

Phonon-assisted optical absorption with EPW

Tutorial Thu. June 15

Hands-on session

Exercise

Before you start, please copy the tutorial tarball to your own scratch directory:

```
$ cp /work2/06868/giustino/EP-SCHOOL/Thu.4.Kioupakis.tar $SCRATCH
```

In this example we are going to calculate the phonon-assisted optical absorption spectrum of silicon. Extract the tarball `Thu.4.Kioupakis.tar`:

```
$ tar -xvf Thu.4.Kioupakis.tar
```

You can find all inputs we will use in this tutorial as well as some output files for verification purposes in the `results` folder. For a complete list of inputs please follow the link:

<https://epwdoc.gitlab.io/source/doc/Inputs.html>

You are advised to prepare the following queue submission script:

```
#!/bin/bash
#SBATCH --nodes=1
#SBATCH --ntasks-per-node=56
#SBATCH --account=EPSchool2022
#SBATCH --partition=small
#SBATCH --reservation=EPSchoolDay4
#SBATCH -t 01:00:00
PATHQE=/work2/06868/giustino/EP-SCHOOL/q-e/bin # this is the path to q-e
cd $PWD
```

Note: The path to the executables are set in the submission script. If you are using your own computer, remember to change the line to:

```
$ export PATHQE='PATH-TO-QE/q-e/bin'
```

► Make a self-consistent calculation for Si.

```
&control
  calculation      = 'scf'
  prefix           = 'si'
  restart_mode     = 'from_scratch'
  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 dense in order to get converged dielectric function and Born effective charge during the following phonon calculation.

```
$ ibrun -np 4 $PATHQE/pw.x < scf.in > scf.out
```

► Compute the vibrational properties of Si on a coarse 3x3x3 q-point grid.

```
$ ibrun -np 56 $PATHQE/ph.x -nk 28 < ph.in > ph.out &
```

The calculation should take about 1 min on 56 cores. During the run, notice the IBZ q-point grid (You can look at the output file or simply use the following command `grep -6 Dynamical ph.out | tail -7`):

```

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 (You can look at the output file or simply use the following command `grep -15 'Dielectric constant in' ph.out | tail -17`):

```

Dielectric constant in cartesian axis

( 12.982914533  0.000000000  0.000000000 )
(  0.000000000  12.982914533 -0.000000000 )
( -0.000000000 -0.000000000  12.982914533 )

```

```

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 of silicon is about 11.9 so that we overestimate it a bit. A smaller value can be obtained with larger k -point grids but DFT will always overestimate 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 a converged calculation you may want to get an even smaller value.

► Like for the previous exercises, run the python post-processing to create the save folder (**No job submission needed, can be ran simply on the login node.**)

```
$ python3 $PATHQE/./EPW/bin/pp.py
```

► Do a non self-consistent calculation on a homogeneous $6 \times 6 \times 6$ **positively defined between 0 and 1** k -point grid.

```
&control
  calculation = 'nscf'
  prefix      = 'si'
  restart_mode = 'from_scratch'
  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
...
```

```
$ ibrun -np 4 $PATHQE/pw.x -npool 4 < nscf.in > nscf.out
```

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

```
--
&inputepw
  prefix      = 'si'
  outdir      = './'

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

  nbndsub     = 8
```

```

eig_read. = .true.

asr_typ   = 'crystal'
use_ws.   = .true.

wannierize = .true.
num_iter  = 1500
iprint    = 2
dis_win_max = 18
dis_froz_max= 9
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.

fsthick    = 1.2 ! eV
temps      = 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
/

```

```
$ ibrun -np 56 $PATHQE/epw.x -npool 56 < epw1.in > epw1.out
```

The calculation should take about 1 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 will produce `band.eig` and `phband.freq` files that contains the electronic and phononic bandstructure along a path given by `filkf` and `filqf`. Note that the tag `eig_read = .true.` asks the code to read in an external set of eigenvalues (see `si.eig`) that needs to be on the same set of k -points grid and number of bands as the `nscf` calculation. Here a set of GW eigenvalues calculated with BerkeleyGW are provided.

Note: An option exists to use QE generated interatomic forces in EPW with setting `lifc = .true.`. This is not recommended, and instead, the combination of `lifc = .false.` (default) and `use_ws = .true.` to ensure construction of the correct Wigner-Seitz cell is always recommended for consistency.

If you want to convert the `band.eig` and `phband.freq` files into a format readable by gnuplot, you can use the `plotband.x` tool by doing: **(No job submission needed, can be ran simply on the login node.)**

```
$ $PATHQE/plotband.x
```

to launch a command line interface for the file generation. Note that the second prompt will define the y-axis bounds. You should check that both bandstructure looks reasonable.

► Do a restart calculation (restarting from the `si.epmatwp` 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 code calculates the imaginary part of the dielectric function due to phonon-assisted optical transitions in the spectral region between the indirect and direct band gaps:

$$\varepsilon_2(\omega) = \frac{8\pi^2 e^2}{\Omega \omega^2} \frac{1}{N_{\mathbf{k}} N_{\mathbf{q}}} \sum_{\nu j \mathbf{k} \mathbf{q}} |\mathbf{e} \cdot (\mathbf{S}_1 + \mathbf{S}_2)|^2 \quad (1)$$

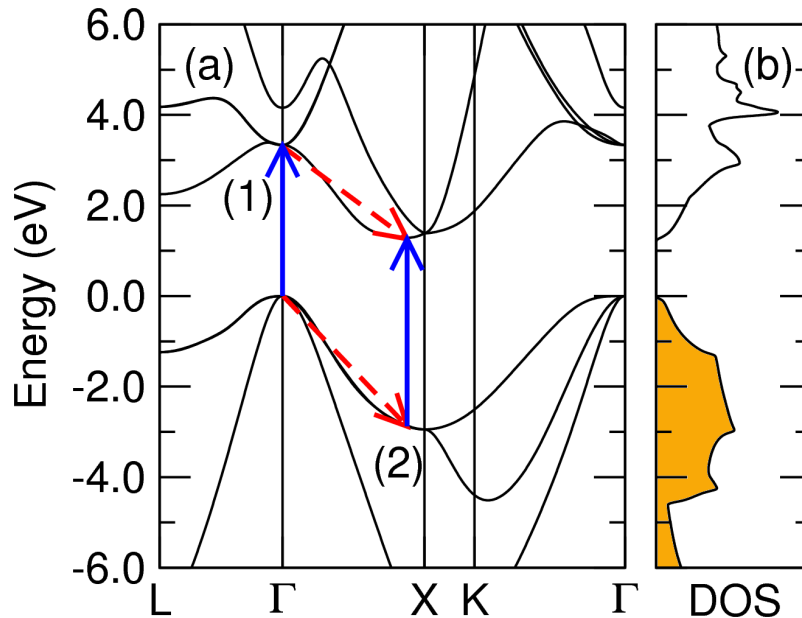
$$\times P \delta(\epsilon_{j, \mathbf{k}+\mathbf{q}} - \epsilon_{i, \mathbf{k}} - \hbar\omega \pm \hbar\omega_{\nu \mathbf{q}}) \quad (2)$$

where $\hbar\omega$ and \mathbf{e} are the energy and polarization of the photon. The generalized optical matrix elements, \mathbf{S}_1 and \mathbf{S}_2 , are given by

$$\mathbf{S}_1(\mathbf{k}, \mathbf{q}) = \sum_m \frac{\mathbf{v}_{im}(\mathbf{k}) g_{mj, \nu}(\mathbf{k}, \mathbf{q})}{\epsilon_{m\mathbf{k}} - \epsilon_{i\mathbf{k}} - \hbar\omega + i\Gamma_{m, \mathbf{k}}}, \quad (3)$$

$$\mathbf{S}_2(\mathbf{k}, \mathbf{q}) = \sum_m \frac{g_{im, \nu}(\mathbf{k}, \mathbf{q}) \mathbf{v}_{mj}(\mathbf{k} + \mathbf{q})}{\epsilon_{m, \mathbf{k}+\mathbf{q}} - \epsilon_{i\mathbf{k}} \pm \hbar\omega_{\nu \mathbf{q}} + i\Gamma_{m, \mathbf{k}+\mathbf{q}}}, \quad (4)$$

and correspond to the two possible paths of the indirect absorption process labelled (1) and (2) in the figure below:



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,

$$P_a = n_{\nu \mathbf{q}} \times f_{i, \mathbf{k}} \times (1 - f_{j, \mathbf{k}+\mathbf{q}}) - (n_{\nu \mathbf{q}} + 1) \times (1 - f_{i, \mathbf{k}}) \times f_{j, \mathbf{k}+\mathbf{q}} \quad (5)$$

$$P_e = (n_{\nu\mathbf{q}} + 1) \times f_{i,\mathbf{k}} \times (1 - f_{j,\mathbf{k}+\mathbf{q}}) - n_{\nu\mathbf{q}} \times (1 - f_{i,\mathbf{k}}) \times f_{j,\mathbf{k}+\mathbf{q}} \quad (6)$$

The P factors can be obtained by considering energy conservation of the absorption/emission process.

The input file is as follows:

```

--                                                                 epw2.in
&inputepw
  prefix      = 'si'
  outdir      = './'

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

! band_plot = .true.

mp_mesh_k = .true.
lindabs = .true.
efermi_read = .true.
fermi_energy = 5.57
eig_read = .true.

omegamin = 0.05
omegamax = 3.0
omegastep = 0.05

eleccselfen = .false.
phonsselfen = .false.
a2f          = .false.

fsthick      = 4.0 ! eV
temps        = 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

use_ws      = .true.
asr_typ     = 'crystal'

wannierize  = .false.
/

```

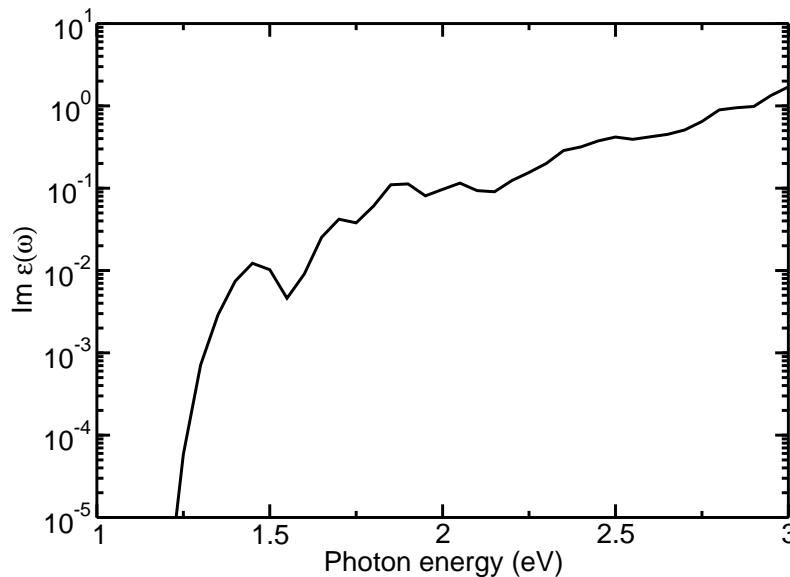
Notes:

- epwread allows for the restart from the si.epmatwp file.

- `lindabs` enables phonon-assisted optical absorption calculations.
- `mp_mesh_k` use only the irr. wedge for the fine electronic mesh. This reduces the computational cost significantly.
- `omegamin`, `omegamax`, `omegastep` are the minimum, maximum, and spacing of the photon energies for which we calculate the absorption coefficient.
- `fermi_energy` = 5.57 sets the Fermi energy for silicon (insulator) in the middle of the gap, and `fsthick` = 4.0 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).
- The code calculates the spectra with nine different broadening parameter values (Γ in the S-parameters, where $\Gamma = 0.001, 0.002, 0.005, 0.01, 0.02, 0.05, 0.1, 0.2, 0.5$ eV). Note that within the indirect region of the spectra, the choice of the broadening of the denominator does not affect the spectra significantly.

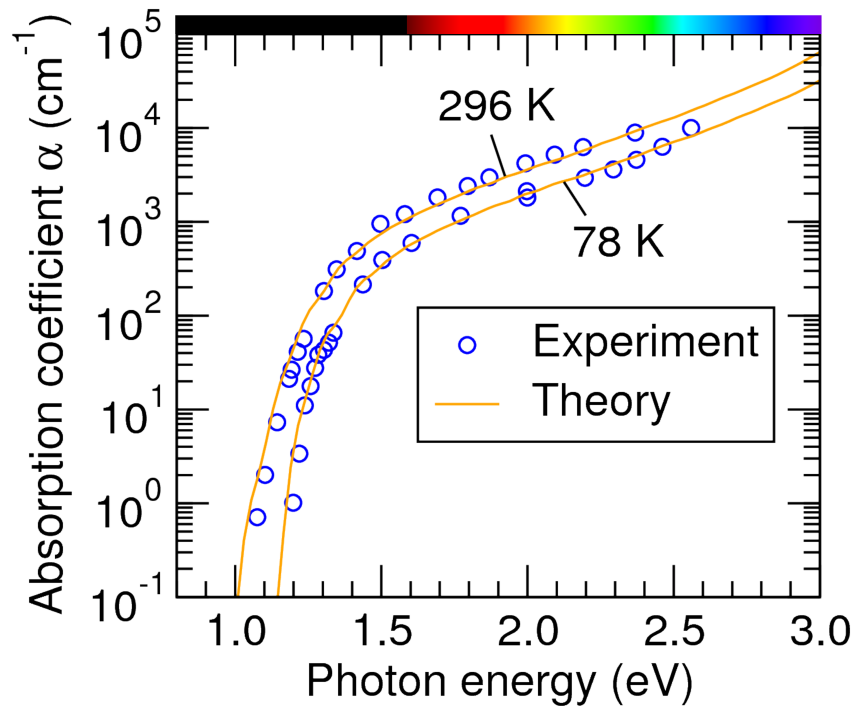
```
$ ibrun -np 56 $PATHQE/epw.x -npool 56 < epw2.in > epw2.out
```

The run should take less than 1 min. You can find the directionally-averaged imaginary part of the phonon-assisted dielectric function for the different broadenings in `epsilon2_indabs_300.0K.dat` (Gaussian broadening for delta function) or `epsilon2_indabs_lorenz300.0K.dat` (Lorentzian broadening for delta function).¹ The first column is photon energy, while the other columns are the corresponding $\epsilon_2(\omega)$ for different Γ s. The result should look like this (for the first Γ with Gaussian broadening for the delta function):



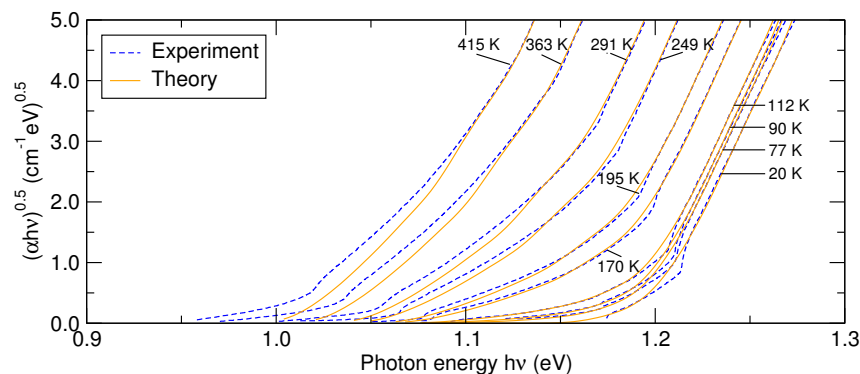
The fine \mathbf{k} and \mathbf{q} point grids need to be denser for production calculations. At convergence you should get a result similar to Fig. 3 of J. Noffsinger *et al.*, *Phys. Rev Lett.* **108**, 167402 (2012). Note that the relationship between $\text{Im } \epsilon(\omega)$ and the absorption coefficient is $\alpha(\omega) = \frac{\omega}{cn_r(\omega)} \text{Im } \epsilon(\omega)$. The paper assumes a constant refractive index of $n_r = 3.4$.

¹Note that direct absorption within the independent particle approximation is also calculated, see `epsilon2_dirabs_300.0K.dat` and `epsilon2_dirabs_lorenz300.0K.dat`. Careful convergence with respect to \mathbf{k} -grid is important.



► Increase the fine grids to improve convergence.

You can also perform calculations to study the onset of phonon-assisted absorption and see the separate 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 phonon-absorption and phonon-emission terms as well as 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 ω_{\min} and ω_{\max} range near the indirect absorption onset and adjusting the `fsthick` window accordingly. The converged result is similar to the spectra below from J. Noffsinger *et al.*, *Phys. Rev. Lett.* **108**, 167402 (2012):



► Optional: phonon-assisted free-carrier absorption (FCA)

In addition to the phonon-assisted optical absorption, you can add the combination of `tags carrier` and `ncarrier` to specify the carrier density in n-type (positive `ncarrier`) or p-type (negative `ncarrier`) semiconductors to study phonon-assisted free-carrier absorption. The input for such a calculation is provided in `epw3.in`.


```
--  
&inputepw  
...  
  
omegamin = 0.05  
omegamax = 3.0  
omegastep = 0.05  
carrier = .true.  
ncarrier = 1e19  
  
...  
  
nkf1      = 16  
nkf2      = 16  
nkf3      = 16  
nqf1      = 16  
nqf2      = 16  
nqf3      = 16  
  
...  
/
```

Note that the \mathbf{k} - and \mathbf{q} -points grid are finer in the input for this optional calculation. Since free-carrier absorption happens close to the conduction band minimum or valence band maximum, a much denser grid is necessary to obtain converged result. In practice, one can typically use a smaller value of `fsthick` to reduce the computational cost due to that free-carrier absorption is dominant only in sub-gap region where photon energy is relatively small compared to cross-gap indirect absorption.

Take a look at the output `epsilon2_indabs_300.0K.dat`, you will notice the $\epsilon_2(\omega)$ now contains sub-gap contributions that results from free-carrier absorption. You may also notice that the spectrum now has a strong dependence on the broadening Γ in Eq.(3) and Eq.(4), which is due to the divergence of the denominator. This divergence is present when direct transition (in this case, inter-conduction bands) is possible, and is a limitation of the second-order perturbation theory itself. It can be reduced by numerical approaches to cancel the diverging term, see e.g. Brown *et al.*, *ACS Nano*, **10.1**, 957-966 (2016).

More details about free-carrier absorption can be found at: <https://arxiv.org/abs/2205.02768>