Phonon-assisted optical absorption with EPW

Tutorial Fri.5

Hands-on session

Exercise

In this example we are going to calculate the phonon-assisted optical absorption spectrum of silicon. This exercise follows the activities of Exercise 2 from Wednesday's tutorial on Conductivities and mobilities.
First copy the tutorial files:

```
$ wget http://epw.org.uk/Documentation/School?action=downloadman&upname=tuto_Fri5.tar
$ tar -xvf tuto_Fri5.tar; cd tuto_Fri/
```

▶ Make a self-consistent calculation for Si.

scf.in

```
 &control
    calculation     = 'scf'
    prefix          = 'si'
    restart_mode    = 'from_scratch'
    wf_collect      = .true.
    pseudo_dir      = './'
    outdir          = './'
 /
 &system
    ibrav           = 2
    celldm(1)       = 10.262
    nat             = 2
    ntyp            = 1
    ecutwfc         = 20
 /
 &electrons
    diagonalization = 'david'
    mixing_beta     = 0.7
    conv_thr        = 1.0d-13
 /
ATOMIC_SPECIES
  Si  28.0855  Si_r.upf
ATOMIC_POSITIONS alat
  Si   0.00  0.00  0.00
  Si   0.25  0.25  0.25
K_POINTS automatic
12 12 12 0 0 0
```

Note: The k-point grid needs to be fairly large in order to get converged dielectric function and Born effective charge during the following phonon calculation.

```
$ mpirun -np 4 q-e/bin/pw.x < scf.in > scf.out
```

▶ Compute the vibrational properties of Si on a coarse 3x3x3 $\mathbf{q}$-point grid.

```
$ mpirun -np 4 q-e/bin/ph.x < ph.in > ph.out &
```

The calculation should take about 15 min on 4 cores. During the run, notice the IBZ q-point grid:

```
 Dynamical matrices for ( 3, 3, 3)  uniform grid of q-points
 (   4 q-points):
   N        xq(1)         xq(2)         xq(3)
   1   0.000000000   0.000000000   0.000000000
   2  -0.333333333   0.333333333  -0.333333333
   3   0.000000000   0.666666667   0.000000000
   4   0.666666667  -0.000000000   0.666666667
```

as well as the dielectric function and Born effective charge tensor:

```
     Dielectric constant in cartesian axis

     (      12.982912147      -0.000000000       0.000000000 )
     (      -0.000000000      12.982912147      -0.000000000 )
     (       0.000000000      -0.000000000      12.982912147 )

     Effective charges (d Force / dE) in cartesian axis

          atom      1   Si
 Ex  (       -0.00778       -0.00000        0.00000 )
 Ey  (       -0.00000       -0.00778        0.00000 )
 Ez  (        0.00000        0.00000       -0.00778 )
          atom      2   Si
 Ex  (       -0.00778       -0.00000       -0.00000 )
 Ey  (       -0.00000       -0.00778        0.00000 )
 Ez  (        0.00000        0.00000       -0.00778 )
```

The experimental dielectric constant in silicon is about 11.9 so that we overestimates it a bit. Smaller value can be obtained with larger $\mathbf{k}$-point grids but DFT will always overestimates experiment. Since Si is a non polar material, the Born effective charges should be 0. Indeed, one can see that we are close to zero. In real calculation you may want to get even smaller values.

▶ Impose the crystal acoustic sum rule and create the interatomic force constant (IFC).

```
&input fildyn='si.dyn', zasr='crystal', flfrc='si.fc' /                    q2r.in
```

```
$  q-e/bin/q2r.x < q2r.in
```

This will create a file named `si.fc` that contain the real space IFC.

▶ Like for the first exercise, run the python post-processing to create the `save` folder

```
$  python pp.py
```

Note: This time the `pp.py` script has an extra line to copy the IFC inside the `save` folder.

▶ Do a non self-consistent calculation on a homogeneous 6x6x6 **positively defined between 0 and 1 k**-point grid.

```
&control                                                                   nscf.in
   calculation     = 'nscf'
   prefix          = 'si'
   restart_mode    = 'from_scratch'
   wf_collect      = .true.
   pseudo_dir      = './'
   outdir          = './'
```

```
 /
 &system
    ibrav           = 2
    celldm(1)       = 10.262
    nat             = 2
    ntyp            = 1
    ecutwfc         = 20
    nbnd            = 12
 /
 &electrons
    diagonalization = 'david'
    mixing_beta     = 0.7
    conv_thr        = 1.0d-10
 /
ATOMIC_SPECIES
  Si  28.0855  Si_r.upf
ATOMIC_POSITIONS alat
  Si   0.00  0.00  0.00
  Si   0.25  0.25  0.25
K_POINTS crystal
216
  0.00000000  0.00000000  0.00000000  4.629630e-03
  0.00000000  0.00000000  0.16666667  4.629630e-03
...
```

```
$ mpirun -np 4 q-e/bin/pw.x -npool 4 < nscf.in > nscf.out
```

▶ Perform an EPW calculation to interpolate the electron-phonon matrix element from a coarse 6x6x6 $\mathbf{k}$ and 3x3x3 $\mathbf{q}$-point grids to real space and then interpolate the electronic and phononic bandstructure along the $L - \Gamma - X$ high symmetry line.

```
--                                                                                epw1.in
&inputepw
  prefix      = 'si'
  amass(1)    = 28.0855
  outdir      = './'

  elph        = .true.
  kmaps       = .false.
  epbwrite    = .true.
  epbread     = .false.
  epwwrite    = .true.
  epwread     = .false.
  etf_mem     = 1

  nbndsub     =  8
  nbndskip    =  0

  lifc        = .true.
  asr_typ     = 'crystal'

  wannierize  = .true.
  num_iter    = 1500
  iprint      = 2
  dis_win_max = 18
  dis_froz_max= 8.5
  proj(1)     = 'Si : sp3'
  wdata(1) = 'bands_plot = .true.'
  wdata(2) = 'begin kpoint_path'
  wdata(3) = 'L 0.50 0.00 0.00 G 0.00 0.00 0.00'
  wdata(4) = 'G 0.00 0.00 0.00 X 0.50 0.50 0.00'
  wdata(5) = 'end kpoint_path'
  wdata(6) = 'bands_plot_format = gnuplot'
  wdata(7) = 'guiding_centres = .true.'
  wdata(8) = 'dis_num_iter      = 500'
  wdata(9) = 'num_print_cycles  = 10'
  wdata(10) = 'dis_mix_ratio     = 1.0'
  wdata(11) = 'use_ws_distance = T'
```

```
  elecselfen  = .false.
  phonselfen  = .false.
  a2f         = .false.

  parallel_k  = .true.
  parallel_q  = .false.

  fsthick     = 1.2 ! eV
  eptemp      = 1 ! K
  degaussw    = 0.005 ! eV

  dvscf_dir   = './save'

  band_plot   = .true.
  filkf       = './LGX.txt'
  filqf       = './LGX.txt'

  nk1         = 6
  nk2         = 6
  nk3         = 6
  nq1         = 3
  nq2         = 3
  nq3         = 3
 /
  4 cartesian
  0.000000000   0.000000000   0.000000000
 -0.333333333   0.333333333  -0.333333333
  0.000000000   0.666666667   0.000000000
  0.666666667  -0.000000000   0.666666667
```

```
$ mpirun -np 4 q-e/bin/epw.x -npool 4 < epw1.in > epw1.out &
```

The calculation should take about 4 min. In the output, notice the additional information related to the crystal ASR. At the end of the calculation, because of the keyword `band_plot = .true.`, the code should produce a `band.eig` and `phband.freq` files that contains the electronic and phononic bandstructure along a path given by `filkf` and `filqf`.
If you want to have files in an easy gnuplot format, you can use the `plotband.x` tool by doing

```
$ q-e/bin/plotbands.x
```

and follow the instructions. You should check that both bandstructure looks reasonable.

▶ Do a restart calculation (restarting from the `si.epmatwp1` file) and compute the phonon-assisted absorption spectrum of silicon in the visible range.
The phonon-assisted optical absorption formalism is presented in J. Noffsinger *et al.*, *Phys. Rev Lett.* **108**, 167402 (2012). The absorption coefficient, with units of inverse length (typicall in cm^{-1}) is calculated according to:

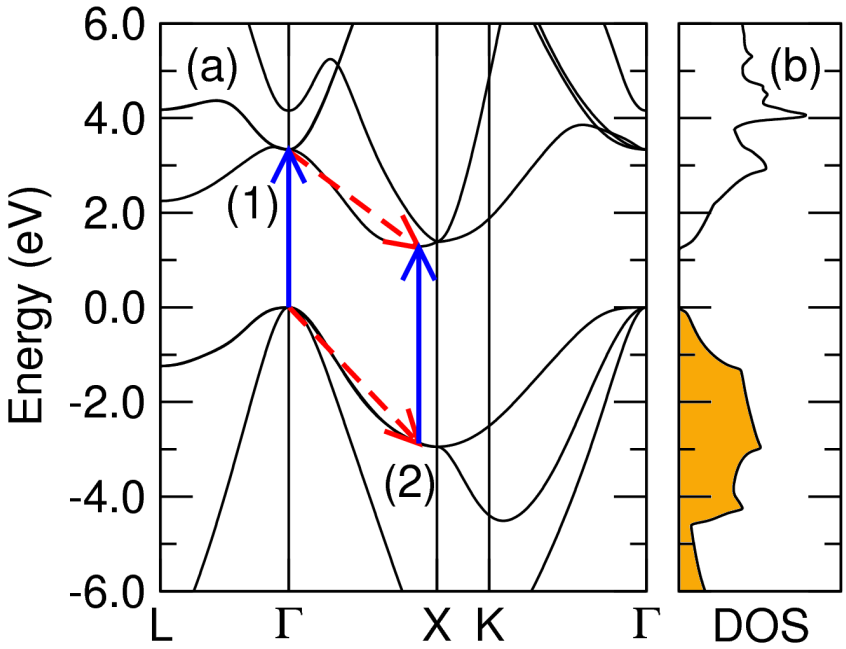
$$\begin{aligned}\alpha(\omega) =& 2\frac{4\pi^2e^2}{\omega c n_r(\omega)}\frac{1}{V_{\text{cell}}}\frac{1}{N_{\mathbf{k}}N_{\mathbf{q}}}\sum_{\nu ij\mathbf{kq}}|\lambda\cdot(\mathbf{S}_1+\mathbf{S}_2)|^2 \\ &\times P\delta(\epsilon_{j,\mathbf{k}+\mathbf{q}}-\epsilon_{i\mathbf{k}}-\hbar\omega\pm\hbar\omega_{\nu\mathbf{q}}),\end{aligned} \tag{1}$$

where $\hbar\omega$ and λ are the energy and polarization of the photon and $n_r(\omega)$ is the refractive index of the material at frequency ω. The generalized optical matrix elements, $\mathbf{S}_1$ and $\mathbf{S}_2$, are given by

$$\mathbf{S}_1(\mathbf{k},\mathbf{q}) = \sum_m \frac{\mathbf{v}_{im}(\mathbf{k})g_{mj,\nu}(\mathbf{k},\mathbf{q})}{\epsilon_{m\mathbf{k}}-\epsilon_{i\mathbf{k}}-\hbar\omega+i\Gamma_{m,\mathbf{k}}}, \tag{2}$$

$$\mathbf{S}_2(\mathbf{k},\mathbf{q}) = \sum_m \frac{g_{im,\nu}(\mathbf{k},\mathbf{q})\mathbf{v}_{mj}(\mathbf{k}+\mathbf{q})}{\epsilon_{m,\mathbf{k}+\mathbf{q}}-\epsilon_{i\mathbf{k}}\pm\hbar\omega_{\nu\mathbf{q}}+i\Gamma_{m,\mathbf{k}+\mathbf{q}}}, \tag{3}$$

and correspond to the two possible paths of the indirect absorption process:



They are determined in terms of the velocity ($\mathbf{v}$) and electron-phonon coupling (g) matrix elements, as well as the real ($\epsilon_{n\mathbf{k}}$) and imaginary ($\Gamma_{n\mathbf{k}}$) parts of the quasiparticle self-energies. The factor P accounts for the carrier and phonon statistics,

$$P = \left(n_{\nu\mathbf{q}} + \frac{1}{2} \pm \frac{1}{2} \right) (f_{i\mathbf{k}} - f_{j,\mathbf{k}+\mathbf{q}}).$$

The upper (lower) sign corresponds to phonon emission (absorption).
The input file is as follows:

```
--                                                                    epw2.in
&inputepw
  prefix      = 'si'
  amass(1)    = 28.0855
  outdir      = './'

  elph        = .true.
  kmaps       = .true.
  epbwrite    = .false.
  epbread     = .false.
  epwwrite    = .false.
  epwread     = .true.
  etf_mem     = 1

!  band_plot = .true.

  lindabs = .true.
  efermi_read = .true.
  fermi_energy = 6.8
  scissor = 0.7

  omegamin = 0.05
  omegamax = 3.0
  omegastep = 0.05
  n_r = 3.4
```

```
 elecselfen  = .false.
 phonselfen  = .false.
 a2f         = .false.

 parallel_k  = .true.
 parallel_q  = .false.

 fsthick     = 4.0 ! eV
 eptemp      = 300 ! K
 degaussw    = 0.05 ! eV

 dvscf_dir   = './save'

 nkf1        = 12
 nkf2        = 12
 nkf3        = 12
 nqf1        = 6
 nqf2        = 6
 nqf3        = 6

 nk1         = 6
 nk2         = 6
 nk3         = 6
 nq1         = 3
 nq2         = 3
 nq3         = 3


 nbndsub     =  8
 nbndskip    =  0

 lifc        = .true.
 asr_typ     = 'crystal'

 wannierize  = .false.
 num_iter    = 1500
 iprint      = 2
 dis_win_max = 18
 dis_froz_max= 8.5
 proj(1)     = 'Si : sp3'
 wdata(1) = 'bands_plot = .true.'
 wdata(2) = 'begin kpoint_path'
 wdata(3) = 'L 0.50 0.00 0.00 G 0.00 0.00 0.00'
 wdata(4) = 'G 0.00 0.00 0.00 X 0.50 0.50 0.00'
 wdata(5) = 'end kpoint_path'
 wdata(6) = 'bands_plot_format = gnuplot'
 wdata(7) = 'guiding_centres = .true.'
 wdata(8) = 'dis_num_iter      = 500'
 wdata(9) = 'num_print_cycles  = 10'
 wdata(10) = 'dis_mix_ratio     = 1.0'
 wdata(11) = 'use_ws_distance = T'


/
 4 cartesian
 0.000000000   0.000000000   0.000000000
-0.333333333   0.333333333  -0.333333333
 0.000000000   0.666666667   0.000000000
 0.666666667  -0.000000000   0.666666667
```

Notes:

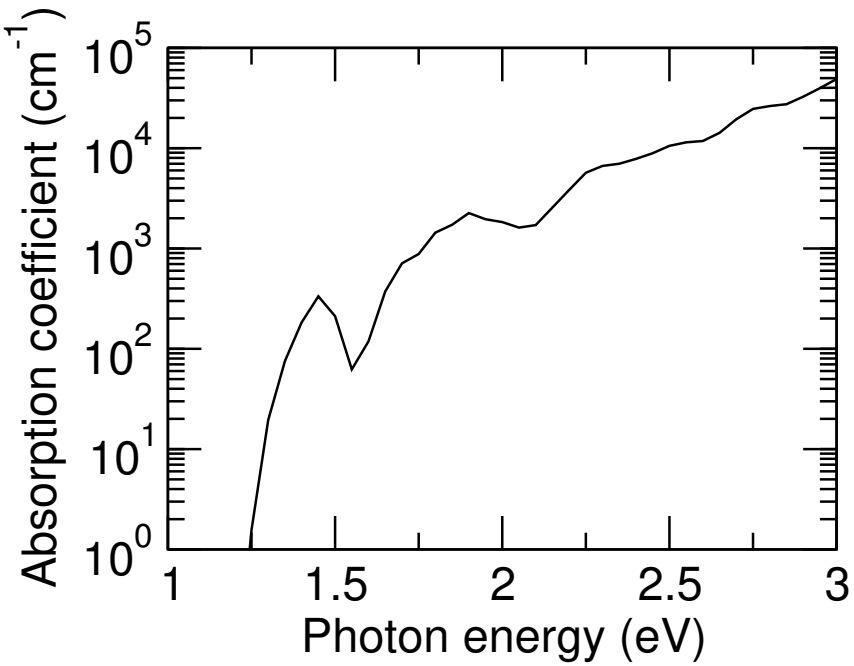
- epwread allow for the restart from the `si.epmatwp1` file.
- `lindabs` enables phonon-assisted optical absorption calculations.
- `scissor` makes a scissor shift to correct for the DFT underestimation of the bandgap.
- `omegamin,omegamax,omegastep` are the minimum, maximum, and spacing of the photon energies for which we calculate the absorption coefficient.
- `fermi_energy = 6.8` sets the Fermi energy for silicon (insulator) in the middle of the gap, and `fsthick` limits

the absorption calculation to states within an energy window around the Fermi level (set to be larger than the maximum photon energy we want the absorption spectra for plus the maximum phonon energy of the material).

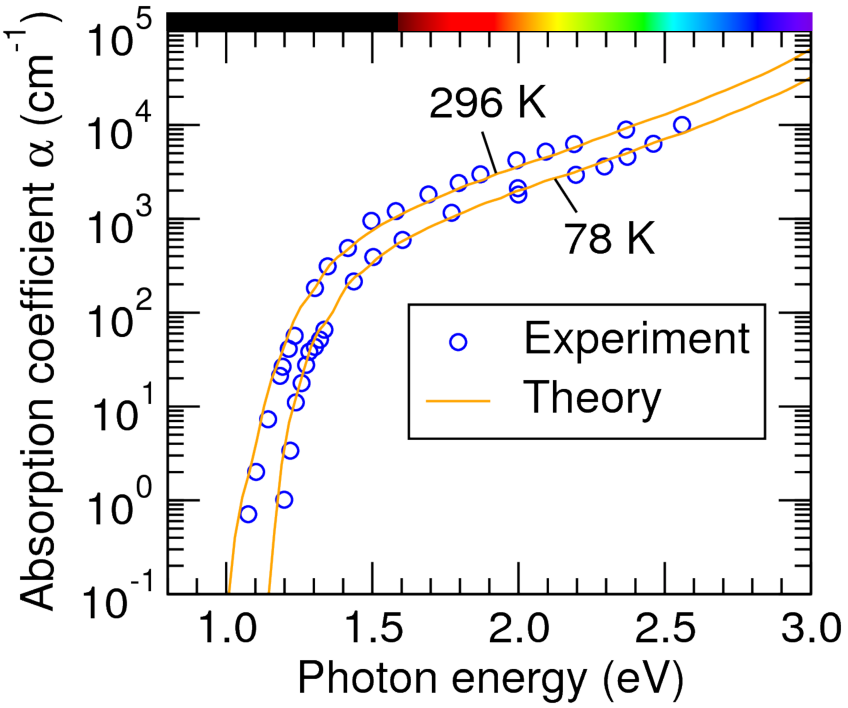
- `n_r` is the refractive index (needed to convert the imaginary part of the dielectric function to the absorption coefficient).
- The imaginary quasiparticle self-energies are taken to be equal to the broadening of the δ function `degaussw`.

```
$ mpirun -np 4 q-e/bin/epw.x -npool 4 < epw2.in > epw2.out &
```

The run should take about 4 min. The result is:



The fine $\mathbf{k}$ and $\mathbf{q}$ point grids need to be denser for production calculations. At convergence you should get a result similar to Fig. 3 of J. Noffsinger *et al.*, *Phys. Rev Lett.* **108**, 167402 (2012):



▶ Increase the fine grids to get closer to convergence.

You can also perform calculations to study the onset of phonon-assisted absorption and see the contributions from the phonon-absorption and the phonon-emission terms. These calculations need a small broadening parameter on the order of 10 meV (smaller than the phonon frequency to distinguish the different onsets of the two terms) and fine $\mathbf{k}$ and $\mathbf{q}$ grids on the order of $40 \times 40 \times 40$. You can accelerate these calculations by selecting a narrow `omegamin` and `omegamax` range and a narrow window for `fsthick`. The converged answer is similar to the spectra below from J. Noffsinger *et al.*, *Phys. Rev Lett.* **108**, 167402 (2012):