QUANTUM ESPRESSO FOUNDATION

QUANTUMESPRESSO

MaX School on Advanced Materials and Molecular Modelling with QUANTUM ESPRESSO

QE-2021: Hands-on session – Day-6 TDDFPT

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Outline

1. Part I – Optical absorption in molecules

2. Part II – EELS in solids

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=.false.).
- 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):

$$(\hat{H}^{\circ} - \varepsilon_v - \hbar\omega)\tilde{\varphi}'_v(\mathbf{r},\omega) + \hat{P}_c\,\hat{V}'_{\mathrm{HXC}}[\tilde{\varphi}'_v(\mathbf{r},\omega), \tilde{\varphi}'^{*}_v(\mathbf{r},-\omega)]\,\varphi^{\circ}_v(\mathbf{r}) = 0$$

$$(\hat{H}^{\circ} - \varepsilon_v + \hbar\omega)\tilde{\varphi}'^{*}_v(\mathbf{r},-\omega) + \hat{P}_c\,\hat{V}'_{\mathrm{HXC}}[\tilde{\varphi}'_v(\mathbf{r},\omega), \tilde{\varphi}'^{*}_v(\mathbf{r},-\omega)]\,\varphi^{\circ}_v(\mathbf{r}) = 0$$

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 $\hat{D} \longrightarrow (\hat{H}^{\circ} - \varepsilon_v)$ and $\hat{K} \longrightarrow \hat{P}_c \hat{V}'_{\mathrm{HXC}} \varphi^{\circ}_v(\mathbf{r})$

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.

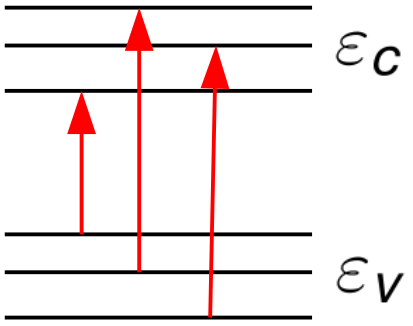
Fermi's golden rule

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



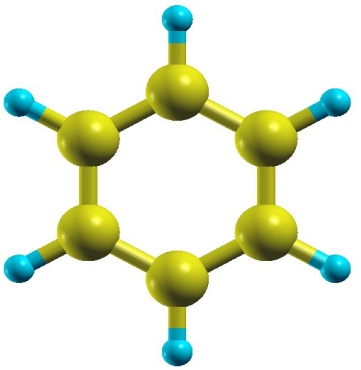
Example 1: Input file for PWscf

```
&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}
```

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)

C_6H_6



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.davidson.in >...
                ...turbo_davidson.benzene.davidson.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.tddfpt_pp.in :

```
&lr_input
  prefix = 'Benzene',
  outdir = './tmp  ,
  td = 'davidson',
  epsil = 0.004,
  start = 0.0d0,
  end   = 1.0d0,
  increment = 0.0001d0,
  eign_file = 'Benzene-dft.eigen'
/
```

The same prefix as in the SCF calculation

Directory for temporary files

Type of previous calculation

The value of Lorenzian smearing in Ry

Minimum value of frequencies for a plot in Ry

Maximum value of frequencies for a plot in Ry

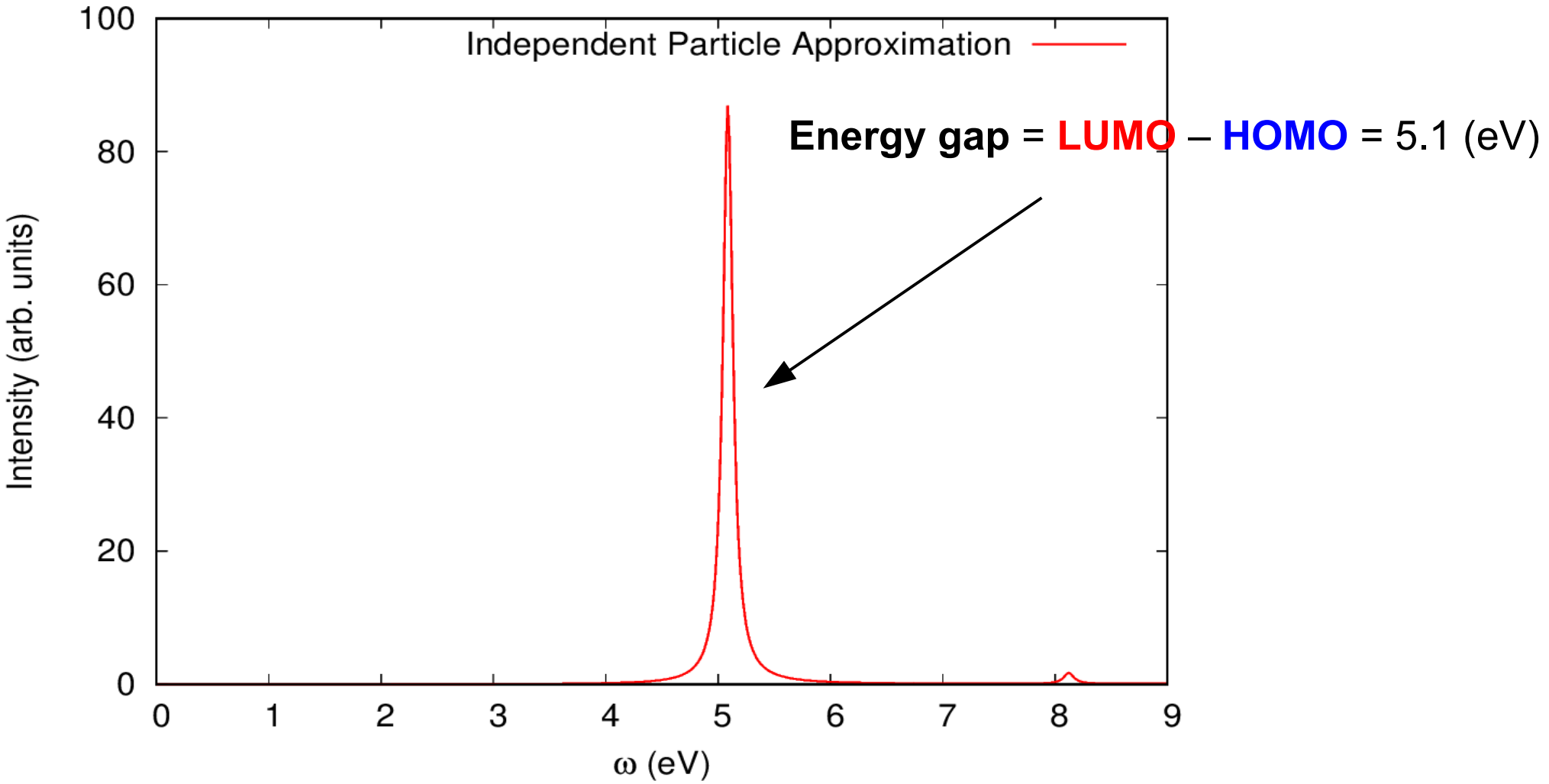
Frequency step in Ry

Frequency with Davidson eigenvalues

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

Example 1: Calculation of absorption spectra in IPA

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



Example 1: Spectra including interactions

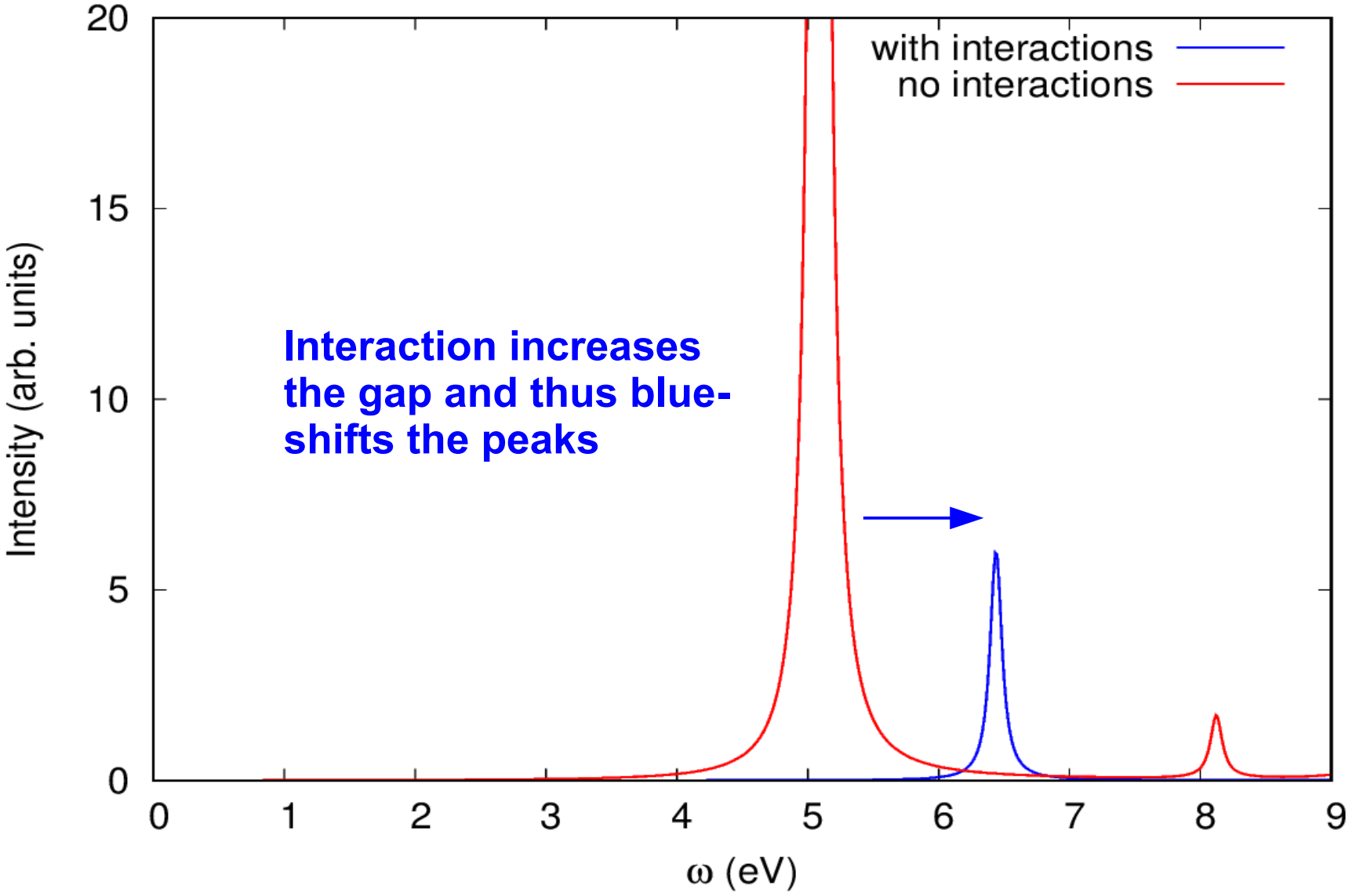
Perform the turboDavidson calculation without the electronic interaction using the **`turbo_davidson.x`** program.

```
&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  = 0.005
  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.davidson.in >...
                ...turbo_davidson.benzene.davidson.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):

perturbation

$$(\hat{H}^{\circ} - \varepsilon_v - \hbar\omega)\tilde{\varphi}'_v(\mathbf{r},\omega) + \hat{P}_c\,\hat{V}'_{\mathrm{HXC}}[\tilde{\varphi}'_v(\mathbf{r},\omega), \tilde{\varphi}'^{*}_v(\mathbf{r},-\omega)]\,\varphi^{\circ}_v(\mathbf{r}) = -\hat{P}_c\,\hat{V}'_{ext}\varphi^{\circ}_v(\mathbf{r})$$

$$(\hat{H}^{\circ} - \varepsilon_v + \hbar\omega)\tilde{\varphi}'^{*}_v(\mathbf{r},-\omega) + \hat{P}_c\,\hat{V}'_{\mathrm{HXC}}[\tilde{\varphi}'_v(\mathbf{r},\omega), \tilde{\varphi}'^{*}_v(\mathbf{r},-\omega)]\,\varphi^{\circ}_v(\mathbf{r}) = -\hat{P}_c\,\hat{V}'_{ext}\varphi^{\circ}_v(\mathbf{r})$$

interaction terms

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

$$(\omega - \mathcal{L}) \cdot \rho'(\omega) = [\hat{V}'_{ext}, \rho^{\circ}]$$

$$\mathcal{L} \cdot \rho' \equiv [\hat{H}^{\circ}, \rho'] + [\hat{V}'_{\mathrm{HXC}}, \rho^{\circ}]$$

Absorption coefficient is computed as:

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

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
  itermax = 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.lanczos.in >...
...turbo_lanczos.benzene.lanczos.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 Lorenzian 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.lanczos.in

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

turbo_spectrum.benzene.lanczos.in

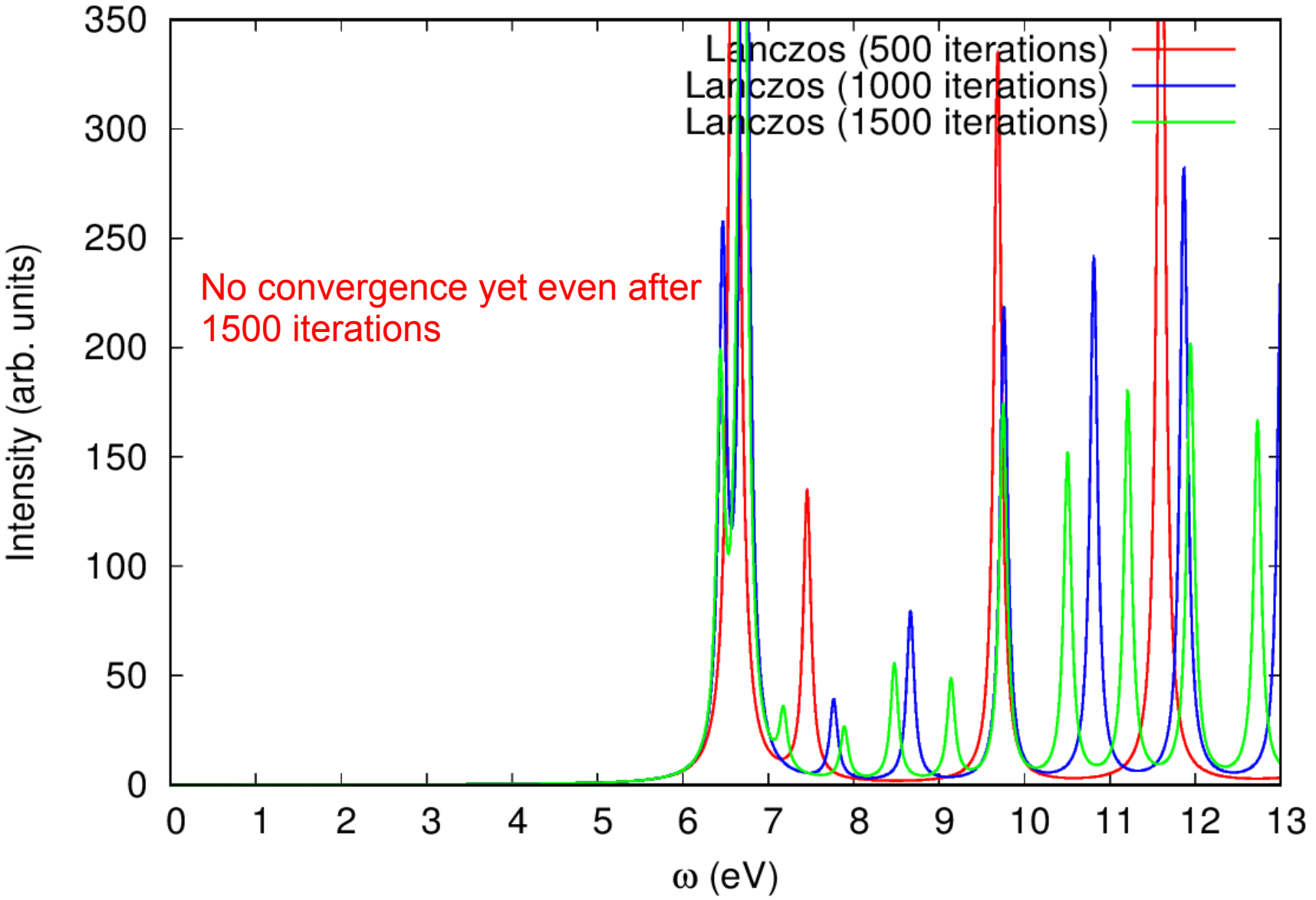
```
&lr_input
  prefix = 'Benzene',
  outdir = './tmp',
  itermax0 = 500,
  itermax  = 500,
  extrapolation = 'no',
  epsil = 0.004,
  start = 0.0d0,
  end   = 1.0d0,
  increment = 0.0001d0,
  ipol = 1
/
```

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.

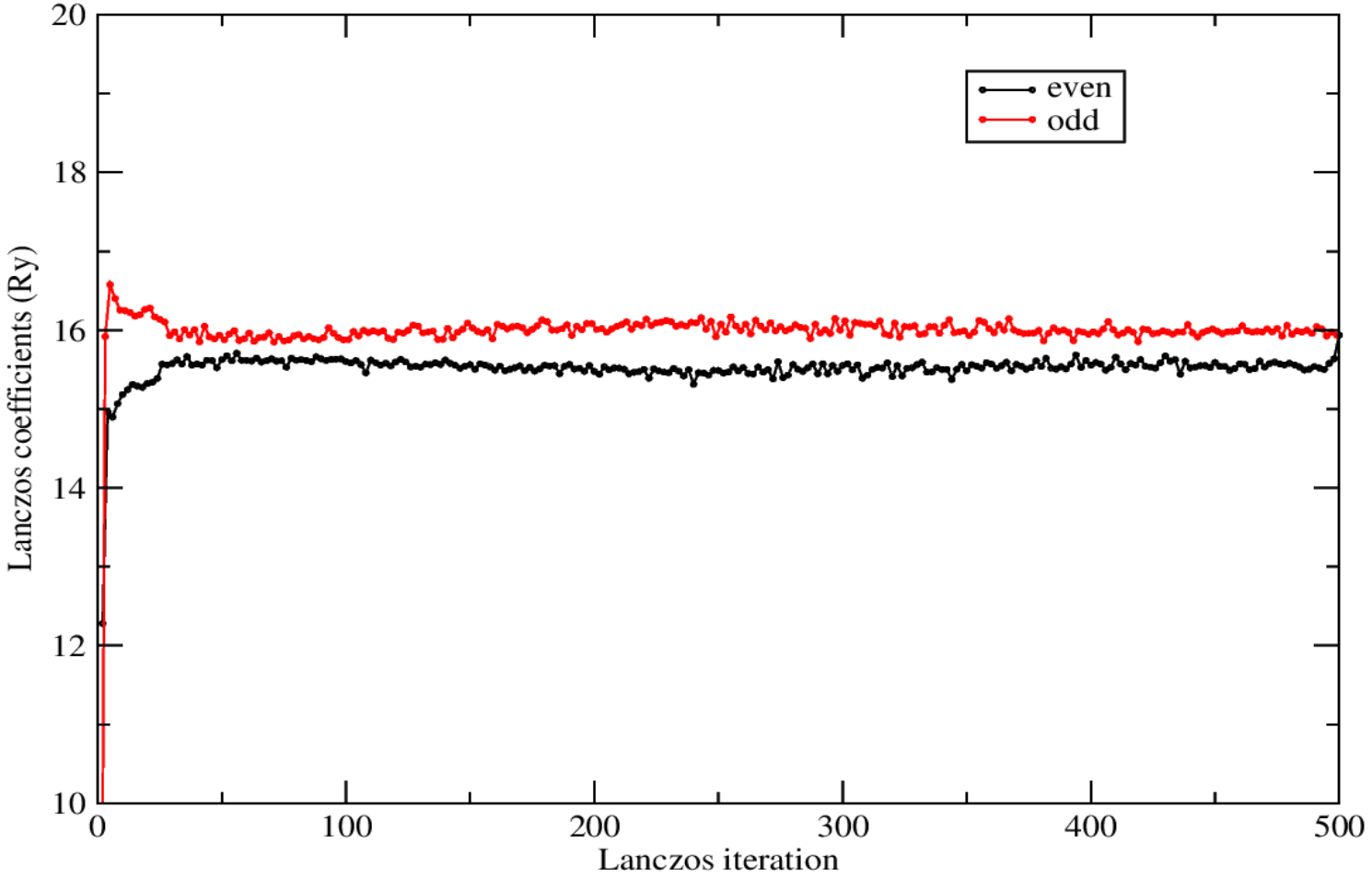
Example 2: Post-processing step

No extrapolation of Lanczos coefficients



Example 2: Lanczos coefficients

Behavior of β Lanczos coefficients



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

Example 2: Extrapolation of Lanczos coefficients

In the Liuoville-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.

$$\hat{T}_N = \begin{pmatrix} 0 & \gamma_2 & 0 & \cdots & 0 \\ \beta_2 & 0 & \gamma_3 & 0 & 0 \\ 0 & \beta_3 & 0 & \ddots & 0 \\ \vdots & 0 & \ddots & \ddots & \gamma_N \\ 0 & \cdots & 0 & \beta_N & 0 \end{pmatrix}$$

Extrapolation

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

$$\langle\beta\rangle = \frac{\beta_1 + \beta_2 + \ldots + \beta_N}{N} \qquad \langle\gamma\rangle = \frac{\gamma_1 + \gamma_2 + \ldots + \gamma_N}{N}$$

$$N = itermax0, \quad N' = itermax$$

Example 2: Post-processing step

With extrapolation of Lanczos coefficients

turbo_lanczos.benzene.lanczos.in

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

turbo_spectrum.benzene.lanczos.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 =
/
```

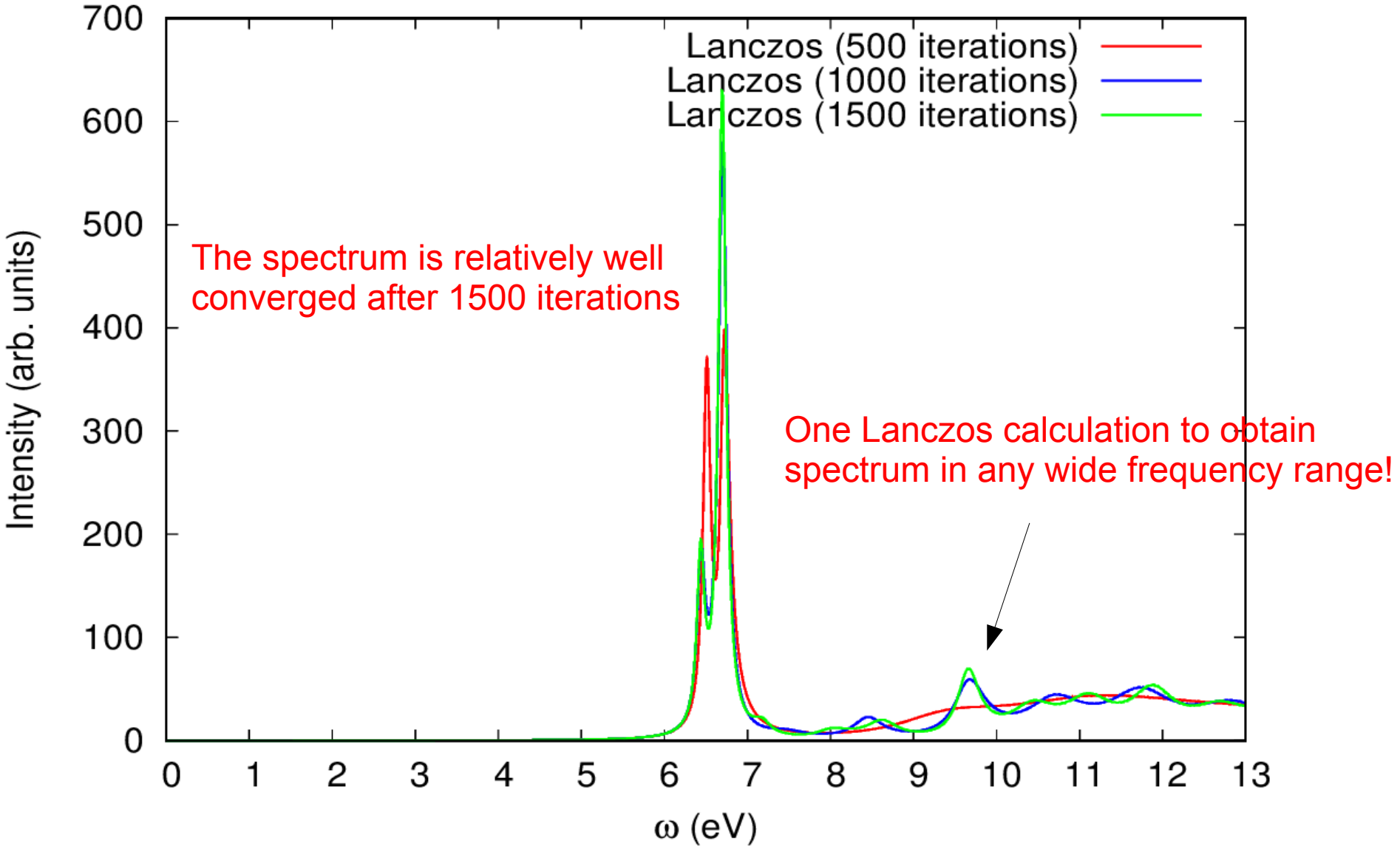
Must be equal !

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:

$$(\hat{H}^{\circ}_{\mathbf{k}+\mathbf{q}} - \varepsilon^{\circ}_{n,\mathbf{k}} - \omega)\,\tilde{u}'_{n,\mathbf{k}+\mathbf{q}}(\mathbf{r},\omega) \;+\; \hat{P}^{\mathbf{k}+\mathbf{q}}_{c}\,\tilde{v}'_{\mathrm{HXC},\mathbf{q}}(\mathbf{r},\omega)\,u^{\circ}_{n,\mathbf{k}}(\mathbf{r}) = -\hat{P}^{\mathbf{k}+\mathbf{q}}_{c}\,\tilde{v}'_{\mathrm{ext},\mathbf{q}}(\mathbf{r},\omega)\,u^{\circ}_{n,\mathbf{k}}(\mathbf{r})$$

$$(\hat{H}^{\circ}_{\mathbf{k}+\mathbf{q}} - \varepsilon^{\circ}_{n,\mathbf{k}} + \omega)\,\tilde{u}'^{*}_{n,-\mathbf{k}-\mathbf{q}}(\mathbf{r},-\omega) + \hat{P}^{\mathbf{k}+\mathbf{q}}_{c}\,\tilde{v}'_{\mathrm{HXC},\mathbf{q}}(\mathbf{r},\omega)\,u^{\circ}_{n,\mathbf{k}}(\mathbf{r}) = -\hat{P}^{\mathbf{k}+\mathbf{q}}_{c}\,\tilde{v}'_{\mathrm{ext},\mathbf{q}}(\mathbf{r},\omega)\,u^{\circ}_{n,\mathbf{k}}(\mathbf{r})$$

interaction terms **perturbation**

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

$$(\omega - \mathcal{L})\cdot\hat{\rho}'_{\mathbf{q}}(\omega) = [\tilde{V}'_{ext,\mathbf{q}}(\omega), \hat{\rho}^{\circ}]$$

$$\mathcal{L}\cdot\hat{\rho}'_{\mathbf{q}} \equiv [\hat{H}^{\circ}, \hat{\rho}'_{\mathbf{q}}] + [\tilde{V}'_{\mathrm{HXC},\mathbf{q}}, \hat{\rho}^{\circ}]$$

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

Susceptibility

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

Loss function

Example 3

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

$$(\hat{H}^{\circ}_{\mathbf{k}+\mathbf{q}} - \varepsilon^{\circ}_{n,\mathbf{k}} - \omega)\,\tilde{u}'_{n,\mathbf{k}+\mathbf{q}}(\mathbf{r},\omega) + \hat{P}^{\mathbf{k}+\mathbf{q}}_{c}\,\tilde{v}'_{\mathrm{HXC},\mathbf{q}}(\mathbf{r},\omega)\,u^{\circ}_{n,\mathbf{k}}(\mathbf{r}) = -\hat{P}^{\mathbf{k}+\mathbf{q}}_{c}\,\tilde{v}'_{\mathrm{ext},\mathbf{q}}(\mathbf{r},\omega)\,u^{\circ}_{n,\mathbf{k}}(\mathbf{r})$$

$$(\hat{H}^{\circ}_{\mathbf{k}+\mathbf{q}} - \varepsilon^{\circ}_{n,\mathbf{k}} + \omega)\,\tilde{u}'^{*}_{n,-\mathbf{k}-\mathbf{q}}(\mathbf{r},-\omega) + \hat{P}^{\mathbf{k}+\mathbf{q}}_{c}\,\tilde{v}'_{\mathrm{HXC},\mathbf{q}}(\mathbf{r},\omega)\,u^{\circ}_{n,\mathbf{k}}(\mathbf{r}) = -\hat{P}^{\mathbf{k}+\mathbf{q}}_{c}\,\tilde{v}'_{\mathrm{ext},\mathbf{q}}(\mathbf{r},\omega)\,u^{\circ}_{n,\mathbf{k}}(\mathbf{r})$$

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:

$$(\omega - \mathcal{L}) \cdot \hat{\rho}'_{\mathbf{q}}(\omega) = [\tilde{V}'_{ext,\mathbf{q}}(\omega), \hat{\rho}^{\circ}]$$

$$\mathcal{L} \cdot \hat{\rho}'_{\mathbf{q}} \equiv [\hat{H}^{\circ}, \hat{\rho}'_{\mathbf{q}}] + [\tilde{V}'_{\mathrm{HXC},\mathbf{q}}, \hat{\rho}^{\circ}]$$

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

Susceptibility

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

Loss function

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.

```
&lr_input
  prefix = 'silicon',
  outdir='./tmp',
  restart_step = 50,
  restart = .false.
/
&lr_control
  calculator = 'lanczos'
  itermax = 500,
  q1 = 0.866
  q2 = 0.000
  q3 = 0.000
/
```

Same as in the PWscf input

Restart keywords

Type of the algorithm that is used

Number of Lanczos iterations

Components of the transferred momentum **q**

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

$$\mathbf{q} = \frac{2\pi}{a_0}\left(\mathrm{q1}, \mathrm{q2}, \mathrm{q3}\right)$$

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

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

Therefore, we obtain:

$$\mathrm{q1} = \frac{|\mathbf{q}|\, a_0}{2\pi} = 0.866$$

$$\mathrm{q2} = 0$$

$$\mathrm{q3} = 0$$

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:

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

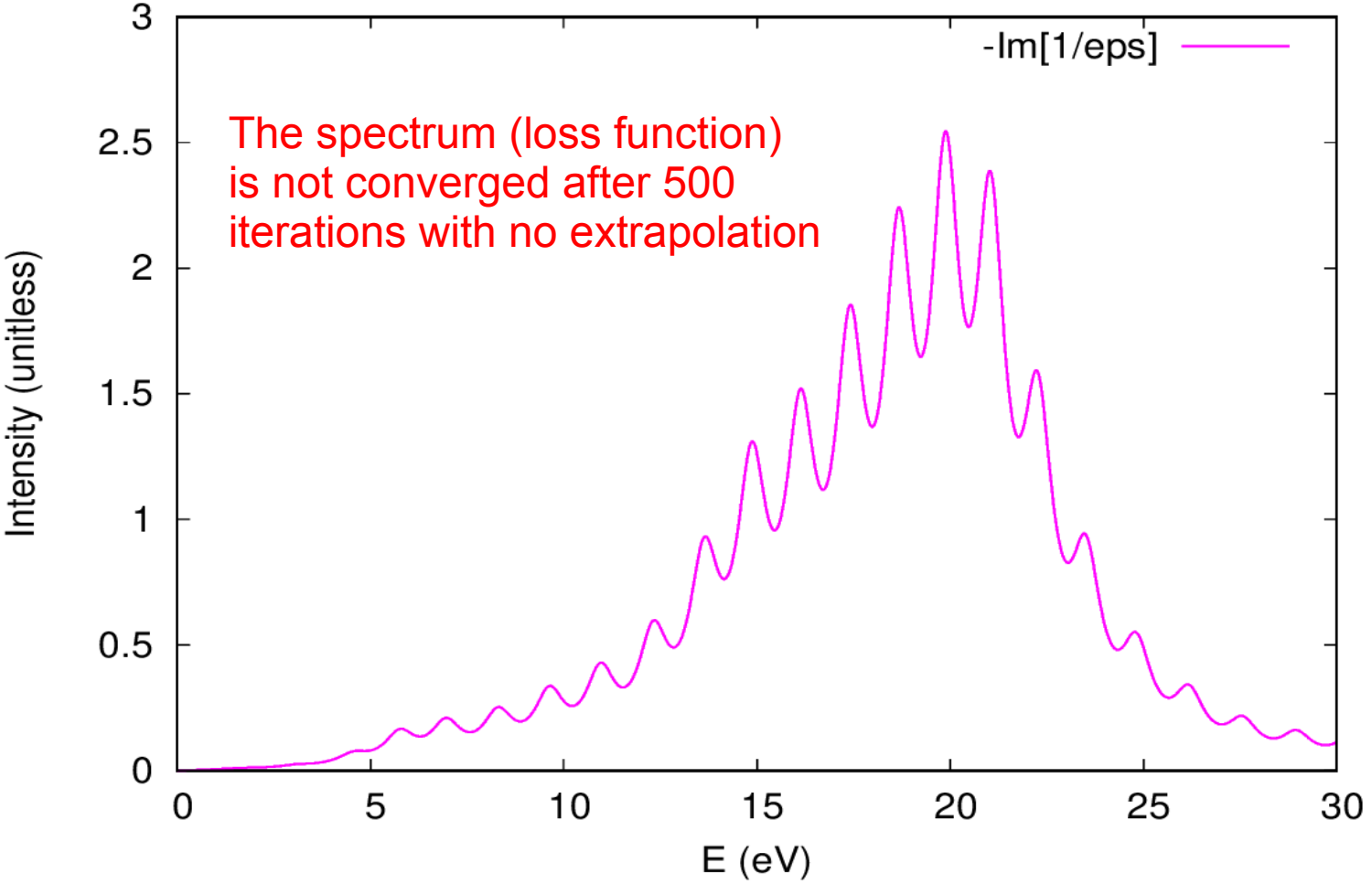
$$\mathrm{Re}[\varepsilon^{-1}(\mathbf{q},\omega)] = 1 + \frac{4\pi e^2}{|\mathbf{q}|^2}\,\mathrm{Re}[\chi(\mathbf{q},\mathbf{q};\omega)]$$

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

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

Example 3: The computed EELS

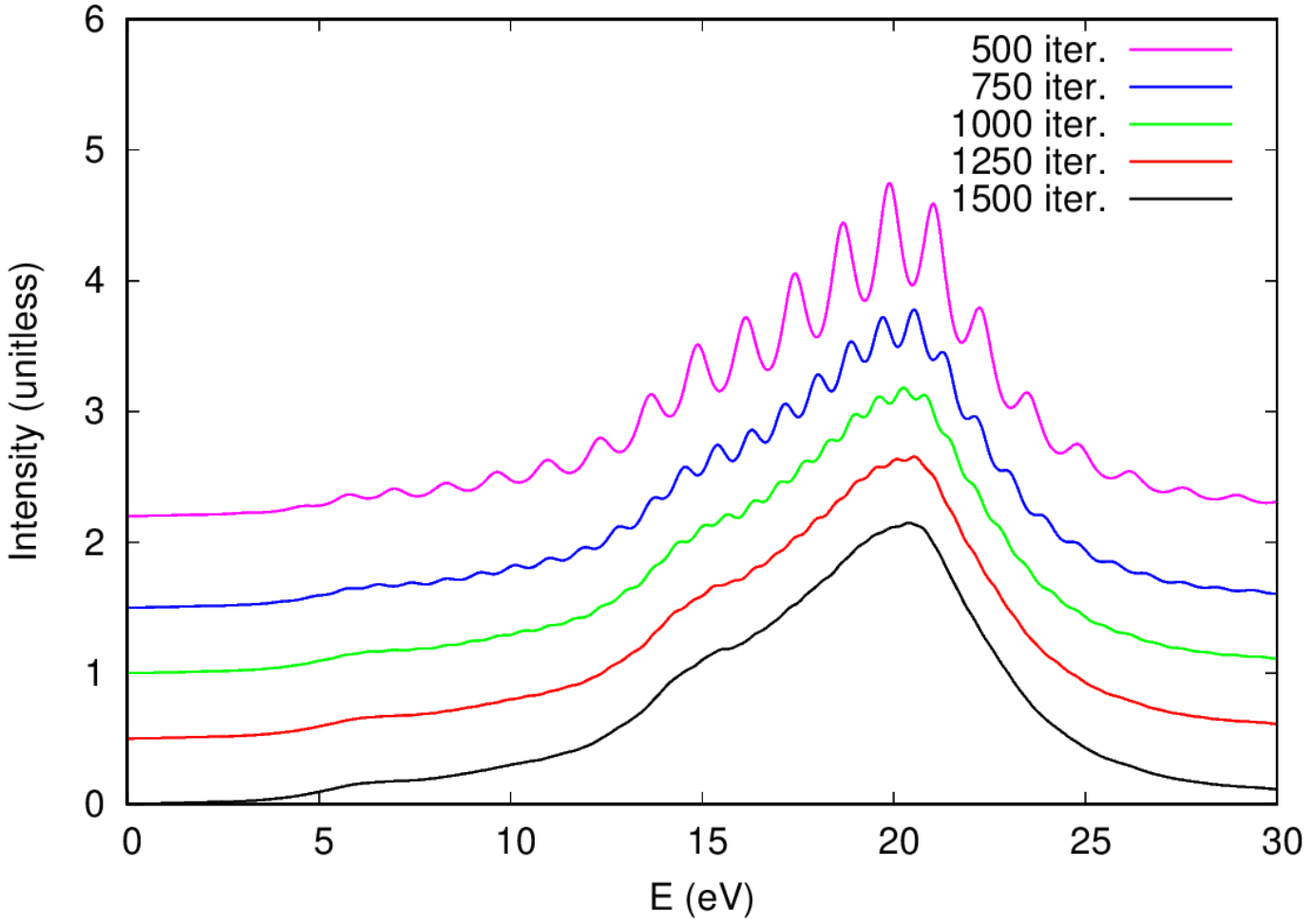
No extrapolation of Lanczos coefficients



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.

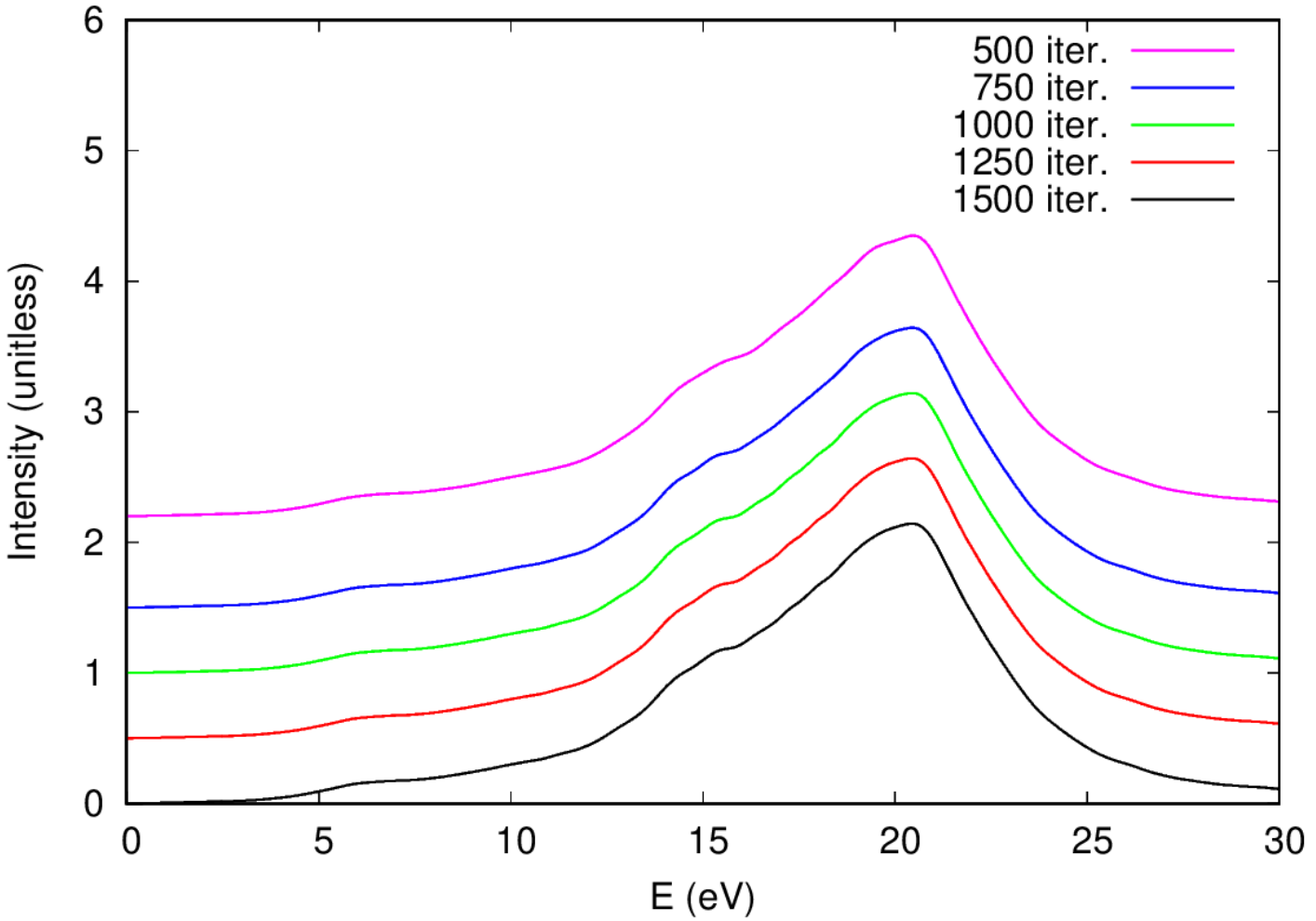
```
&lr_input
  prefix = 'silicon',
  outdir = './tmp',
  eels = .true.
  itermax0 = 500,
  itermax  = 20000
  extrapolation = 'osc'
  epsil = 0.035,
  units = 1,
  start = 0.0d0,
  end   = 50.0d0,
  increment = 0.01d0
/
```

- 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
```

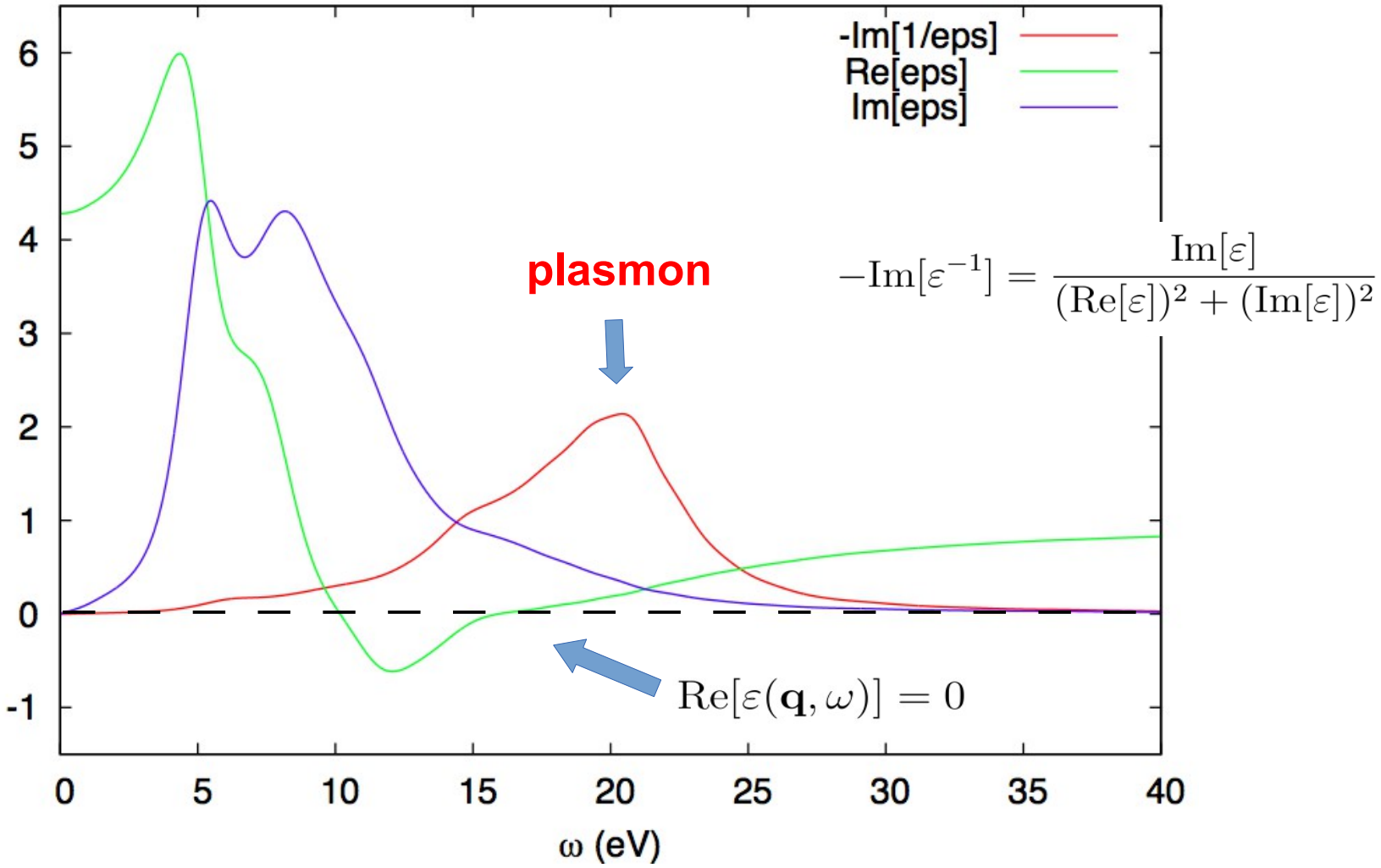
Example 3: Convergence of EELS

With extrapolation of Lanczos coefficients



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

Example 3: Where is the plasmon peak?



Example 4

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

$$(\hat{H}^{\circ}_{\mathbf{k}+\mathbf{q}} - \varepsilon^{\circ}_{n,\mathbf{k}} - \omega)\,\tilde{u}'_{n,\mathbf{k}+\mathbf{q}}(\mathbf{r},\omega) + \hat{P}^{\mathbf{k}+\mathbf{q}}_{c}\,\tilde{v}'_{\mathrm{HXC},\mathbf{q}}(\mathbf{r},\omega)\,u^{\circ}_{n,\mathbf{k}}(\mathbf{r}) = -\hat{P}^{\mathbf{k}+\mathbf{q}}_{c}\,\tilde{v}'_{\mathrm{ext},\mathbf{q}}(\mathbf{r},\omega)\,u^{\circ}_{n,\mathbf{k}}(\mathbf{r})$$

$$(\hat{H}^{\circ}_{\mathbf{k}+\mathbf{q}} - \varepsilon^{\circ}_{n,\mathbf{k}} + \omega)\,\tilde{u}'^{*}_{n,-\mathbf{k}-\mathbf{q}}(\mathbf{r},-\omega) + \hat{P}^{\mathbf{k}+\mathbf{q}}_{c}\,\tilde{v}'_{\mathrm{HXC},\mathbf{q}}(\mathbf{r},\omega)\,u^{\circ}_{n,\mathbf{k}}(\mathbf{r}) = -\hat{P}^{\mathbf{k}+\mathbf{q}}_{c}\,\tilde{v}'_{\mathrm{ext},\mathbf{q}}(\mathbf{r},\omega)\,u^{\circ}_{n,\mathbf{k}}(\mathbf{r})$$

interaction terms **perturbation**

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

$$(\omega - \mathcal{L})\cdot\hat{\rho}'_{\mathbf{q}}(\omega) = [\tilde{V}'_{\mathrm{HXC},\mathbf{q}}(\omega), \hat{\rho}^{\circ}]$$

$$\mathcal{L}\cdot\hat{\rho}'_{\mathbf{q}} \equiv [\hat{H}^{\circ}, \hat{\rho}'_{\mathbf{q}}] + [\tilde{V}'_{\mathrm{HXC},\mathbf{q}}, \hat{\rho}^{\circ}]$$

Let's use the Sternheimer algorithm

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

Susceptibility

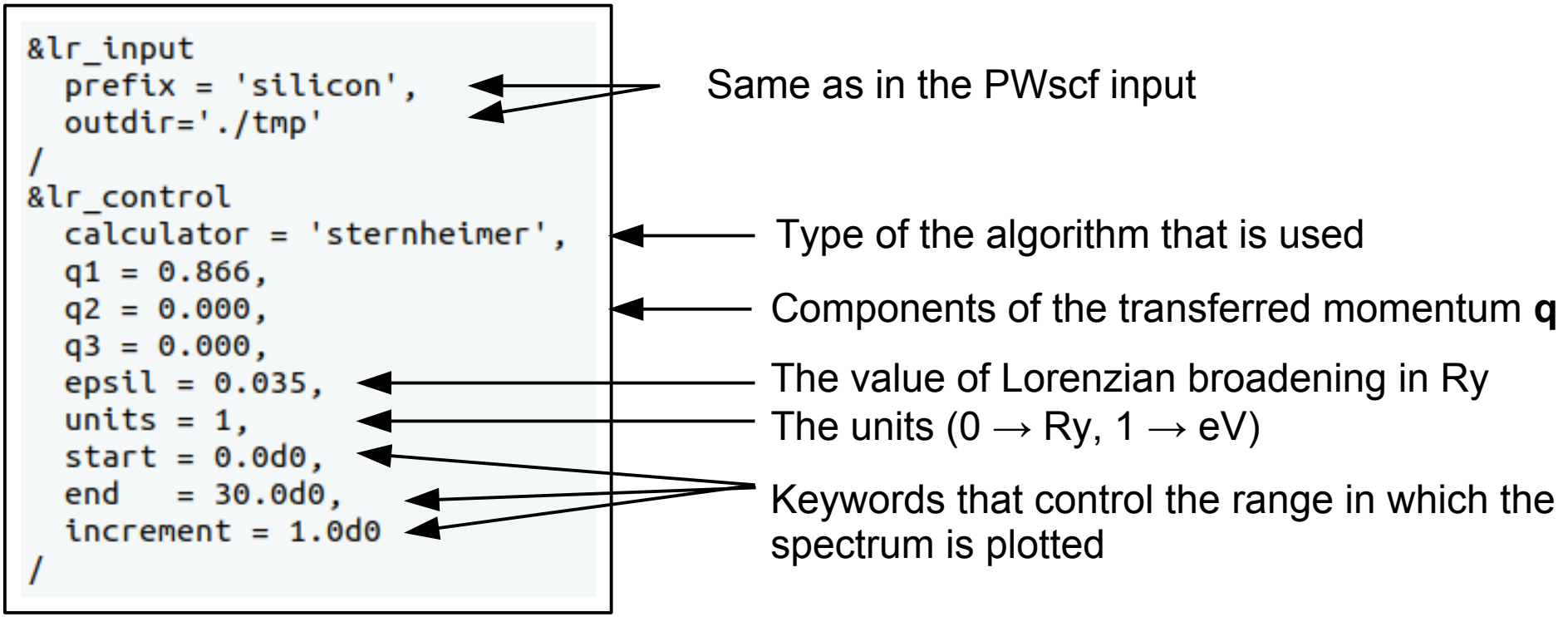
$$-\mathrm{Im}[\varepsilon^{-1}(\mathbf{q},\omega)] = -\frac{4\pi e^2}{|\mathbf{q}|^2}\,\mathrm{Im}[\chi(\mathbf{q},\mathbf{q};\omega)]$$

Loss function

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**



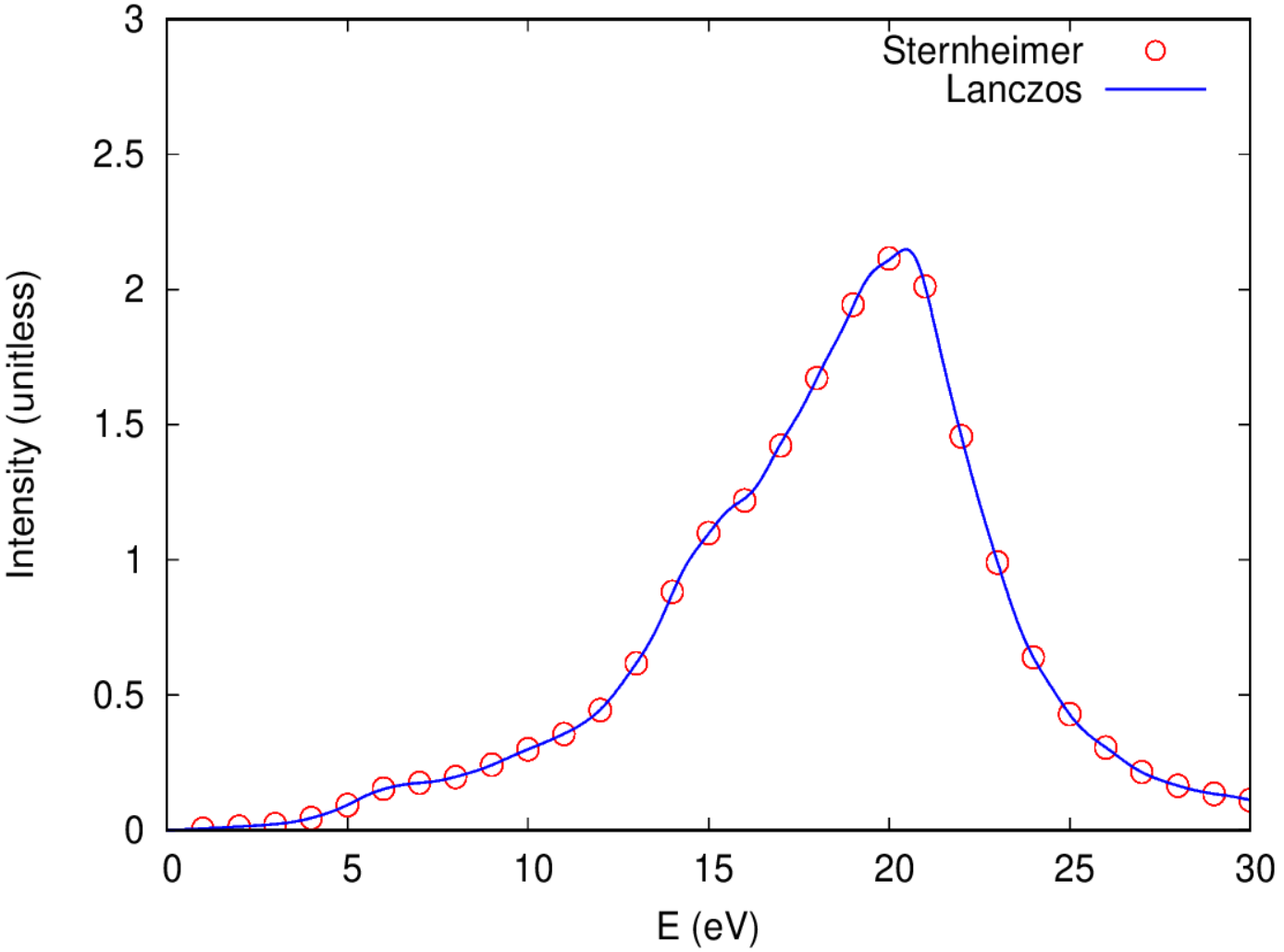

```
turbo_eels.x < turbo_eels.si.sternheimer.in > ...

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

Example 4: The computed EELS

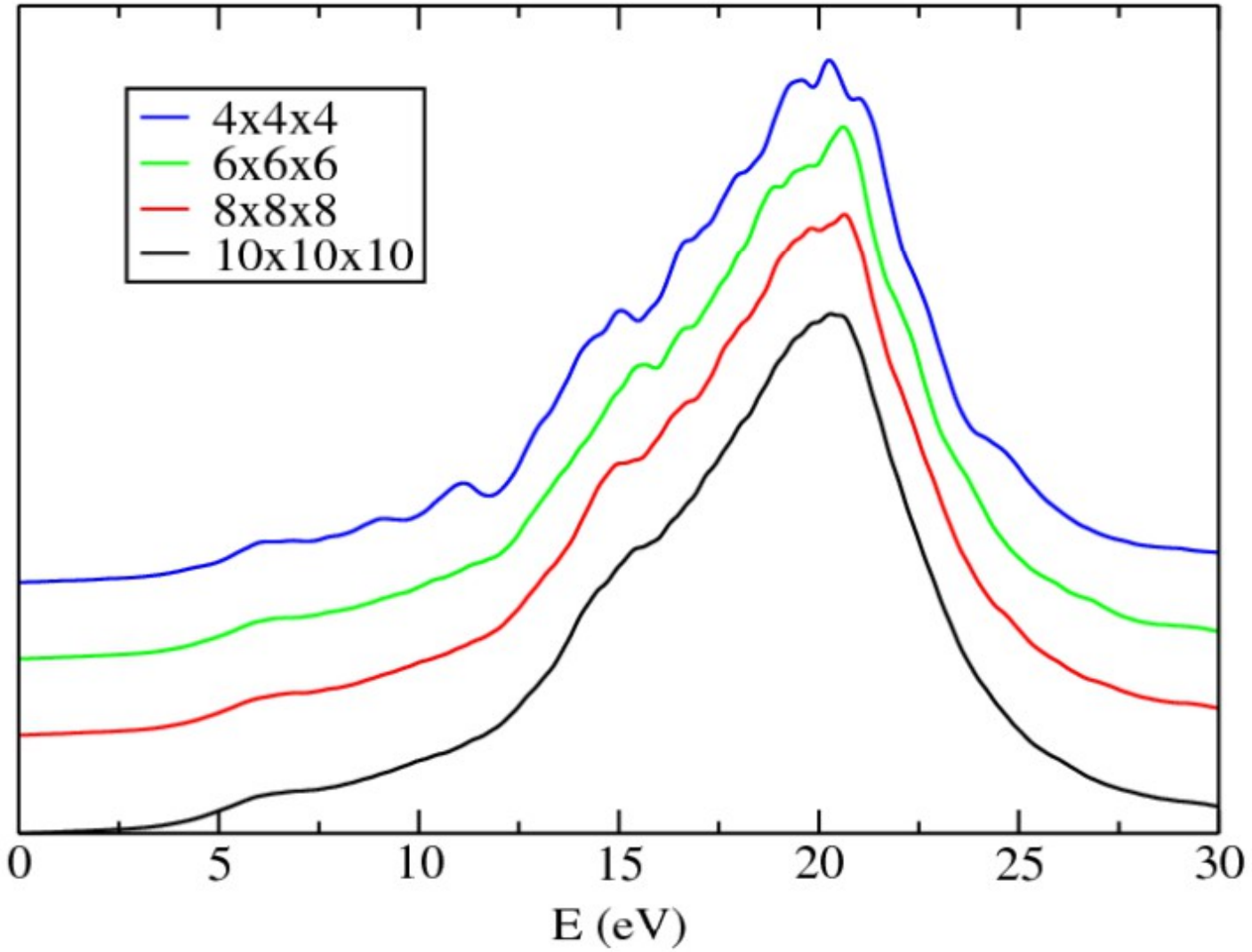
The Sternheimer and Lanczos algorithms give exactly the same spectrum.

Sternheimer is much slower than Lanczos!



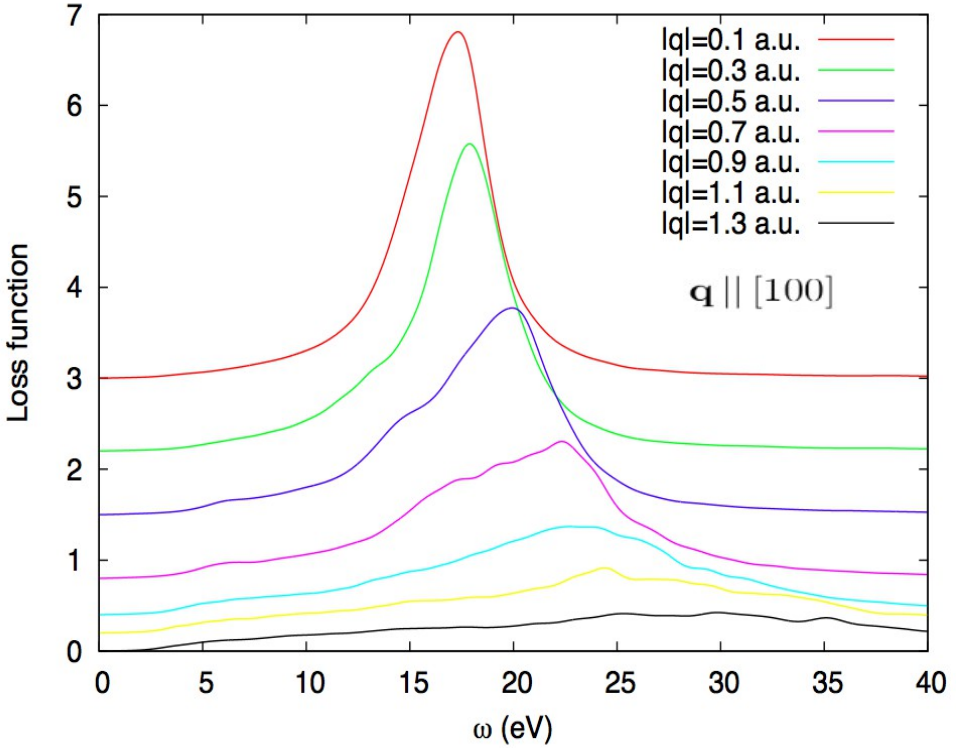
Example 4: Convergence w.r.t. **k** mesh

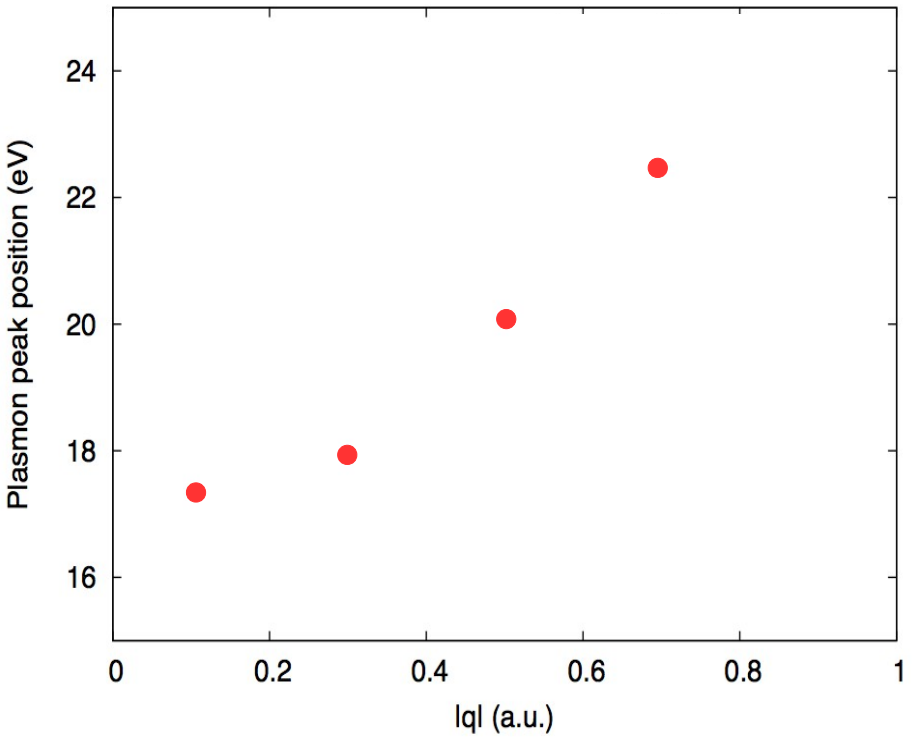
Convergence of EELS with respect to the size of the **k** points mesh



Example 4: Plasmon dispersion

Plasmon dispersion in bulk silicon

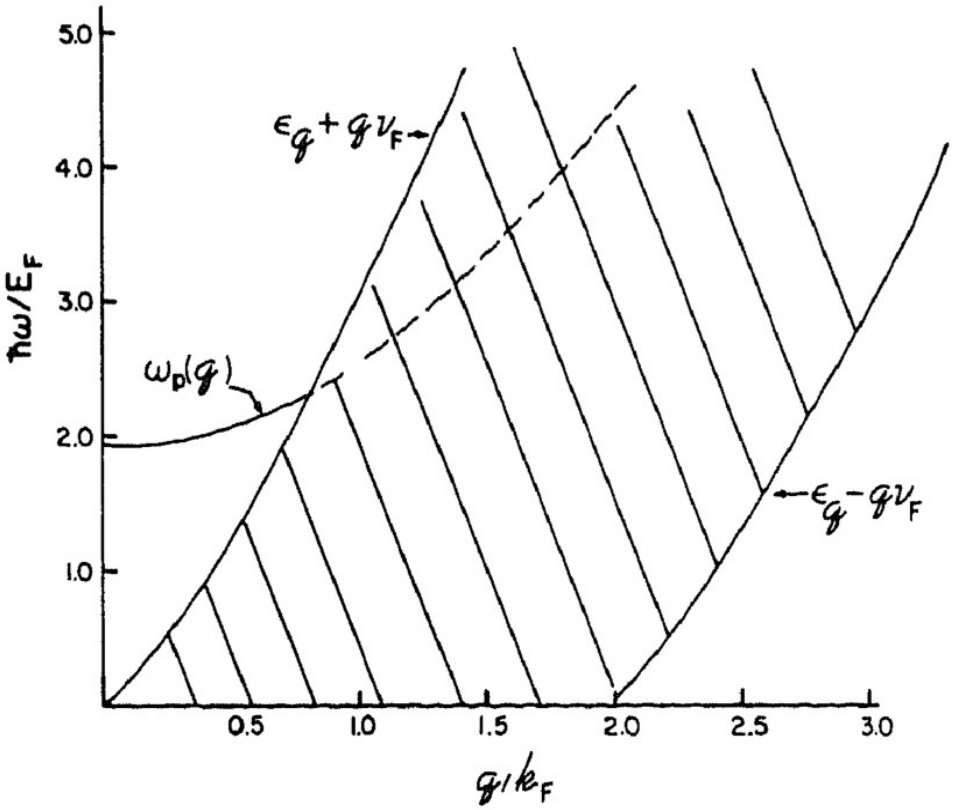




By increasing **q**, the plasmon peak blue-shifts and broadens, because it enters in the electron-hole continuum.

Example 4: Plasmon dispersion and e-h continuum

The excitation region of the electron gas in (**q**,w) 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)