
MAX School on Advanced Materials and Molecular Modelling
with **QUANTUM ESPRESSO**

QE-2021: Hands-on session – Day-6

TDDFPT

Iurii Timrov (EPFL, Switzerland)

Oscar Baseggio (SISSA, Italy)

Outline

1. **Part I** – Optical absorption in molecules
2. **Part II** – EELS in solids

(We will use HPC for this hands-on, because many examples are quite heavy)

Part I – Optical absorption in molecules

1. **Example 1:** **turboDavidson** – from the Independent Particle Approximation (IPA) to interacting electrons
2. **Example 2:** **turboLanczos** – total spectra at low cost for interacting electrons

turboDavidson program for calculations of absorption spectra

- The **turbo_davidson.x** program allows us to calculate absorption spectra of molecules using time-dependent density functional perturbation theory (TDDFpT).
- The interactions of electrons (**Hartree** and **Exchange-Correlation effects**) are taken into account fully *ab initio* and self-consistently (or they can be neglected **if_dft_spectrum=.true.**).
- The electronic transitions from occupied to empty states can be analyzed by selecting a frequency range in which the transitions occur.
- However, calculations of overall absorption spectra in a wide frequency range are computationally rather expensive, because many eigenvalues of the Hamiltonian must be computed.

turboDavidson program for calculations of absorption spectra

Coupled linear-response TDDFpT equations (**resonant** and **anti-resonant**):

$$\begin{aligned} (\hat{H}^o - \varepsilon_v - \hbar\omega) \tilde{\varphi}'_v(\mathbf{r}, \omega) + \hat{P}_c \hat{V}'_{\text{HXC}}[\tilde{\varphi}'_v(\mathbf{r}, \omega), \tilde{\varphi}'_v^*(\mathbf{r}, -\omega)] \varphi_v^o(\mathbf{r}) &= 0 \\ (\hat{H}^o - \varepsilon_v + \hbar\omega) \tilde{\varphi}'_v^*(\mathbf{r}, -\omega) + \hat{P}_c \hat{V}'_{\text{HXC}}[\tilde{\varphi}'_v(\mathbf{r}, \omega), \tilde{\varphi}'_v^*(\mathbf{r}, -\omega)] \varphi_v^o(\mathbf{r}) &= 0 \end{aligned}$$

These equations can be re-written as Casida's matrix equation:

$$\begin{pmatrix} 0 & \hat{D} \\ \hat{D} + \hat{K} & 0 \end{pmatrix} \begin{pmatrix} Q \\ P \end{pmatrix} = \omega \begin{pmatrix} Q \\ P \end{pmatrix}$$

interaction terms

where $\hat{D} \longrightarrow (\hat{H}^o - \varepsilon_v)$ and $\hat{K} \longrightarrow \hat{P}_c \hat{V}'_{\text{HXC}} \varphi_v^o(\mathbf{r})$

Davidson algorithm is used (the same algorithm as in the ground state SCF calculation) to solve the Casida's equations and to obtain the eigenvalues which are used for a calculation of the absorption coefficient.

Independent Particle Approximation

The simplest approximation: Independent Particle Approximation (IPA) - a sum of independent excitations from occupied to empty states.

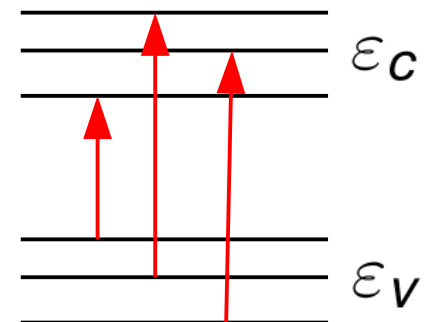
Fermi's golden rule

The transition probability per unit time from occupied states $|\varphi_v\rangle$ to empty states $|\varphi_c\rangle$ reads:

$$T(\omega) = \frac{2\pi}{\hbar} \sum_{v,c} \delta(\varepsilon_c - \varepsilon_v - \hbar\omega) \left| \langle \varphi_c | V'_{ext} | \varphi_v \rangle \right|^2$$

$V'_{ext} = -e\mathbf{E} \cdot \mathbf{r}$ is the external potential induced by the electric field.

$\varepsilon_v, \varepsilon_c$ and $|\varphi_v\rangle, |\varphi_c\rangle$ are the eigenvalues and the eigenfunctions of the ground-state Kohn-Sham equation

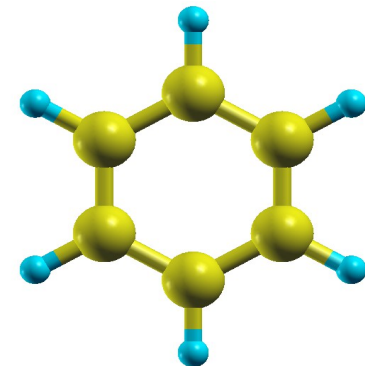
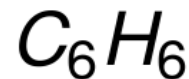


Example 1: Input file for PWscf

Step 1. Perform a Self-Consistent Field ground-state calculation for benzene at the equilibrium structure using the **pw.x** program.

Specify the total number of Kohn-Sham bands (occupied + some empty states)

```
&CONTROL
  calculation = 'scf'
  restart_mode='from_scratch',
  prefix='Benzene'
  pseudo_dir = '../..//pseudo'
  outdir=' /tmp',
/
&SYSTEM
 ibrav = 6,
  celldm(1) = 32,
  celldm(3) = 0.83,
  nat = 12,
  ntyp = 2,
  ecutwfc = 30,
  nbnd = 20
/
&ELECTRONS
  conv_thr = 1.0d-8
  mixing_beta = 0.6,
/
ATOMIC_SPECIES
H 1.0 H.blyp-vbc.UPF
C 12.01 C.blyp-mt.UPF
ATOMIC_POSITIONS {Angstrom}
C 5.633200899 6.320861303 5.000000000
C 6.847051545 8.422621957 5.000000000
C 8.060751351 7.721904557 5.000000000
C 8.060707879 6.320636665 5.000000000
C 6.846898786 5.620067381 5.000000000
C 5.633279551 7.722134449 5.000000000
H 6.847254360 9.512254789 5.000000000
H 9.004364510 8.266639340 5.000000000
H 9.004297495 5.775895755 5.000000000
H 6.846845929 4.530522778 5.000000000
H 4.689556006 5.776237709 5.000000000
H 4.689791688 8.267023318 5.000000000
K_POINTS {gamma}
```



Input

Output

pw.x < pw.benzene.scf.in > pw.benzene.scf.out

Example 1: Output file of PWscf

The output SCF file **pw.benzene.scf.out** :

```
End of self-consistent calculation
```

```
k = 0.0000 0.0000 0.0000 ( 37796 PWs)   bands (ev):
```

```
-21.1410 -18.3897 -18.3884 -14.6742 -14.6729 -12.5121 -11.0334 -10.4379  
-9.8983  -9.8963  -8.5697  -7.8759  -7.8751  -5.8257  -5.8251  -0.7364  
-0.7362  -0.3332   0.2501   0.3207
```

```
highest occupied, lowest unoccupied level (ev):  -5.8251  -0.7364
```

HOMO **LUMO**

HOMO – Highest Occupied Molecular Orbital

LUMO – Lowest Unoccupied Molecular Orbital

Energy gap = **LUMO** – **HOMO** = 5.1 (eV)

Example 1: Calculation of absorption spectra using turboDavidson (IPA)

Perform the turboDavidson calculation without the electronic interaction using the **turbo_davidson.x** program.

```
&lr_input  
  prefix = 'Benzene',  
  outdir = './tmp'  
/  
&lr_dav  
  if_dft_spectrum = .true.  
  num_init        = 30  
/
```

Same as in PWscf

This means we are using IPA

Obsolete variable for the IPA case
(will not be needed in future version of
QE for the IPA case)

```
turbo_davidson.x < turbo_davidson.benzene.in > turbo_davidson.benzene.out
```

Example 1: Post-processing step

Perform a spectrum calculation using the **turbo_spectrum.x** program and using the eigenvalues computed in the previous step.

turbo_spectrum.benzene.in :

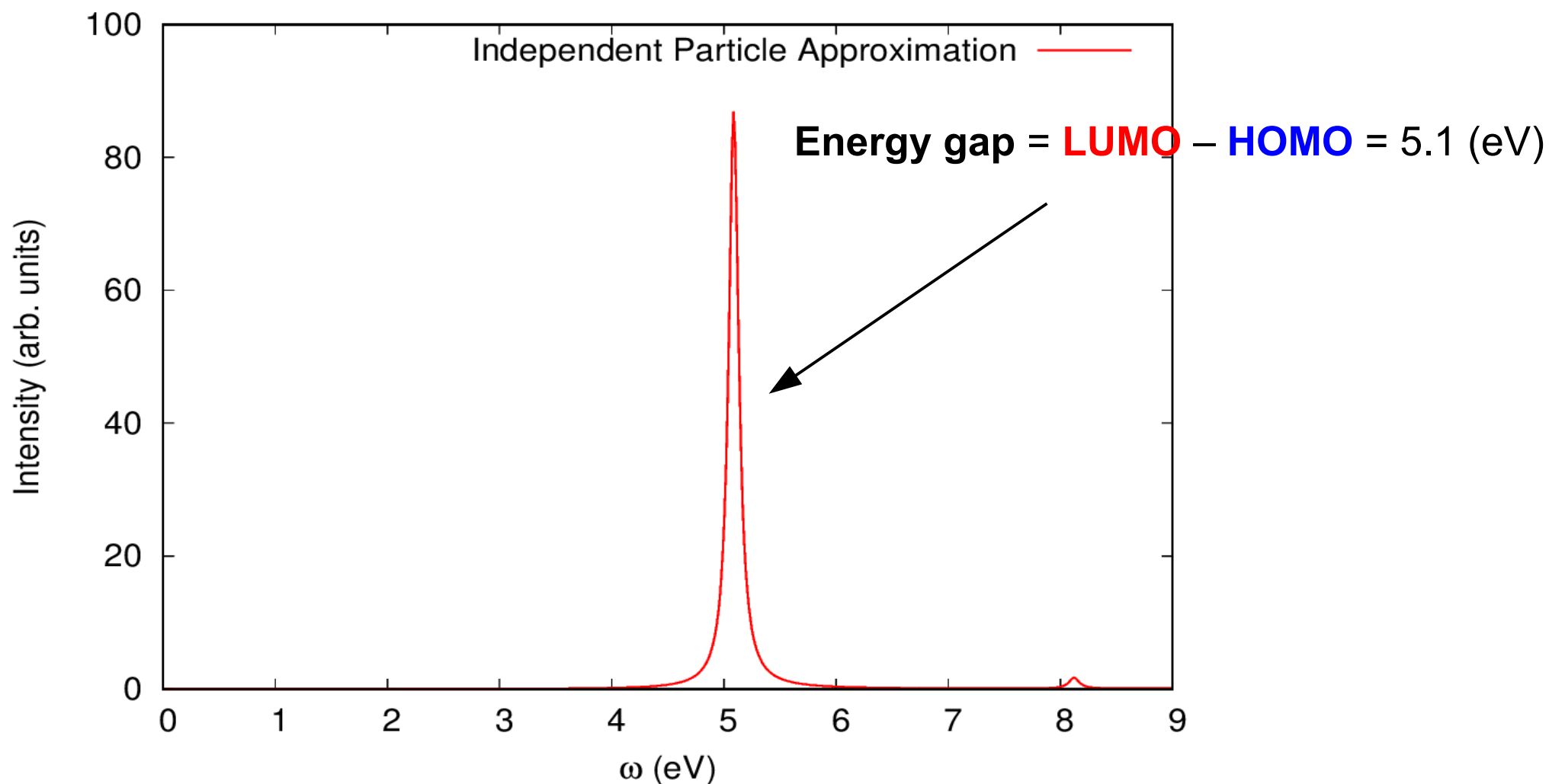
<code>&lr_input</code>	
<code>prefix = 'Benzene',</code>	← Prefix the same as in PWscf
<code>outdir = './tmp',</code>	← Directory for temporary (same as in PWscf)
<code>td = 'davidson',</code>	← Type of previous calculation
<code>start = 0.0,</code>	← Starting value of the freq. for the plot
<code>end = 1.0,</code>	← End value of the freq. for the plot
<code>increment = 0.001,</code>	← Freq. step for the plot
<code>epsil = 0.004,</code>	← Lorentzian broadening in Ry
<code>eign_file = 'Benzene-dft.eigen'</code>	← File with Davidson eigenvalues
<code>/</code>	

turbo_spectrum.x < turbo_spectrum.benzene.in > turbo_spectrum.benzene.out

Example 1: Calculation of absorption spectra in IPA

Absorption spectrum of benzene in the Independent Particle Approximation (file `Benzene_spectrum.eps`):

Use the script `plot_spectrum.gp` to produce this figure.



Example 1: Spectra including interactions

Perform the turboDavidson calculation without the electronic interaction using the **turbo_davidson.x** program.

```
&lr_input
  prefix = 'Benzene',
  outdir=' /tmp'
/
&lr_dav
  if_dft_spectrum = .false.
  num_eign = 15
  num_init = 30
  num_basis_max = 90
  residue_conv_thr = 1.0E-4
  start = 0.0
  finish = 1.0
  step = 0.001
  broadening = 0.004
  reference = 0.3
/
```

← The same prefix as in the SCF calculation

← Directory for temporary files

← **Switch on the interactions**

← Number of eigenvalues to be calculated

← Number of initial vectors

← Maximum number of basis allowed for the sub-basis

← Convergence threshold

← Minimum value of frequencies for a plot in Ry

← Maximum value of frequencies for a plot in Ry

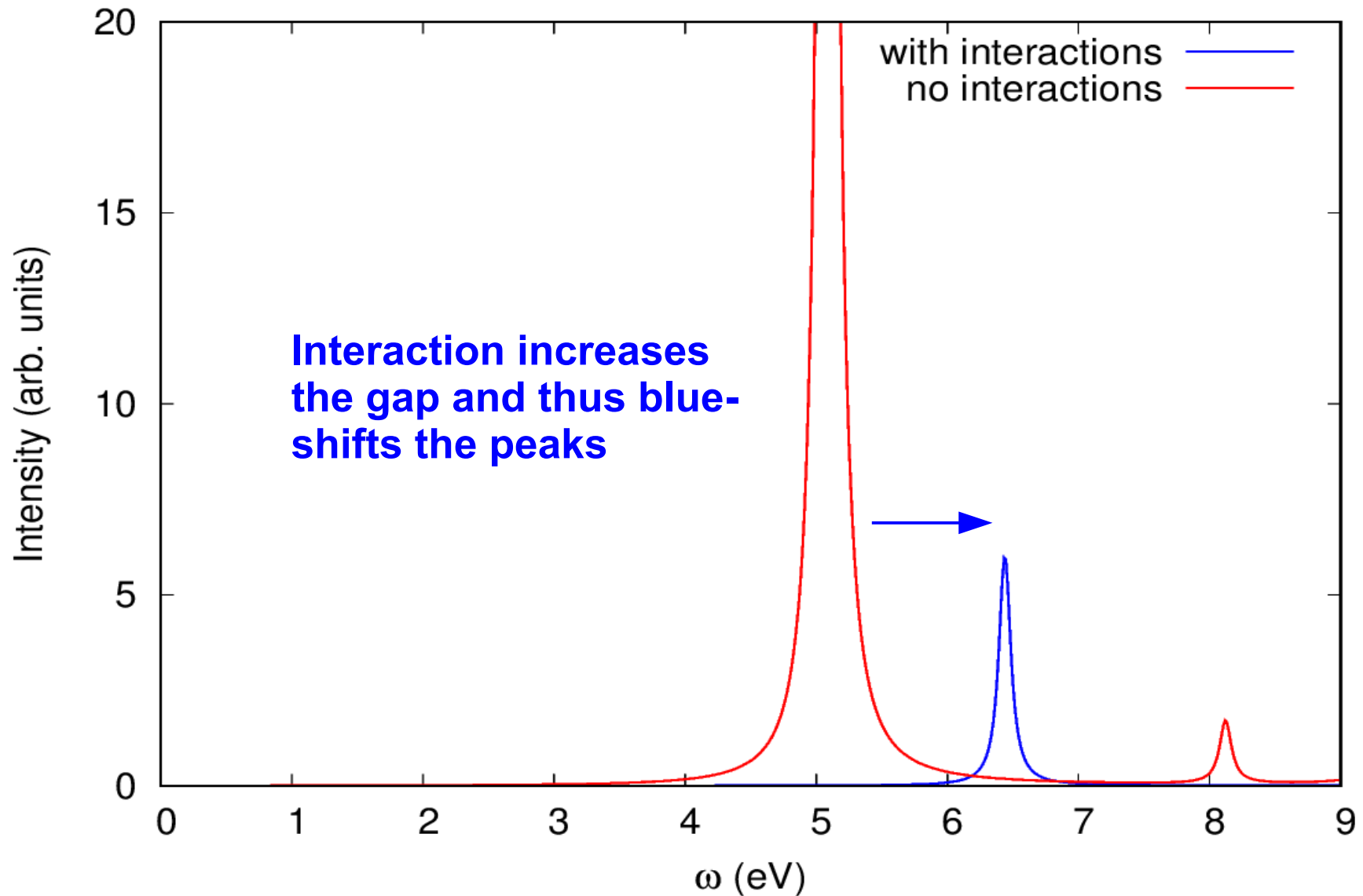
← Frequency step in Ry

← Lorentzian broadening parameter in Ry

← Reference frequency in Ry where the peak is expected

turbo_davidson.x < turbo_davidson.benzene.in > turbo_davidson.benzene.out

Example 1: Comparison of spectra with and without interactions



turboLanczos program for calculation of absorption spectra

- The **turbo_lanczos.x** program allows us to calculate absorption spectra of molecules using time-dependent density functional perturbation theory (TDDFpT) **without computing empty states!**
- The interactions of electrons (**Hartree** and **Exchange-Correlation effects**) are taken into account fully *ab initio* and self-consistently.
- The electronic transitions from occupied to empty states cannot be analyzed (use **turbo_davidson.x** for this purpose).
- The overall absorption spectrum in a wide frequency range **can be calculated at once!**

turboLanczos program for calculation of absorption spectra

Coupled linear-response TDDFpT equations (**resonant** and **anti-resonant**):

$$\begin{aligned}
 (\hat{H}^o - \varepsilon_v - \hbar\omega) \tilde{\varphi}'_v(\mathbf{r}, \omega) + \hat{P}_c \hat{V}'_{\text{HXC}}[\tilde{\varphi}'_v(\mathbf{r}, \omega), \tilde{\varphi}'_v^*(\mathbf{r}, -\omega)] \varphi_v^o(\mathbf{r}) &= -\hat{P}_c \hat{V}'_{\text{ext}} \varphi_v^o(\mathbf{r}) \\
 (\hat{H}^o - \varepsilon_v + \hbar\omega) \tilde{\varphi}'_v^*(\mathbf{r}, -\omega) + \hat{P}_c \hat{V}'_{\text{HXC}}[\tilde{\varphi}'_v(\mathbf{r}, \omega), \tilde{\varphi}'_v^*(\mathbf{r}, -\omega)] \varphi_v^o(\mathbf{r}) &= -\hat{P}_c \hat{V}'_{\text{ext}} \varphi_v^o(\mathbf{r})
 \end{aligned}$$

perturbation

These equations can be re-written as a quantum Liouville equation: **interaction terms**

$$\begin{aligned}
 (\omega - \mathcal{L}) \cdot \rho'(\omega) &= [\hat{V}'_{\text{ext}}, \rho^o] \\
 \mathcal{L} \cdot \rho' &\equiv [\hat{H}^o, \rho'] + [\hat{V}'_{\text{HXC}}, \rho^o]
 \end{aligned}$$

Absorption coefficient is computed as:

$$\alpha(\omega) = -(\mathbf{r}, (\omega - \mathcal{L})^{-1} [\mathbf{r}, \rho^o])$$

Lanczos algorithm is used to solve recursively quantum Liouville equation in the standard batch representation. This allows us to avoid inversions and multiplications of large matrices.

Example 2: Calculation of absorption spectra using turboLanczos

Step 1. Perform a SCF ground-state calculation (no **nbnd** in the input):

```
pw.x < pw.benzene.scf.in > pw.benzene.scf.out
```

Step 2. Perform Lanczos recursions using the **turbo_lanczos.x** program.

```
&lr_input  
  prefix = 'Benzene',  
  outdir=' /tmp ',  
  restart_step = 100,  
  restart = .false.  
/  
&lr_control  
  itermx = 500,  
  ipol = 1  
/
```

← The same prefix as in the SCF calculation

← Directory for temporary files

← The code writes restart files every restart_step iterations

← Restart iterations after previous calculation

← Number of Lanczos iterations

← Polarization direction of incoming light, 1=x

```
turbo_lanczos.x < turbo_lanczos.benzene.in > turbo_lanczos.benzene.out
```


Example 2: Post-processing step

Perform a spectrum calculation using the post-processing program **turbo_spectrum.x** and using the Lanczos coefficients computed in the previous step.

```
&lr_input
  prefix = 'Benzene',
  outdir = '/tmp',
  itermax0 = 500,
  itermax = 500,
  extrapolation = 'no',
  epsil = 0.004,
  start = 0.0d0,
  end = 1.0d0,
  increment = 0.0001d0,
  ipol = 1
/
```

- ← The same prefix as in the SCF calculation
- ← Directory for temporary files
- ← Number of calculated Lanczos coefficient
- ← Number of extrapolated Lanczos coefficient
- ← Type of extrapolation
- ← The value of Lorentzian smearing in Ry
- ← Minimum value of frequencies for a plot in Ry
- ← Maximum value of frequencies for a plot in Ry
- ← Frequency step in Ry
- ← Polarization direction (same as in turbo_lanczos.x)

```
turbo_spectrum.x < turbo_spectrum.benzene.in >...
...turbo_spectrum.benzene.out
```

Example 2: Post-processing step

No extrapolation of Lanczos coefficients

turbo_lanczos.benzene.in

```
&lr_input
  prefix = 'Benzene',
  outdir=' /tmp ',
  restart_step = 100,
  restart = .false.
/
&lr_control
  itermax = 500,
  ipol = 1
/
```

turbo_spectrum.benzene.in

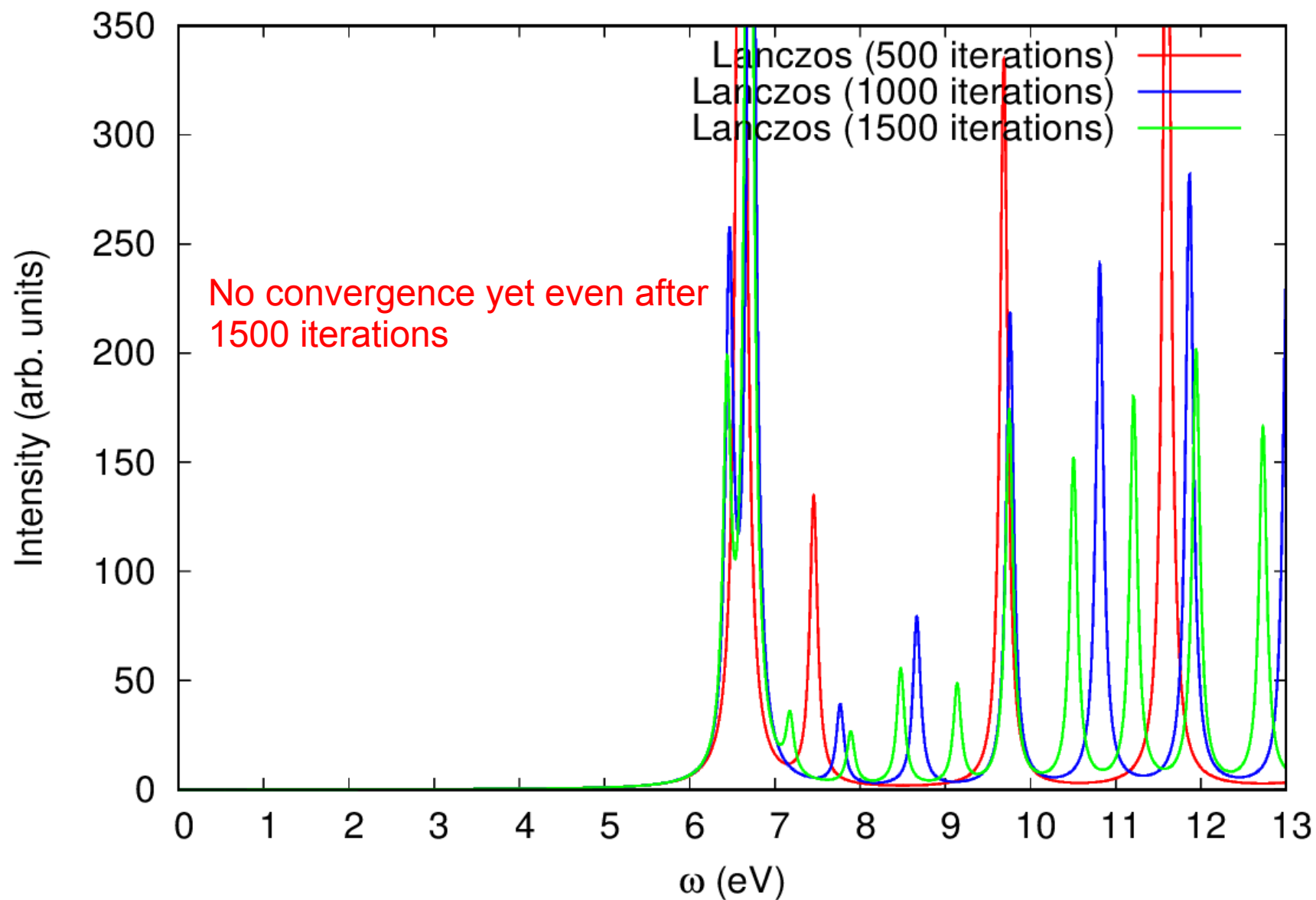
```
&lr_input
  prefix = 'Benzene',
  outdir = ' /tmp ',
  itermax0 = 500,
  itermax = 500,
  extrapolation = 'no',
  epsil = 0.004,
  start = 0.0d0,
  end   = 1.0d0,
  increment = 0.0001d0,
  ipol = 1
/
```

Must be equal !

You can use **restart = .true.** option in order not to start from scratch, when you want to increase the number of Lanczos iterations.

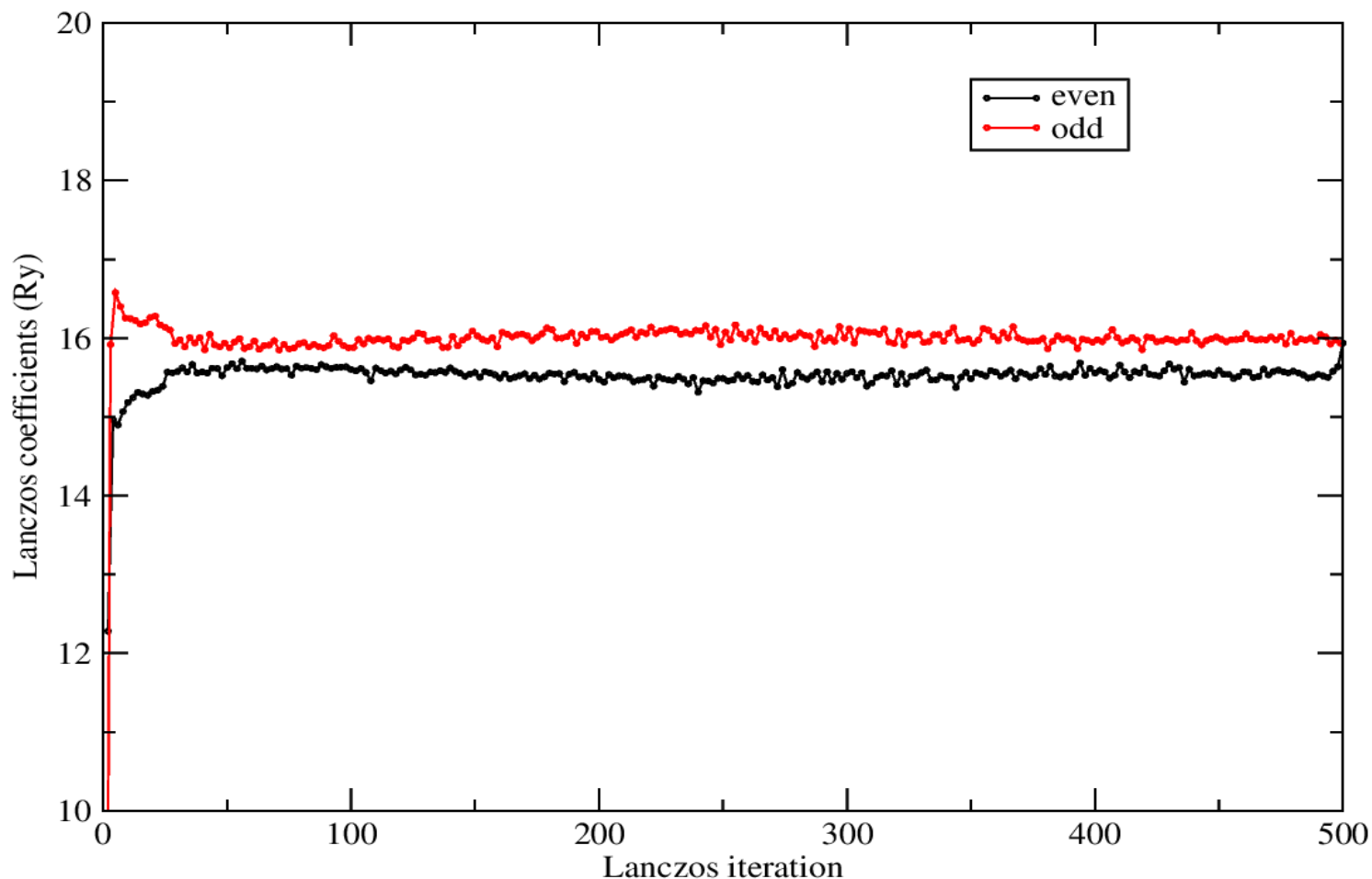
Example 2: Post-processing step

No extrapolation of Lanczos coefficients



Example 2: Lanczos coefficients

Behavior of β Lanczos coefficients



Lanczos coefficients oscillate around half of the kinetic-energy cutoff ($\sim 30/2 = 15$ Ry in this case). Hence, we can extrapolate these coefficients.

Example 2: Extrapolation of Lanczos coefficients

In the Liouville-Lanczos approach, the absorption coefficient is computed as:

$$\alpha(\omega) = (\zeta_N, (\omega - \hat{T}_N)^{-1} \cdot \mathbf{e}_1^N)$$

where \hat{T}_N is the tridiagonal matrix composed of the Lanczos coefficients.

$$\hat{T}_N = \begin{pmatrix} 0 & \gamma_2 & 0 & \cdots & 0 \\ \beta_2 & 0 & \gamma_3 & 0 & 0 \\ 0 & \beta_3 & 0 & \ddots & 0 \\ \vdots & 0 & \ddots & \ddots & \gamma_N \\ 0 & \cdots & 0 & \beta_N & 0 \end{pmatrix} \xrightarrow{\text{Extrapolation}} \hat{T}_{N'} = \begin{pmatrix} 0 & \gamma_2 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ \beta_2 & 0 & \gamma_3 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & \beta_3 & 0 & \ddots & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & \ddots & \ddots & \gamma_N & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & \beta_N & 0 & \langle \gamma \rangle & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & \langle \beta \rangle & 0 & \langle \gamma \rangle & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & \ddots & 0 & \ddots & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & \langle \beta \rangle & 0 & \langle \gamma \rangle \end{pmatrix}$$

$$\langle \beta \rangle = \frac{\beta_1 + \beta_2 + \dots + \beta_N}{N}$$

$$\langle \gamma \rangle = \frac{\gamma_1 + \gamma_2 + \dots + \gamma_N}{N}$$

$$N = \text{itermax0}, \quad N' = \text{itermax}$$

Example 2: Post-processing step

With extrapolation of Lanczos coefficients

turbo_lanczos.benzene.in

```
&lr_input
  prefix = 'Benzene',
  outdir=' /tmp ',
  restart_step = 100,
  restart = .false.
/
&lr_control
  itermax = 500,
  ipol = 1
/
```

turbo_spectrum.benzene.in

```
&lr_input
  prefix = 'Benzene',
  outdir = ' /tmp ',
  itermax0 = 500,
  itermax = 20000,
  extrapolation = 'osc',
  epsil = 0.004,
  start = 0.0d0,
  end = 1.0d0,
  increment = 0.0001d0,
  ipol = 1
/
```

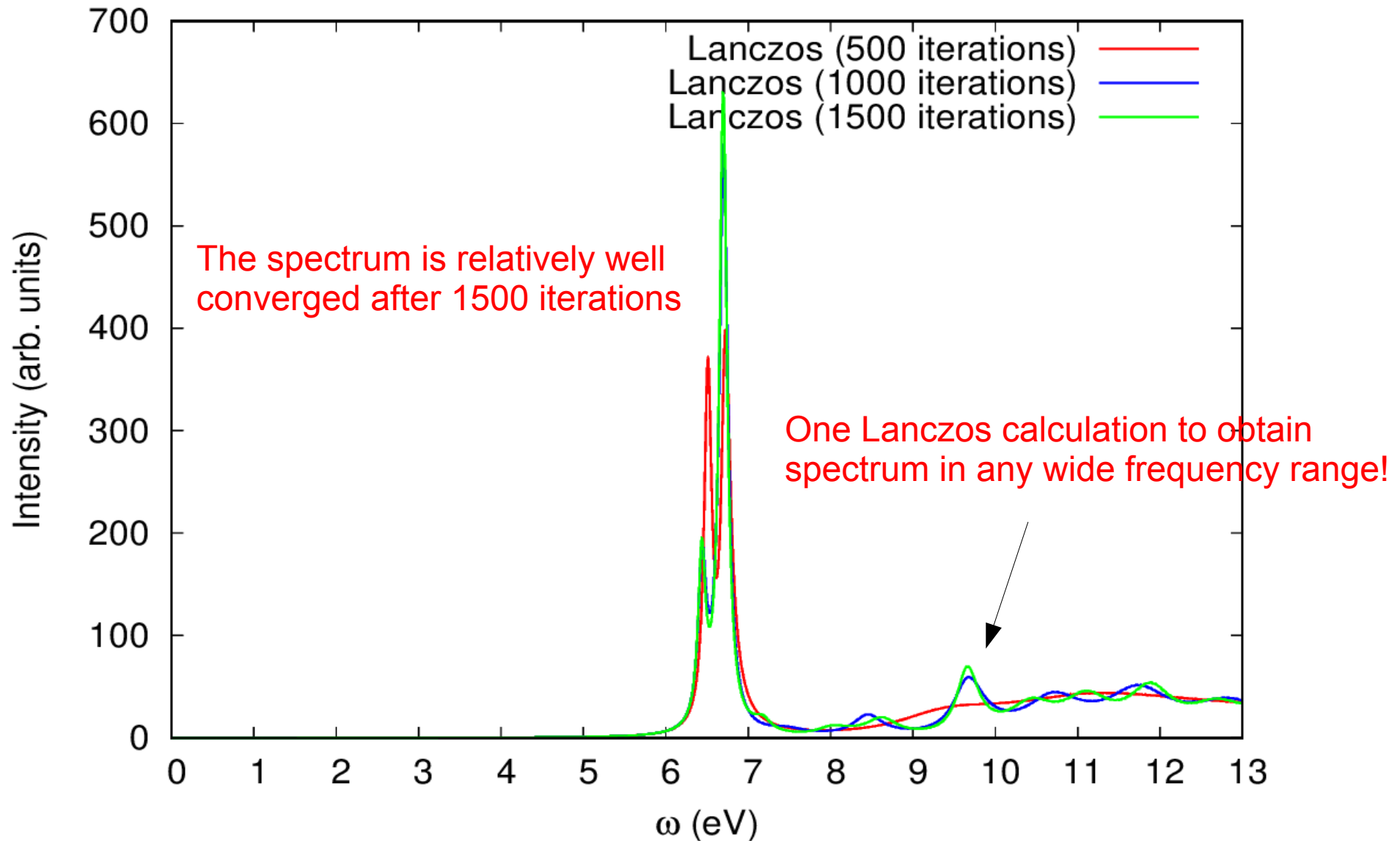
Must be equal !

Extrapolation until 20000

You can use `restart = .true.` option in order not to start from scratch, when you want to increase the number of Lanczos iterations.

Example 2: Post-processing step

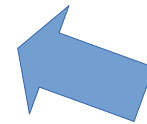
With extrapolation of Lanczos coefficients



Part II – EELS in solids

1. **Example 3:** EELS spectrum of Si using the **turboEELS** code (**Lanczos algorithm**)

2. **Example 4:** EELS spectrum of Si using the **turboEELS** code (**Sternheimer algorithm**)



OPTIONAL
(very slow)

Basic equations

Coupled (**resonant** and **anti-resonant**) frequency-dependent **Sternheimer** equations:

$$\begin{aligned}
 (\hat{H}_{\mathbf{k}+\mathbf{q}}^{\circ} - \varepsilon_{n,\mathbf{k}}^{\circ} - \omega) \tilde{u}'_{n,\mathbf{k}+\mathbf{q}}(\mathbf{r}, \omega) + \boxed{\hat{P}_c^{\mathbf{k}+\mathbf{q}} \tilde{v}'_{\text{HXC},\mathbf{q}}(\mathbf{r}, \omega) u_{n,\mathbf{k}}^{\circ}(\mathbf{r})} &= \boxed{-\hat{P}_c^{\mathbf{k}+\mathbf{q}} \tilde{v}'_{\text{ext},\mathbf{q}}(\mathbf{r}, \omega) u_{n,\mathbf{k}}^{\circ}(\mathbf{r})} \\
 (\hat{H}_{\mathbf{k}+\mathbf{q}}^{\circ} - \varepsilon_{n,\mathbf{k}}^{\circ} + \omega) \tilde{u}'_{n,-\mathbf{k}-\mathbf{q}}(\mathbf{r}, -\omega) + \boxed{\hat{P}_c^{\mathbf{k}+\mathbf{q}} \tilde{v}'_{\text{HXC},\mathbf{q}}(\mathbf{r}, \omega) u_{n,\mathbf{k}}^{\circ}(\mathbf{r})} &= \boxed{-\hat{P}_c^{\mathbf{k}+\mathbf{q}} \tilde{v}'_{\text{ext},\mathbf{q}}(\mathbf{r}, \omega) u_{n,\mathbf{k}}^{\circ}(\mathbf{r})}
 \end{aligned}$$

interaction terms
perturbation

These equations can be re-written as a quantum Liouville equation and solved using the **Lanczos** algorithm:

$$\begin{aligned}
 (\omega - \mathcal{L}) \cdot \hat{\rho}'_{\mathbf{q}}(\omega) &= [\tilde{V}'_{\text{ext},\mathbf{q}}(\omega), \hat{\rho}^{\circ}] \\
 \mathcal{L} \cdot \hat{\rho}'_{\mathbf{q}} &\equiv [\hat{H}^{\circ}, \hat{\rho}'_{\mathbf{q}}] + [\tilde{V}'_{\text{HXC},\mathbf{q}}, \hat{\rho}^{\circ}]
 \end{aligned}$$

$\chi(\mathbf{q}, \mathbf{q}; \omega)$
Susceptibility

$$-\text{Im}[\varepsilon^{-1}(\mathbf{q}, \omega)] = -\frac{4\pi e^2}{|\mathbf{q}|^2} \text{Im}[\chi(\mathbf{q}, \mathbf{q}; \omega)]$$

Loss function

Example 3

Coupled (**resonant** and **anti-resonant**) frequency-dependent **Sternheimer** equations:

$$\begin{aligned}
 (\hat{H}_{\mathbf{k}+\mathbf{q}}^{\circ} - \varepsilon_{n,\mathbf{k}}^{\circ} - \omega) \tilde{u}'_{n,\mathbf{k}+\mathbf{q}}(\mathbf{r}, \omega) + \hat{P}_c^{\mathbf{k}+\mathbf{q}} \tilde{v}'_{\text{HXC},\mathbf{q}}(\mathbf{r}, \omega) u_{n,\mathbf{k}}^{\circ}(\mathbf{r}) &= -\hat{P}_c^{\mathbf{k}+\mathbf{q}} \tilde{v}'_{\text{ext},\mathbf{q}}(\mathbf{r}, \omega) u_{n,\mathbf{k}}^{\circ}(\mathbf{r}) \\
 (\hat{H}_{\mathbf{k}+\mathbf{q}}^{\circ} - \varepsilon_{n,\mathbf{k}}^{\circ} + \omega) \tilde{u}'_{n,-\mathbf{k}-\mathbf{q}}(\mathbf{r}, -\omega) + \hat{P}_c^{\mathbf{k}+\mathbf{q}} \tilde{v}'_{\text{HXC},\mathbf{q}}(\mathbf{r}, -\omega) u_{n,\mathbf{k}}^{\circ}(\mathbf{r}) &= -\hat{P}_c^{\mathbf{k}+\mathbf{q}} \tilde{v}'_{\text{ext},\mathbf{q}}(\mathbf{r}, -\omega) u_{n,\mathbf{k}}^{\circ}(\mathbf{r})
 \end{aligned}$$

Let's use the Lanczos algorithm




interaction terms

perturbation


These equations can be re-written as a quantum Liouville equation and solved using the **Lanczos** algorithm:

$$\begin{aligned}
 (\omega - \mathcal{L}) \cdot \hat{\rho}'_{\mathbf{q}}(\omega) &= [\tilde{V}'_{\text{ext},\mathbf{q}}(\omega), \hat{\rho}^{\circ}] \\
 \mathcal{L} \cdot \hat{\rho}'_{\mathbf{q}} &\equiv [\hat{H}^{\circ}, \hat{\rho}'_{\mathbf{q}}] + [\tilde{V}'_{\text{HXC},\mathbf{q}}, \hat{\rho}^{\circ}]
 \end{aligned}$$



$\chi(\mathbf{q}, \mathbf{q}; \omega)$

Susceptibility



Loss function

$$-\text{Im}[\varepsilon^{-1}(\mathbf{q}, \omega)] = -\frac{4\pi e^2}{|\mathbf{q}|^2} \text{Im}[\chi(\mathbf{q}, \mathbf{q}; \omega)]$$

Example 3: Input file for PWscf

```
&CONTROL
  calculation = 'scf'
  restart_mode='from_scratch',
  prefix='silicon'
  pseudo_dir = '../..../pseudo',
  outdir='./tmp'
/
&SYSTEM
 ibrav = 2,
celldm(1) = 10.26,
nat = 2,
ntyp = 1,
ecutwfc = 16.0
/
&ELECTRONS
  conv_thr = 1.0d-8
  mixing_beta = 0.7,
/
ATOMIC_SPECIES {alat}
Si 28.08 Si.pz-vbc.UPF
ATOMIC_POSITIONS {alat}
Si 0.00 0.00 0.00
Si 0.25 0.25 0.25
K_POINTS {automatic}
10 10 10 1 1 1
```

Step 1. Perform a Self-Consistent Field ground-state calculation for silicon using the **pw.x** program.

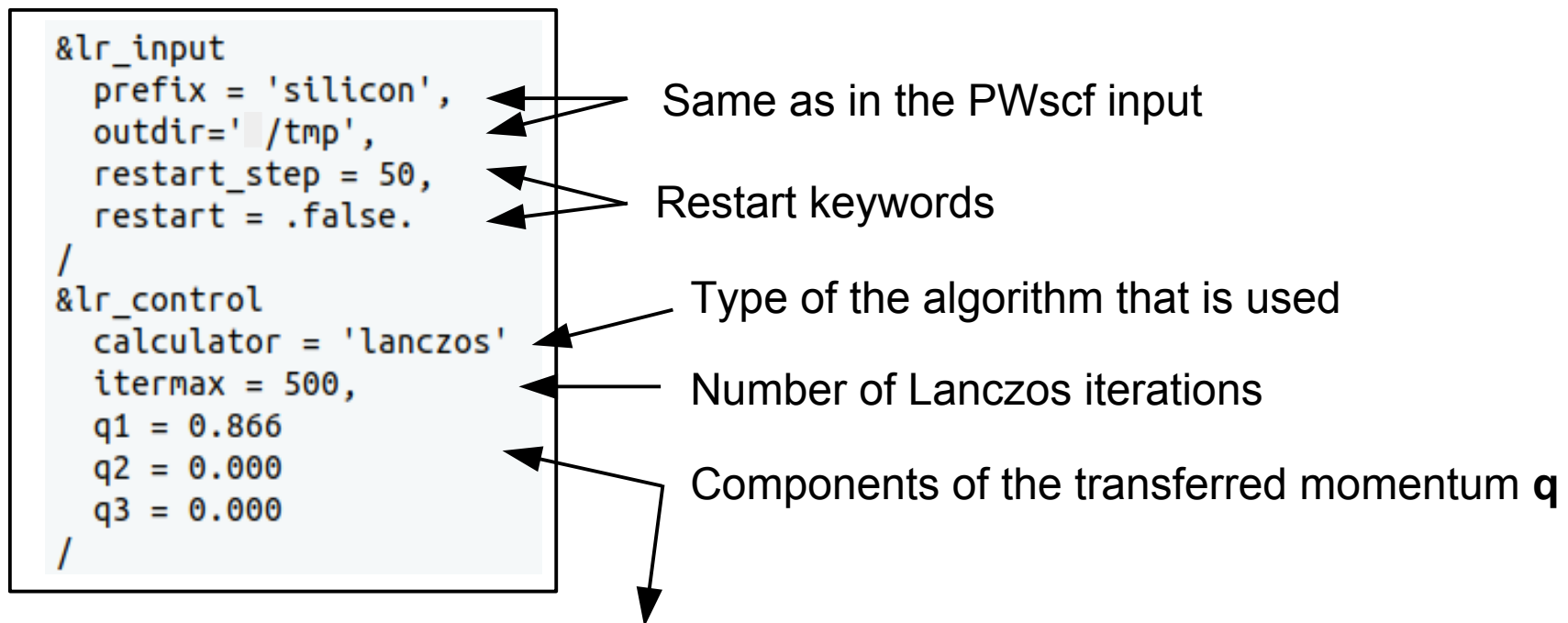
Input

Output

pw.x < pw.si.scf.in > pw.si.scf.out

Example 3 : Input file for turboEELS

Step 2. Perform Lanczos recursions using the **turbo_eels.x** program in order to compute Lanczos coefficients, which will be needed in Step 3.



How to specify q1, q2, q3 ? -> See next slide

turbo_eels.x < turbo_eels.si.lanczos.in > turbo_eels.si.lanczos.out

Example 3: Transferred momentum specification

$$\mathbf{q} = \frac{2\pi}{a_0} (q_1, q_2, q_3)$$

$$a_0 = \text{celldm}(1) = 10.26 \text{ Bohr} \quad - \text{ lattice parameter}$$

Example: $|\mathbf{q}| = 0.53 \text{ Bohr}^{-1}$ and $\mathbf{q} \parallel [100]$.

Therefore, we obtain:

$$q_1 = \frac{|\mathbf{q}| a_0}{2\pi} = 0.866$$

$$q_2 = 0$$

$$q_3 = 0$$

Example 3: Post-processing step

Step 3. Perform a spectrum calculation using the post-processing program **turbo_spectrum.x** and using the Lanczos coefficients computed in the previous step.

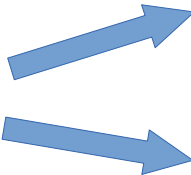
```
&lr_input
  prefix = 'silicon',
  outdir = '/tmp',
  eels = .true.
  itermax0 = 500,
  itermax = 500,
  extrapolation = 'no',
  epsil = 0.035,
  units = 1,
  start = 0.0d0,
  end = 50.0d0,
  increment = 0.01d0
/
```

- ← The same prefix as in the SCF calculation
- ← Directory for temporary files
- ← **Must be .true. for EELS, otherwise absorption**
- ← Number of calculated Lanczos coefficient
- ← Number of extrapolated Lanczos coefficient
- ← Type of extrapolation (bi-constant)
- ← The value of Lorentzian smearing in Ry
- ← The units for start, end and increment
- ← Minimum value of frequencies for a plot in eV
- ← Maximum value of frequencies for a plot in eV
- ← Frequency step in eV

turbo_spectrum.x < turbo_spectrum.si.in > turbo_spectrum.si.out

Example 3: Computed quantities

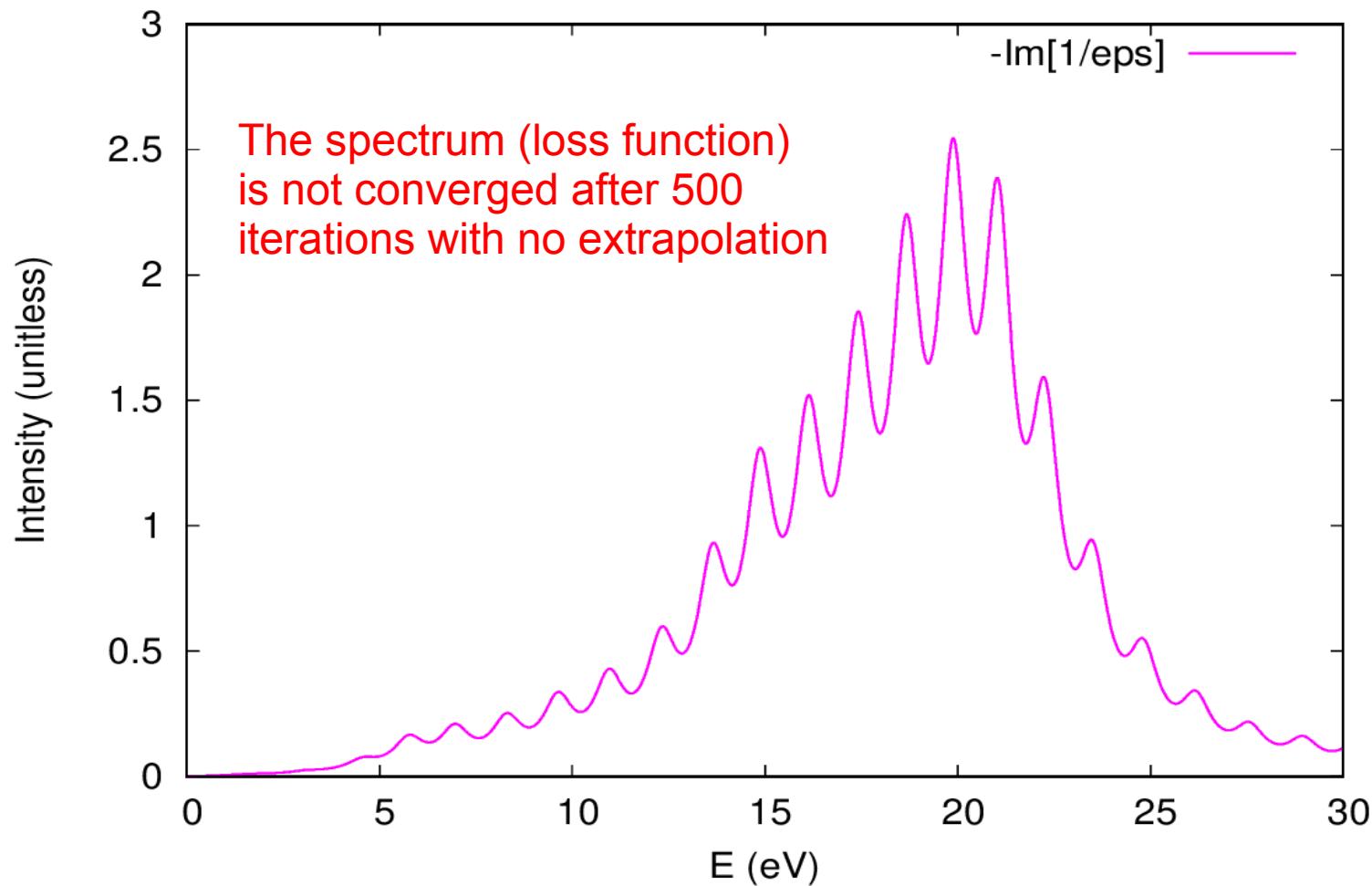
The code `turbo_spectrum.x` produces a file `silicon.plot_eps.dat` which contains the real and imaginary parts of the dielectric function and its inverse:

$$\varepsilon^{-1}(\mathbf{q}, \omega) = 1 + \frac{4\pi e^2}{|\mathbf{q}|^2} \chi(\mathbf{q}, \mathbf{q}; \omega)$$

$$\begin{aligned}\operatorname{Re}[\varepsilon^{-1}(\mathbf{q}, \omega)] &= 1 + \frac{4\pi e^2}{|\mathbf{q}|^2} \operatorname{Re}[\chi(\mathbf{q}, \mathbf{q}; \omega)] \\ -\operatorname{Im}[\varepsilon^{-1}(\mathbf{q}, \omega)] &= -\frac{4\pi e^2}{|\mathbf{q}|^2} \operatorname{Im}[\chi(\mathbf{q}, \mathbf{q}; \omega)]\end{aligned}$$

$$\varepsilon(\mathbf{q}, \omega) = \frac{1}{\varepsilon^{-1}(\mathbf{q}, \omega)} = \underbrace{\frac{\operatorname{Re}[\varepsilon^{-1}]}{(\operatorname{Re}[\varepsilon^{-1}])^2 + (\operatorname{Im}[\varepsilon^{-1}])^2}}_{\operatorname{Re}[\varepsilon(\mathbf{q}, \omega)]} + i \underbrace{\frac{-\operatorname{Im}[\varepsilon^{-1}]}{(\operatorname{Re}[\varepsilon^{-1}])^2 + (\operatorname{Im}[\varepsilon^{-1}])^2}}_{\operatorname{Im}[\varepsilon(\mathbf{q}, \omega)]}$$

Example 3: The computed EELS

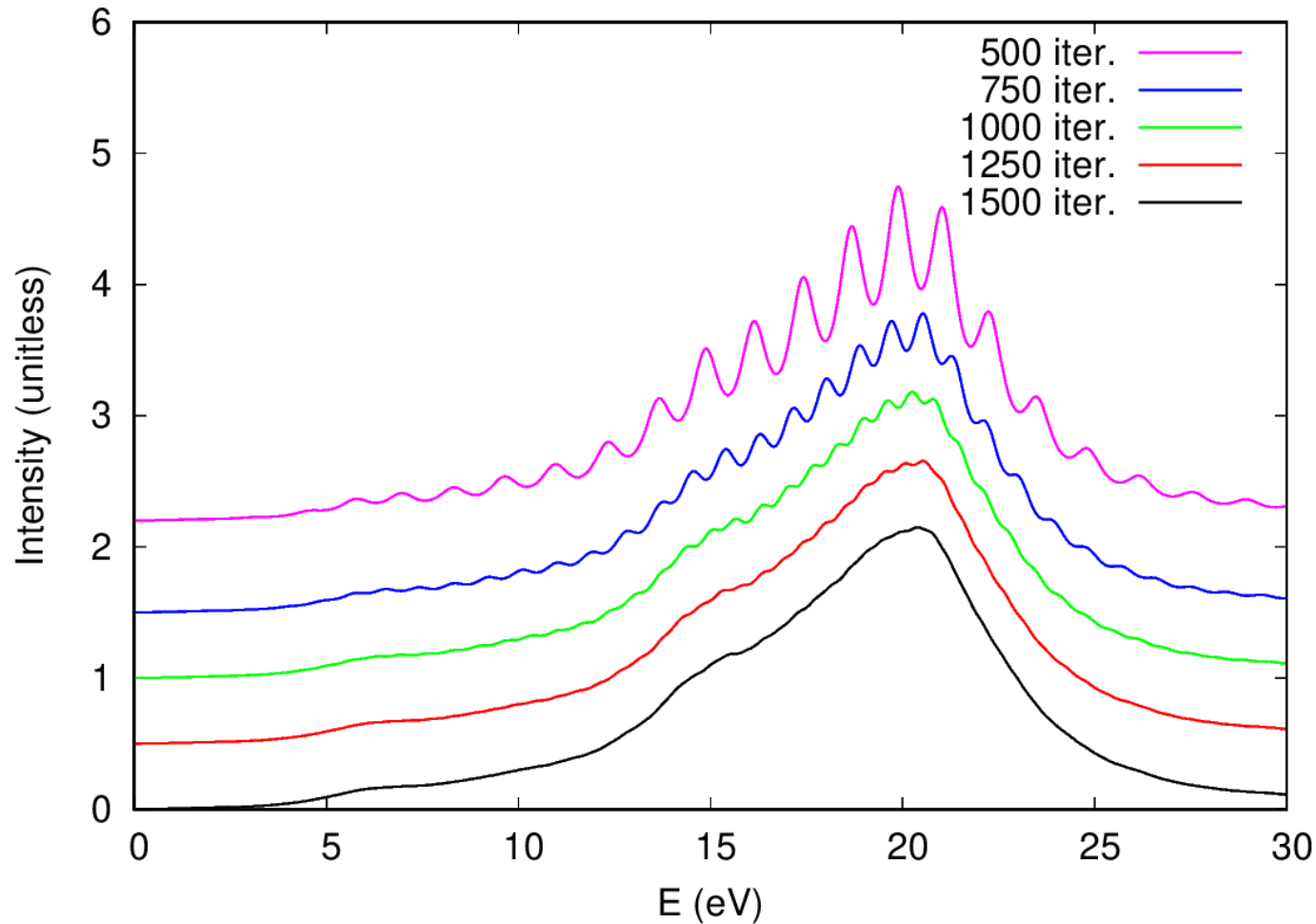
No extrapolation of Lanczos coefficients



Here, **k** points mesh 10x10x10 1 1 1 is used.

Example 3: Convergence of EELS

No extrapolation of Lanczos coefficients



Here, **k** points mesh 10x10x10 1 1 1 is used.

Example 3: Post-processing step

Step 3. Perform a spectrum calculation using the post-processing program **turbo_spectrum.x** and using the Lanczos coefficients computed in the previous step.

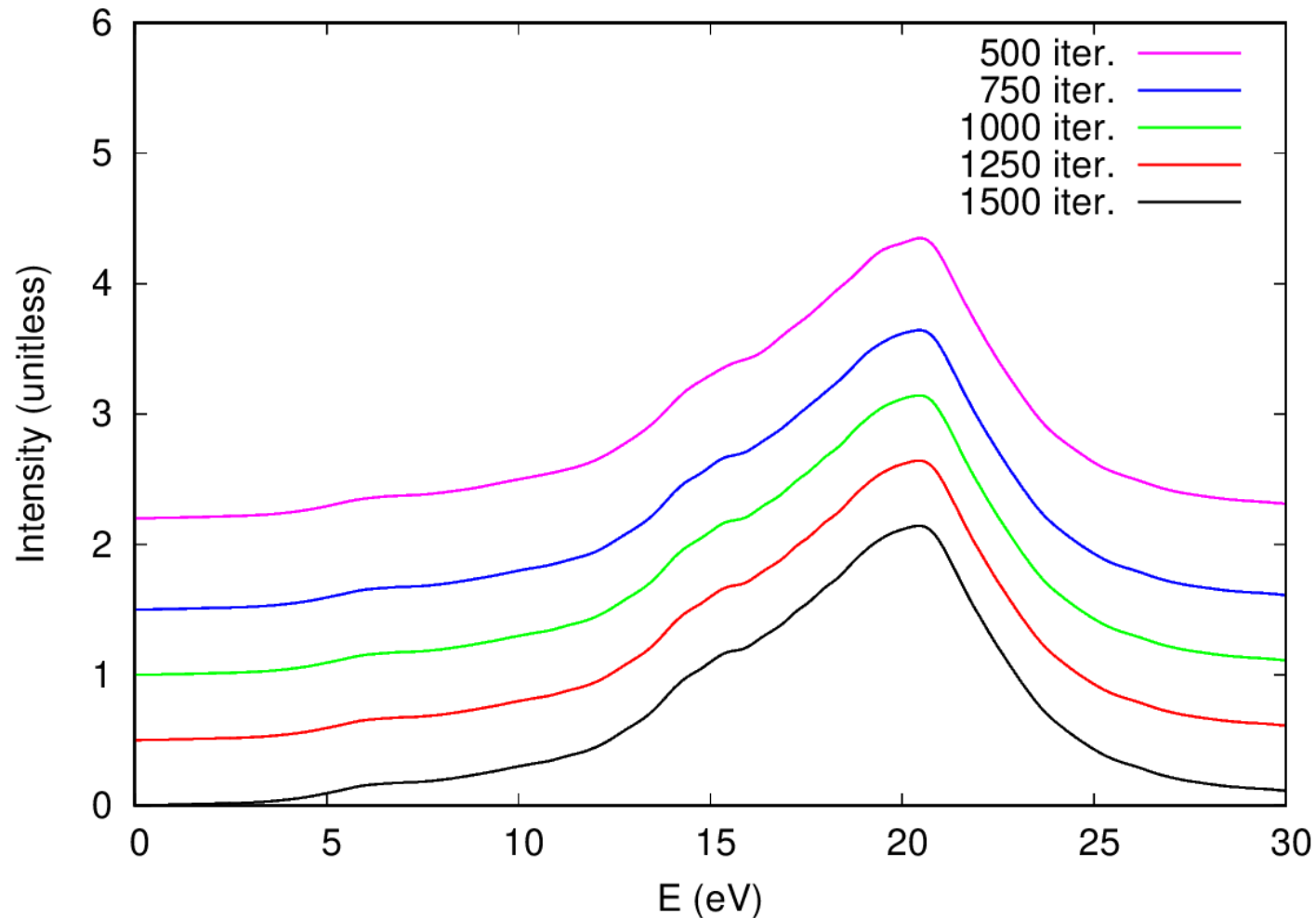
```
&lr_input
  prefix = 'silicon',
  outdir = '/tmp',
  eels = .true.
  itermax0 = 500,
  itermax = 20000
  extrapolation = 'osc'
  epsil = 0.035,
  units = 1,
  start = 0.0d0,
  end = 50.0d0,
  increment = 0.01d0
/
```

- ← The same prefix as in the SCF calculation
- ← Directory for temporary files
- ← **Must be .true. for EELS, otherwise absorption**
- ← Number of calculated Lanczos coefficient
- ← Number of extrapolated Lanczos coefficient
- ← Type of extrapolation (bi-constant)
- ← The value of Lorentzian smearing in Ry
- ← The units for start, end and increment
- ← Minimum value of frequencies for a plot in eV
- ← Maximum value of frequencies for a plot in eV
- ← Frequency step in eV

turbo_spectrum.x < turbo_spectrum.si.in > turbo_spectrum.si.out

Example 3: Convergence of EELS

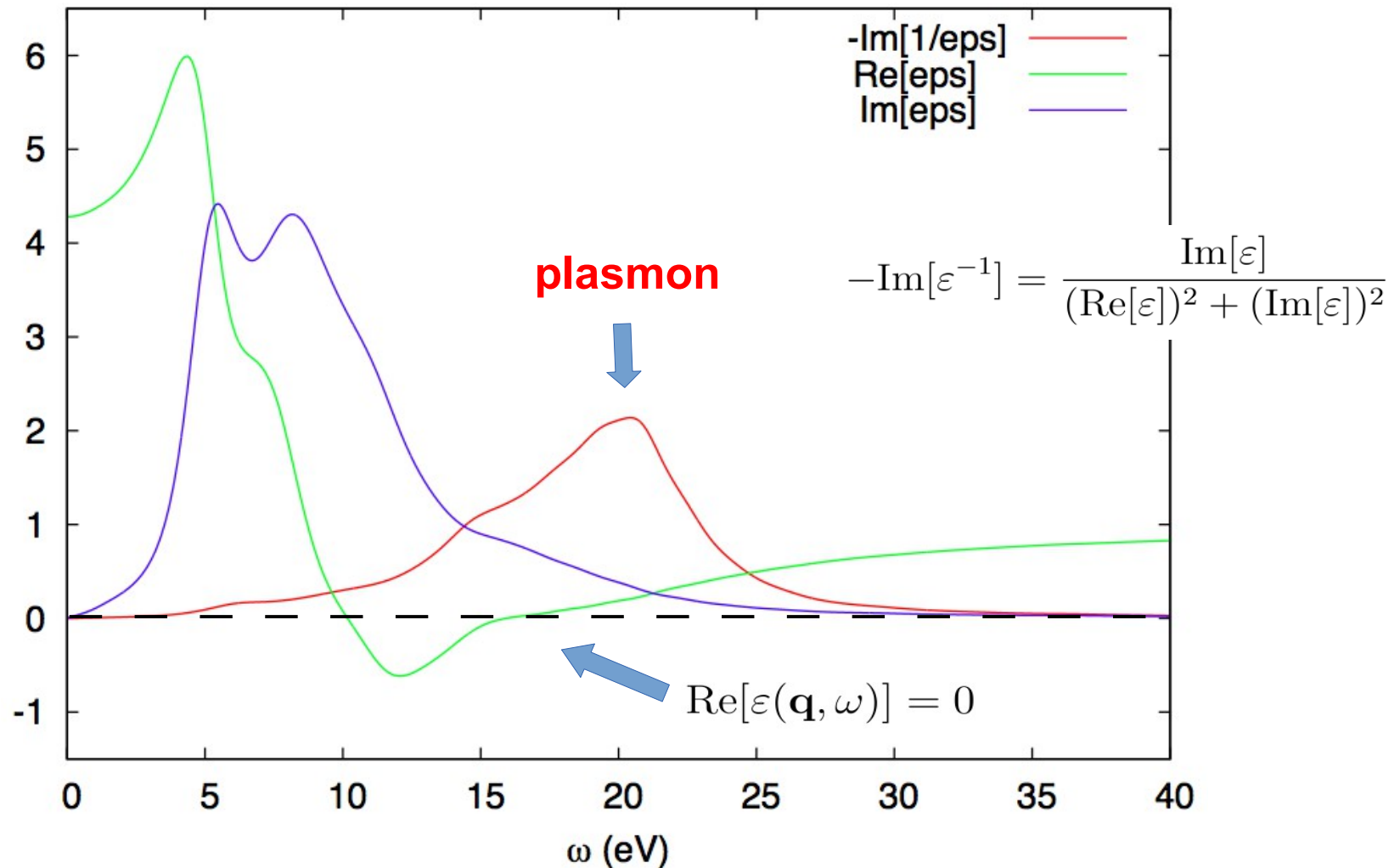
With extrapolation of Lanczos coefficients



Here, k points mesh 10x10x10 1 1 1 was used.

Example 3: Where is the plasmon peak?

Modify the script **plot_spectrum.gp** and use the file **silicon.plot_eps.dat** to plot this figure



Example 4

Coupled (**resonant** and **anti-resonant**) frequency-dependent **Sternheimer** equations:

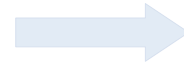
$$\begin{aligned}
 (\hat{H}_{\mathbf{k}+\mathbf{q}}^{\circ} - \varepsilon_{n,\mathbf{k}}^{\circ} - \omega) \tilde{u}'_{n,\mathbf{k}+\mathbf{q}}(\mathbf{r}, \omega) + \boxed{\hat{P}_c^{\mathbf{k}+\mathbf{q}} \tilde{v}'_{\text{HXC},\mathbf{q}}(\mathbf{r}, \omega) u_{n,\mathbf{k}}^{\circ}(\mathbf{r})} &= \boxed{-\hat{P}_c^{\mathbf{k}+\mathbf{q}} \tilde{v}'_{\text{ext},\mathbf{q}}(\mathbf{r}, \omega) u_{n,\mathbf{k}}^{\circ}(\mathbf{r})} \\
 (\hat{H}_{\mathbf{k}+\mathbf{q}}^{\circ} - \varepsilon_{n,\mathbf{k}}^{\circ} + \omega) \tilde{u}'_{n,-\mathbf{k}-\mathbf{q}}(\mathbf{r}, -\omega) + \boxed{\hat{P}_c^{\mathbf{k}+\mathbf{q}} \tilde{v}'_{\text{HXC},\mathbf{q}}(\mathbf{r}, \omega) u_{n,\mathbf{k}}^{\circ}(\mathbf{r})} &= \boxed{-\hat{P}_c^{\mathbf{k}+\mathbf{q}} \tilde{v}'_{\text{ext},\mathbf{q}}(\mathbf{r}, \omega) u_{n,\mathbf{k}}^{\circ}(\mathbf{r})}
 \end{aligned}$$

interaction terms
perturbation

These equations can be re-written as a quantum Liouville equation and solved using the **Lanczos** algorithm:

Let's use the Sternheimer algorithm

$$\begin{aligned}
 (\omega - \mathcal{L}) \cdot \hat{\rho}'_{\mathbf{q}}(\omega) &= [\tilde{V}'_{\text{HXC},\mathbf{q}}(\omega), \hat{\rho}^{\circ}] \\
 \mathcal{L} \cdot \hat{\rho}'_{\mathbf{q}} &\equiv [\hat{H}^{\circ}, \hat{\rho}'_{\mathbf{q}}] + [\tilde{V}'_{\text{HXC},\mathbf{q}}, \hat{\rho}^{\circ}]
 \end{aligned}$$



$\chi(\mathbf{q}, \mathbf{q}; \omega)$
Susceptibility



$$-\text{Im}[\varepsilon^{-1}(\mathbf{q}, \omega)] = -\frac{4\pi e^2}{|\mathbf{q}|^2} \text{Im}[\chi(\mathbf{q}, \mathbf{q}; \omega)]$$

Loss function

Example 4

The implementation of the Sternheimer algorithm in turboEELS is very recent.

This algorithm is not fully optimized, therefore the calculation is much slower than in the previous examples.

We will need to use HPC for this exercise.

Moreover, the disc space must be enough, because the code writes quite large files on disc and it may fail if there is not enough space.

Use the parallelization of \mathbf{k} point pools to speed up the calculation.

Example 4 : Input file for turboEELS

Step 1. Perform a SCF ground-state calculation for Si.

Step 2. Solve the Sternheimer equations using **turbo_eels.x**

```
&lr_input  
  prefix = 'silicon',  
  outdir=' /tmp'
```

Same as in the PWscf input

```
/
```

```
&lr_control  
  calculator = 'sternheimer',  
  q1 = 0.866,  
  q2 = 0.000,  
  q3 = 0.000,  
  epsil = 0.035,  
  units = 1,  
  start = 0.0d0,  
  end   = 30.0d0,  
  increment = 1.0d0
```

Type of the algorithm that is used

Components of the transferred momentum \mathbf{q}

The value of Lorentzian broadening in Ry

The units (0 → Ry, 1 → eV)

Keywords that control the range in which the spectrum is plotted

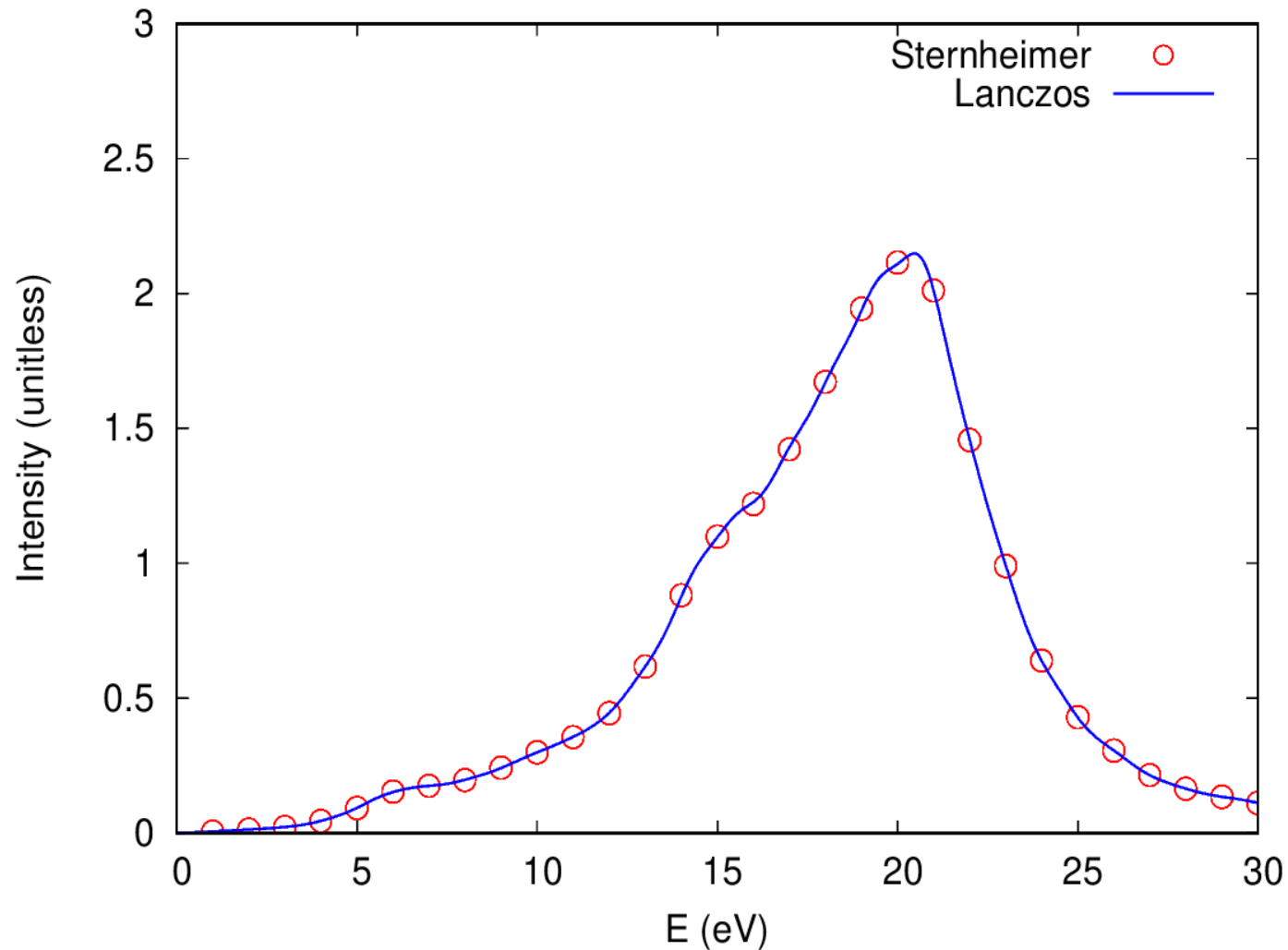
```
turbo_eels.x < turbo_eels.si.sternheimer.in > ...
```

```
...turbo_eels.si.sternheimer.out
```

Example 4: The computed EELS

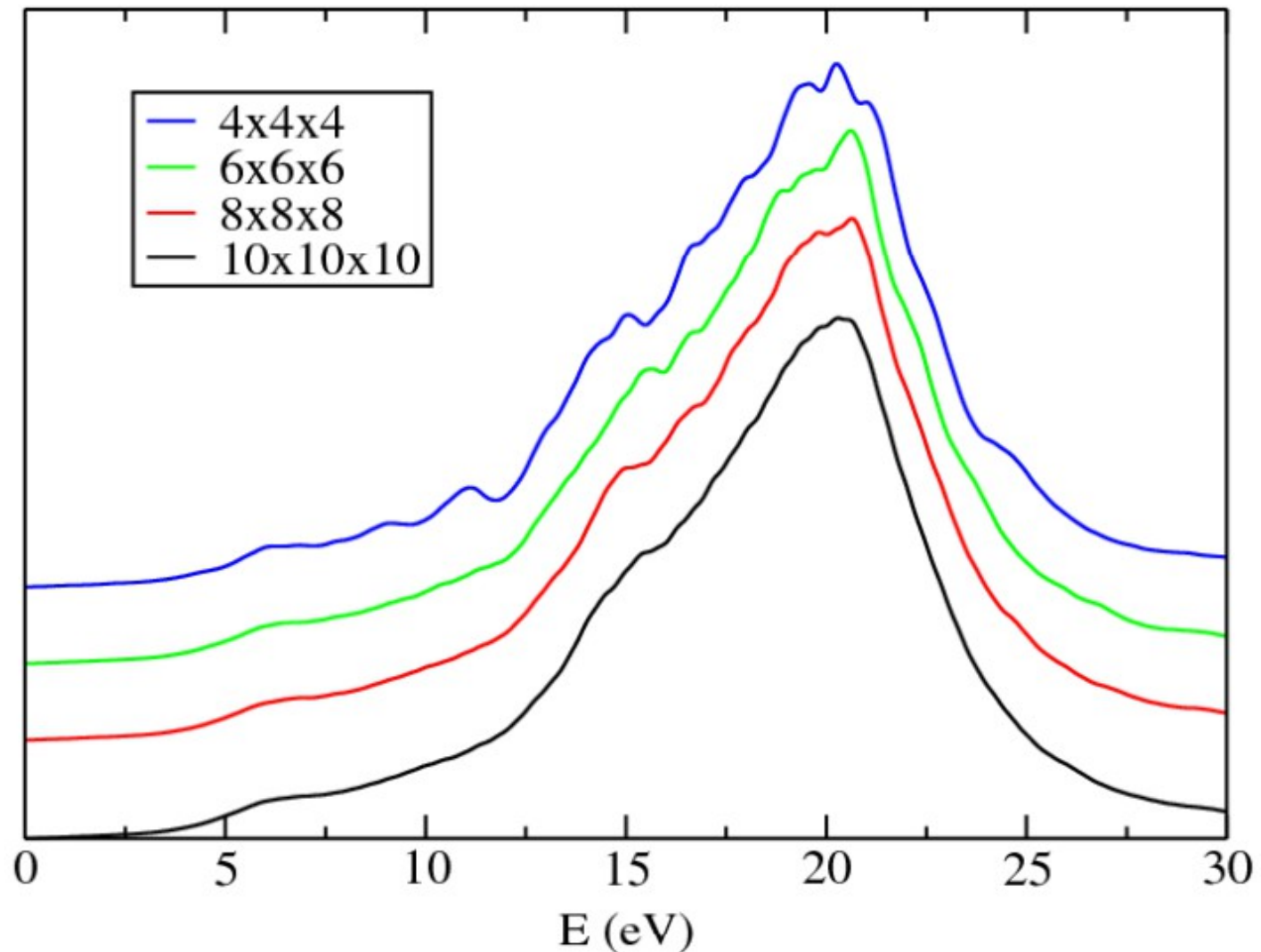
The Sternheimer and Lanczos algorithms give exactly the same spectrum.

Sternheimer is much slower than Lanczos!



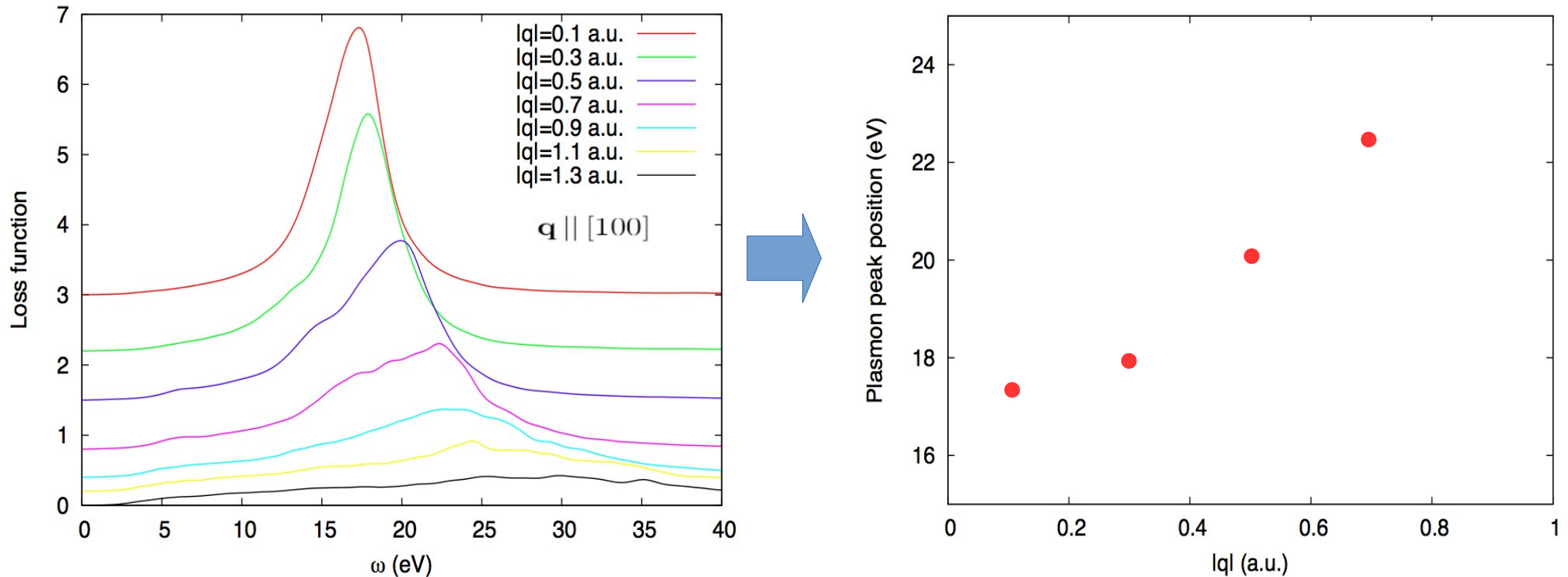
Example 4: Convergence w.r.t. **k** mesh

Convergence of EELS with respect to the size of the **k** points mesh



Example 4: Plasmon dispersion

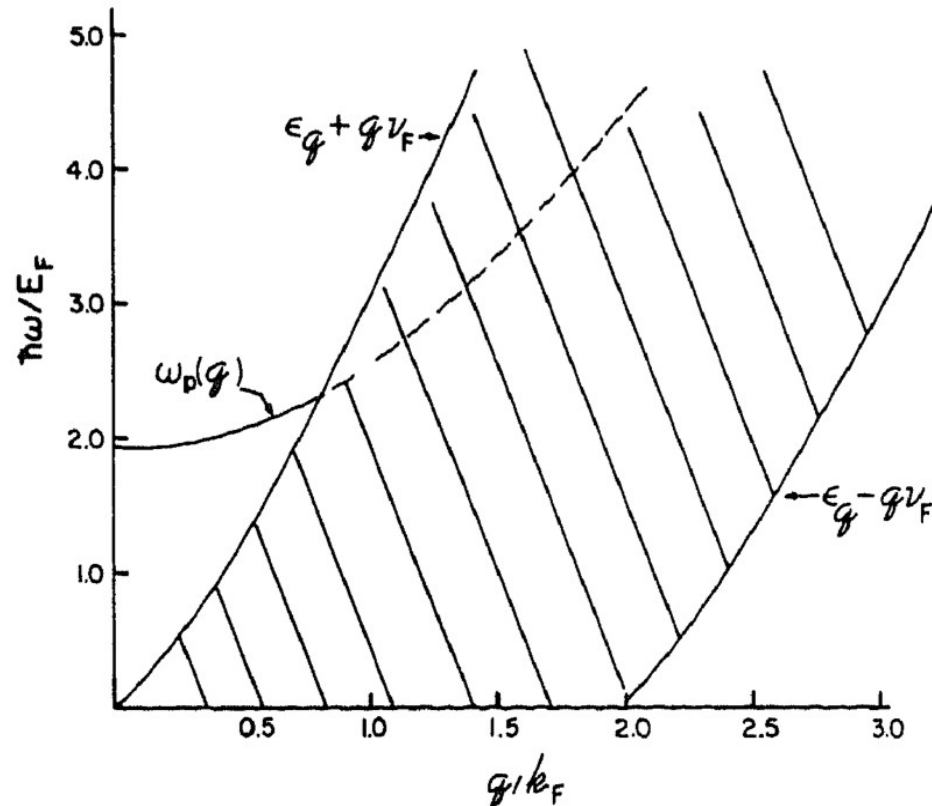
Plasmon dispersion in bulk silicon



By increasing q , the plasmon peak blue-shifts and broadens, because it enters in the electron-hole continuum.

Example 4: Plasmon dispersion and e-h continuum

The excitation region of the electron gas in (\mathbf{q}, ω) space



The plasmon line becomes strongly damped in a region of electron-hole pairs.

G. D. Mahan, Many-Particle Physics, Plenum Press, 2nd ed. New York, (1975)