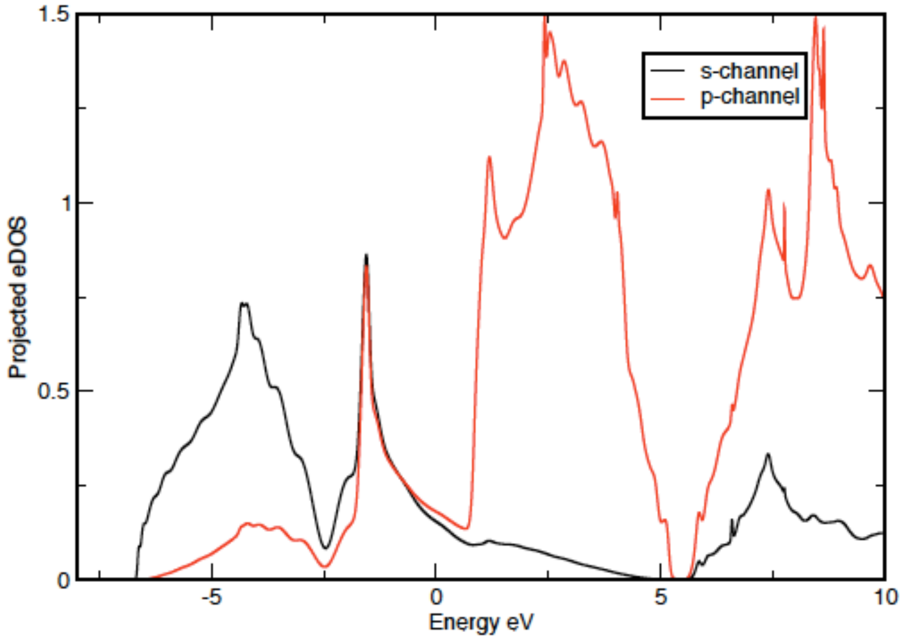

Figure 1: DOS of Silicon generated by adaptive broadening projected onto LCAO momentum states

Other projections to try are:

- `PDOS : Si1;Si2(s)` -- Output the PDOS on Si atom 1 and the PDOS on the s-channel of Si atom 2. (Resulting in two projectors)
- `PDOS : sum:Si1-2(s)` -- Output the sum of the s-channels on the two Si atoms. (Resulting in one projector)
- `PDOS : Si1(p)` -- Output the p-channel on Si atom 1. (Resulting in one projector)

3. Core Loss EELS

Outline

This is a simple example of using `optados` for calculating core level absorption spectra for crystalline silicon.

INSTRUCTIONS:

We begin by running a castep calculation using the files provided in examples/Si2_CORE. Note that we specify a pseudopotential file for one atom, and an on-the-fly pseudopotential for the other atom. This looks a bit weird! It is simply a way to only compute the EELS for one atomic site (core-loss spectra can only be computed for atoms described by on-the-fly potentials)

Execute `optados` using the input files provided and the file `Si2_CORE_core_edge.dat` will be created. The file contains two columns, the first is the energy and the second is the spectrum. This file contains the following edges:

```
 # Si 1    K1
 # Si 1    L1
 # Si 1  L2,3
 # Si 2    K1
 # Si 2    L1
 # Si 2  L2,3
```

i.e. all edges from the atom are produced.

`optados` has also written a grace file

```
$ xmgrace Si2_CORE_core_edge.agr
```

This spectrum contains lots of fine detail. To compare with experiment we can include lifetime and instrument broadening effects. First let's add some Gaussian broadening to simulate instrument effects. Add the following the `.odi` file and re-run.

```
CORE_LAI_BROADENING : true
LAI_GAUSSIAN_WIDTH : 1.0
```

To compare the broadened and un-broadened spectra

```
$ xmgrace Si2_CORE_core_edge_broad.agr Si2_CORE_core_edge.agr
```

Now add some lifetime broadening (look up the meaning of the keywords in the optados user guide

```
LAI_LORENTZIAN_WIDTH : 0.5
LAI_LORENTZIAN_SCALE : 0.1
```

Including a Core hole

To include a core-hole in the calculation, first one atom is chosen to have the excitation. To begin, we will keep two atoms in the unit cell and distinguish one atom by changing the

```
%BLOCK POSITIONS_FRAC
Si:1  0.0     0.0     0.0
Si:2 0.25    0.25    0.25
%ENDBLOCK POSITIONS_FRAC

%BLOCK SPECIES_POT
Si:1 2|1.8|1.8|1.3|2|3|4|30:31:32LGG{1s1.00}(qc=4) ! 1s core hole
Si:2 Si_STD_OTF.usp
%ENDBLOCK SPECIES_POT
```

in the `Si2_CORE.cell` file. The atom `Si:1` is the one to have a core-hole. To create a core-hole we remove a 1s electrons from the electronic configuration used in the generation of the pseudopotential. Information about the pseudopotentials is included at the top of the `Si2_CORE.castep` file:

```
 ============================================================
 | Pseudopotential Report-Date of generation 16-05-2012     |
 ------------------------------------------------------------
 | Element: Si Ionic charge:  4.00 Level of theory: LDA     |
 |                                                          |
 |              Reference Electronic Structure              |
 |         Orbital         Occupation          Energy       |
 |            3s              2.000            -0.400       |
 |            3p              2.000            -0.153       |
 |                                                          |
 |                Pseudopotential Definition                |
 |        Beta      l      e       Rc     scheme   norm    |
 |          1       0   -0.400   1.797     qc      0       |
 |          2       0    0.250   1.797     qc      0       |
 |          3       1   -0.153   1.797     qc      0       |
 |          4       1    0.250   1.797     qc      0       |
 |         loc      2    0.000   1.797     pn      0       |
 |                                                          |
 | Augmentation charge Rinner = 1.298                       |
 | Partial core correction Rc = 1.298                       |
 ------------------------------------------------------------
 | "2|1.8|1.8|1.3|2|3|4|30:31:32LGG(qc=4)"                  |
 ------------------------------------------------------------
 |      Author: Chris J. Pickard, Cambridge University      |
 ============================================================
```

The line

```
  2|1.8|1.8|1.3|2|3|4|30:31:32LGG(qc=4)
```

specifies the parameters used to create the pseudopotential. We use this as the starting point and then remove one of the core 1s electrons to create a core-hole pseudopotential. This is done by including {1s1.00} in the pseudopotential string as shown:

```
  2|1.8|1.8|1.3|2|3|4|30:31:32LGG{1s1.00}(qc=4)
```

If, instead of removing a 1s electron, we wanted to remove a 2s electron from the core, we would have included {2s1.00} instead of {1s1.00} in the pseudopotential string.
To maintain the neutrality of the cell, we include

```
CHARGE : +1
```

in the `Si2_CORE.param` file. Run the calculation. Compare the K-edge from the core-hole calculation with the previous non-core-hole calculation.

The periodic images of the core-hole will interact with one another. As this is unphysical, we need to increase the distance between the core-holes. This is done by creating a supercell. To start with we use a face-centred unit cell rather than the primitive unit cell. This is done by changing the lattice parameters and fractional co-ordinates to:

```
%BLOCK LATTICE_CART
      5.46  0.00 0.00
      0.00  5.46 0.00
      0.00  0.00 5.46
%ENDBLOCK  LATTICE_CART

%BLOCK POSITIONS_FRAC
     Si:1      0.0000000000    0.0000000000    0.0000000000
     Si:2      0.5000000000    0.5000000000    0.0000000000
     Si:2      0.5000000000    0.0000000000    0.5000000000
     Si:2      0.0000000000    0.5000000000    0.5000000000
     Si:2      0.2500000000    0.2500000000    0.2500000000
     Si:2      0.7500000000    0.2500000000    0.7500000000
     Si:2      0.2500000000    0.7500000000    0.7500000000
     Si:2      0.7500000000    0.7500000000    0.2500000000
%ENDBLOCK POSITIONS_FRAC
```

Run `optados` and compare the spectrum from the face-centred unit cell with that from the primitive unit cell. Continue constructing larger unit cells until the core-hole spectrum stops changing with increasing separation between the periodic images.

Extension

Try changing the geometry from polycrystalline to polarized.
Try repeating this for Graphite (or graphene)

4. JDOS

Outline

This is a simple example of using `optados` for calculating joint electronic density of states. We choose to recalculate the Fermi level using the calculated DOS, rather than use the Fermi level suggested by castep, and so **`EFERMI: OPTADOS`** is included in the `Si2.odi` file.

Execute `castep` and `optados` using the example files. The JDOS is written to `Si2.jadaptive.dat`. A file suitable for plotting using xmgrace is written to `Si2.jadaptive.agr`.

Check the effect of changing the sampling by increasing and decreasing the value of **`JDOS_SPACING`** in the `Si2.odi` file.

OPTICS

Two sets of example files are provided for calculations of optical properties. For each example, the `castep` files containing all the cell and simulation parameters are included, along with an `optados` input file.

Example 1 – Silicon

Execute `optados` to calculate the optical properties. Several *.dat files are produced:

1. `Si2_OPTICS_absorption.dat` : This file contains the absorption coefficient (second column) as function of energy (first column).
2. `Si2_OPTICS_conductivity.dat` : This file contains the conductivity outputted in SI units (Siemens per metre). The columns are the energy, real part and imaginary part of the conductivity respectively.
3. `Si2_OPTICS_epsilon.dat` : This file contains the dielectric function. The columns are the energy and real and imaginary parts of the dielectric function respectively. The file header also includes the result of the sum rule

$$\int_o^{\omega'} Im\epsilon(\omega)d\omega = N_{eff}(\omega')$$

where N_{eff} is the effective number of electrons contributing to the absorption process, and is a function of energy.

4. `Si2_OPTICS_loss_fn.dat` : This file contains the loss function (second column) as a function of energy (first column). The header of the file shows the results of the two sum rules associated with the loss function

$$\int_o^{\omega'} Im\left(\frac{-1}{\epsilon(\omega)}\right)\omega\, d\omega = N_{eff}(\omega')$$

and

$$\int_o^{\omega'} Im\left(\frac{-1}{\epsilon(\omega)}\right)\frac{1}{\omega}\, d\omega = \frac{\pi}{2}$$

5. `Si2_OPTICS_reflection.dat` : This file contains the reflection coefficient (second column) as a function of energy (first column).
6. `Si2_OPTICS_refractive_index.dat` : This file contains the refractive index. The columns are the energy and real and imaginary parts of the refractive index respectively.

*Corresponding *.agr files are also generated which can be plotted easily using xmgrace.*

INSTRUCTIONS:
1. Change parameters **`JDOS_SPACING`** and **`JDOS_MAX`** and check the effect on the optical properties. Note: all of the other optical properties are derived from the dielectric function.

2. The `optados` input file has been set up to calculate the optical properties in the polycrystalline geometry (**`optics_geom = polycrystalline`**). It is possible to calculate either polarised or unpolarised geometries, or to calculate the full dielectric tensor. To calculate the full dielectric tensor set **`optics_geom = tensor`**. This time only the file `Si2_OPTICS_epsilon.dat` is generated. The format of this file is the same as before (the columns are the energy and the real and imaginary parts of the dielectric function respectively), but this time the six different components of the tensor are listed sequentially in the order ε_{xx}, ε_{yy}, ε_{zz}, ε_{xy}, ε_{xz} and ε_{yz}.

3. Additional broadening can be included in the calculation of the loss function. This is done by including the keyword **`optics_lossfn_broadening`** in the `optados` input file. If you include this keyword and re-run `optados`, you will find that the file `Si2_OPTICS_loss_fn.dat` now has three columns. These are the energy, unbroadened spectrum and broadened spectrum respectively.

Example 2 – Aluminium

Aluminium is a metal so we need to include both the interband and intraband contributions to the dielectric function. To include the intraband contribution **`optics_intraband = true`** must be included in the `optados` input file. When you run `optados`, the same files are generated as when only the interband term is included.

The `Al_OPTICS_epsilon.dat` file has the same format as before, but it now contains sequentially the interband contribution, the intraband contribution and the total dielectric function. The file `Al_OPTICS_epsilon.agr` only contains the interband term. In the same way, `Al_OPTICS_loss_fn.dat` contains the interband contribution, intraband contribution and total loss function. All other optical properties are calculated from the total dielectric function and the format of the output files remains the same.

In the case where the dielectric tensor is calculated and the intraband term is included, only the `Al_OPTICS_epsilon.dat` file is generated. As before it contains each component, but this time it lists sequentially the interband contribution, intraband contribution and total dielectric function for each component.

This time, if additional broadening for the loss function is included by using the key word **`optics_lossfn_broadening`** then `AL_OPTICS_loss_fn.dat` will contains four sequential data sets. These are the interband contribution, the intraband contribution, the total loss function without the additional broadening and the broadened total loss function.