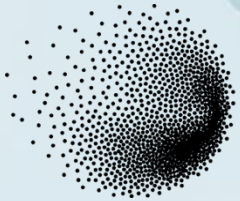
Hands-on: Time-dependent density functional theory (TDDFT) for solids

Presenter: Iurii Timrov (PSI)



PSI

MARVEL

NATIONAL CENTRE OF COMPETENCE IN RESEARCH

Electron energy loss spectra (EELS) of solids

exercise1: EELS spectrum of Si using the **turboEELS** code (Lanczos algorithm)

example2: EELS spectrum of Si using the **turboEELS** code (Sternheimer algorithm)

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:

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

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

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

exercise1: 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

Input file for turboEELS

Step 2. Perform Lanczos recursions using the **turbo_eels.x** program to compute Lanczos coefficients, which will be needed for the next step.

```
&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

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

Therefore, we obtain:

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

$$\mathrm{q2} = 0$$

$$\mathrm{q3} = 0$$

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 = '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
/
```

- Same as in the PWscf input
- EELS calculation
- Number of Lanczos iterations
- Number of Lanczos iterations
- Extrapolation technique
- Lorentzian broadening parameter (in Ry)
- Units for the spectrum plotting (1 = eV)
- Initial energy for plotting spectrum
- Final energy for plotting spectrum
- Energy step for plotting spectrum

Documentation: https://www.quantum-espresso.org/Doc/INPUT_Spectrum.html

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

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:

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

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

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

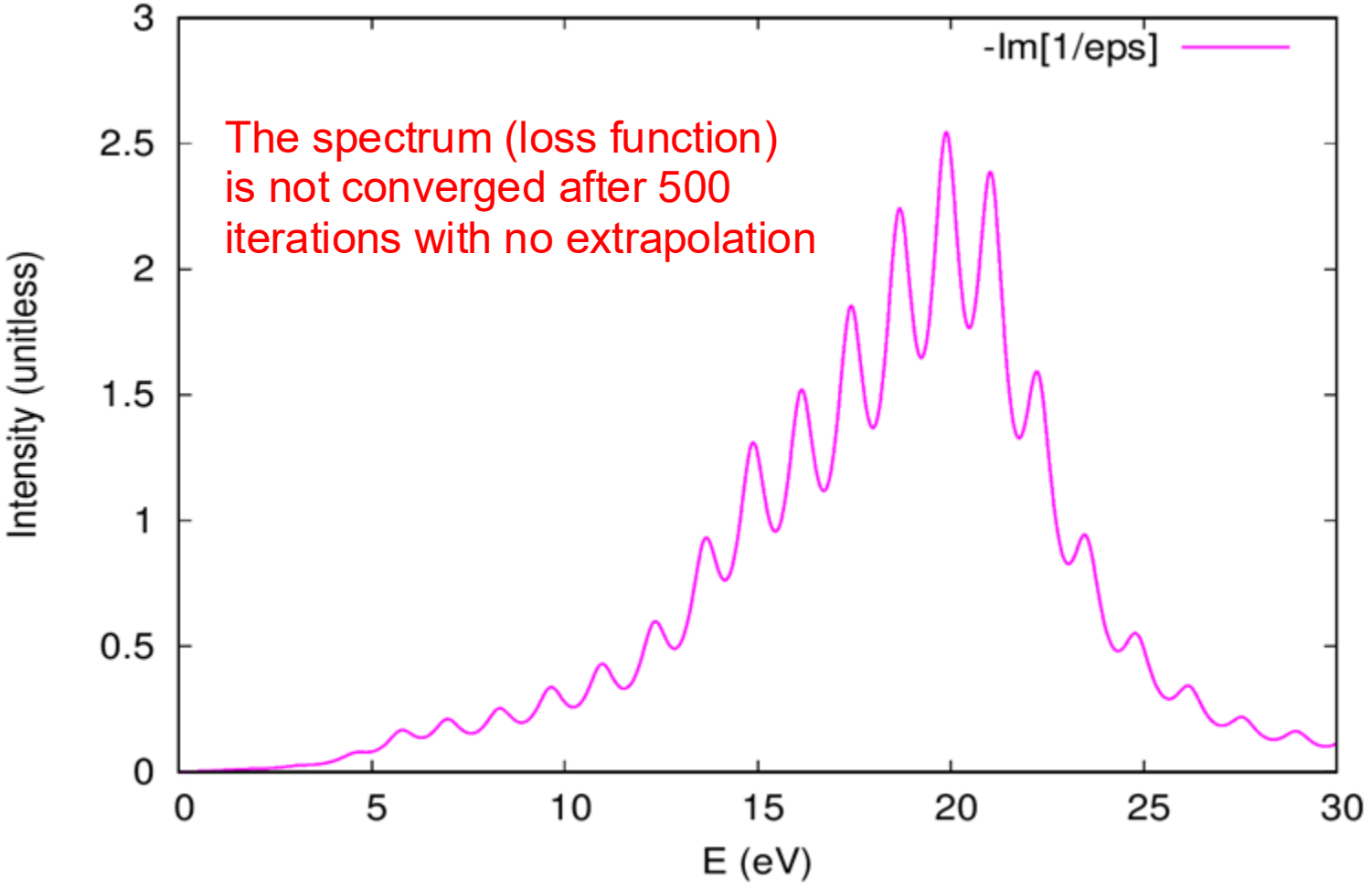
$$\varepsilon(\mathbf{q},\omega) = \frac{1}{\varepsilon^{-1}(\mathbf{q},\omega)} = \underbrace{\frac{\mathrm{Re}[\varepsilon^{-1}]}{(\mathrm{Re}[\varepsilon^{-1}])^2 + (\mathrm{Im}[\varepsilon^{-1}])^2}}_{\mathrm{Re}[\varepsilon(\mathbf{q},\omega)]} + i\,\underbrace{\frac{-\mathrm{Im}[\varepsilon^{-1}]}{(\mathrm{Re}[\varepsilon^{-1}])^2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

macroscopic

(local field effects are included)

The computed EELS

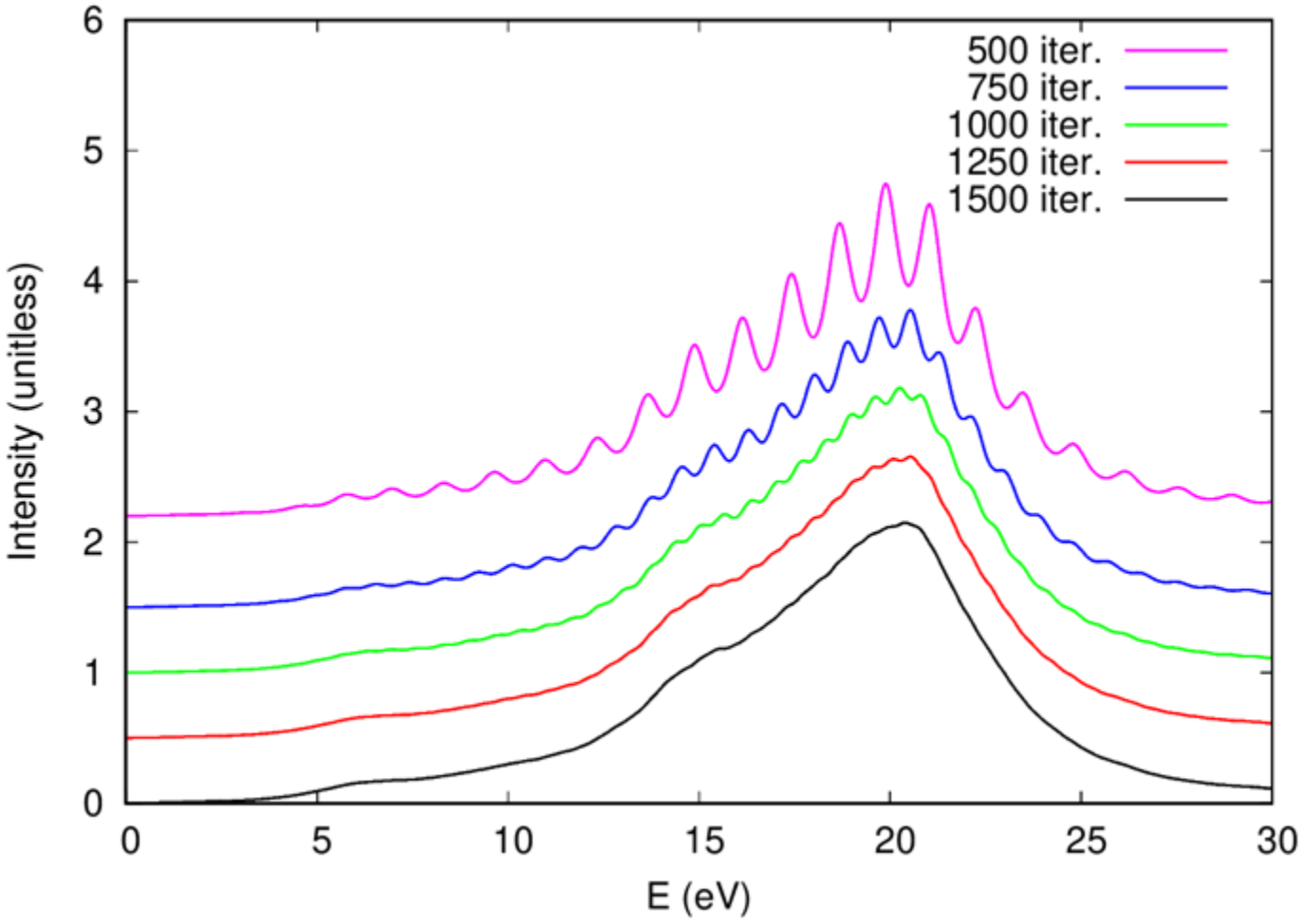
No extrapolation of Lanczos coefficients



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

Convergence of EELS

No extrapolation of Lanczos coefficients



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

Extrapolation of Lanczos coefficients

In the Liuoville-Lanczos approach, the EELS spectrum is computed as:

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

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

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

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

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

Post-processing step (with extrapolation)

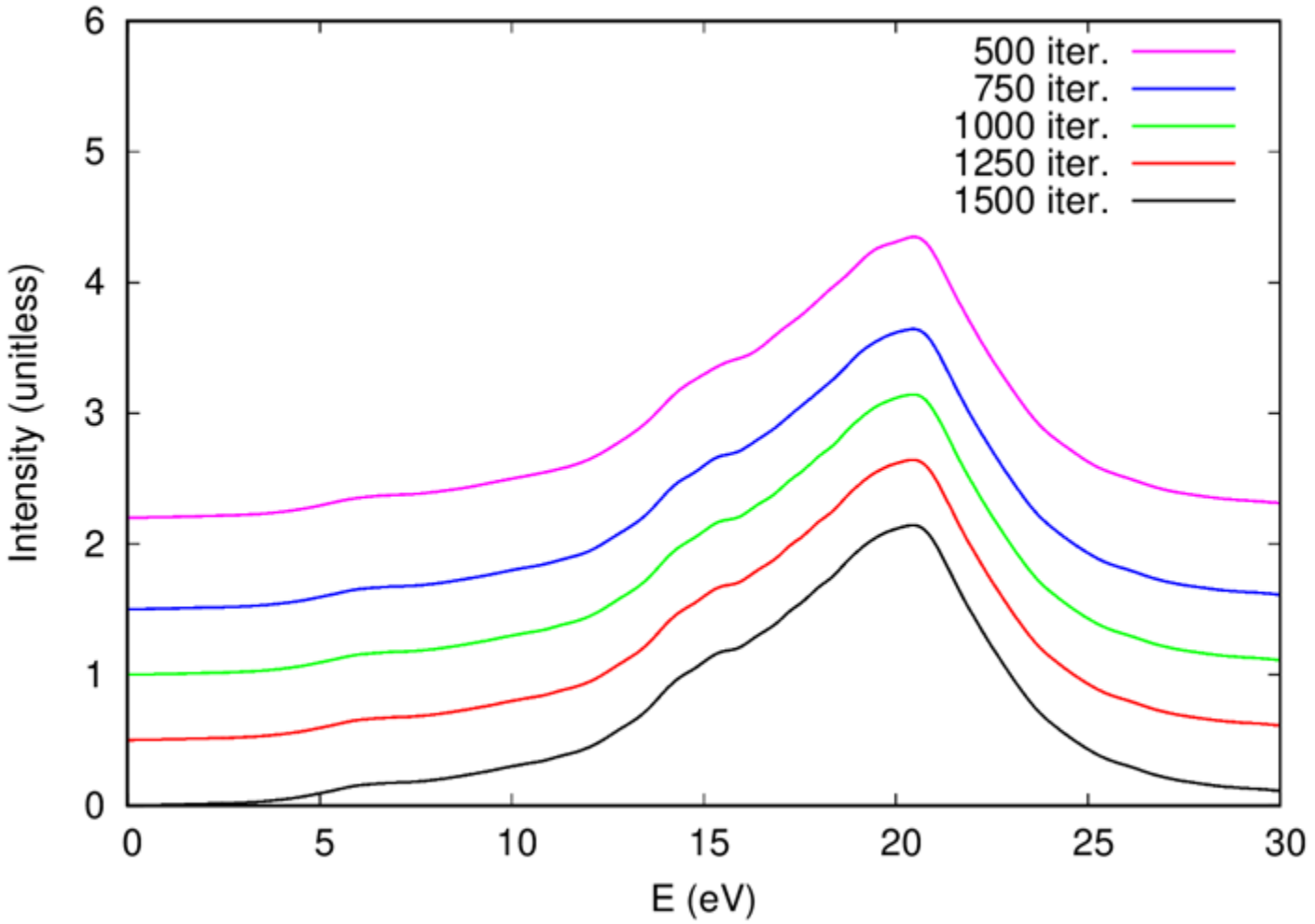
Perform a spectrum calculation using the post-processing program **turbo_spectrum.x** and using the Lanczos coefficients computed in the previous step.

```
&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
/
```

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

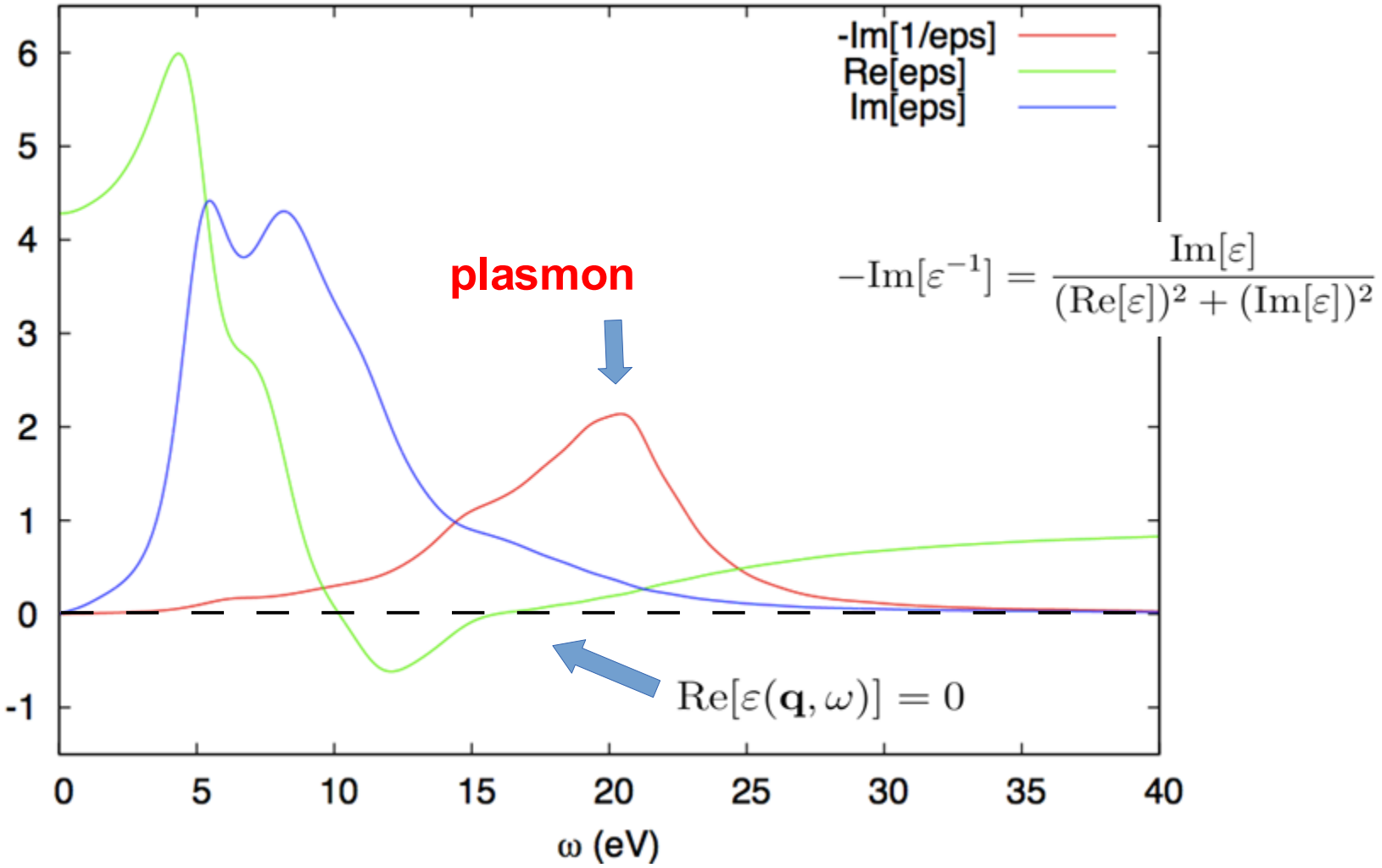
Convergence of EELS

With extrapolation of Lanczos coefficients



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

Where is the plasmon peak?



Exercise 2

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

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

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

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

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

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

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

Exercise 2

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

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

The use of HPC resources is recommended.

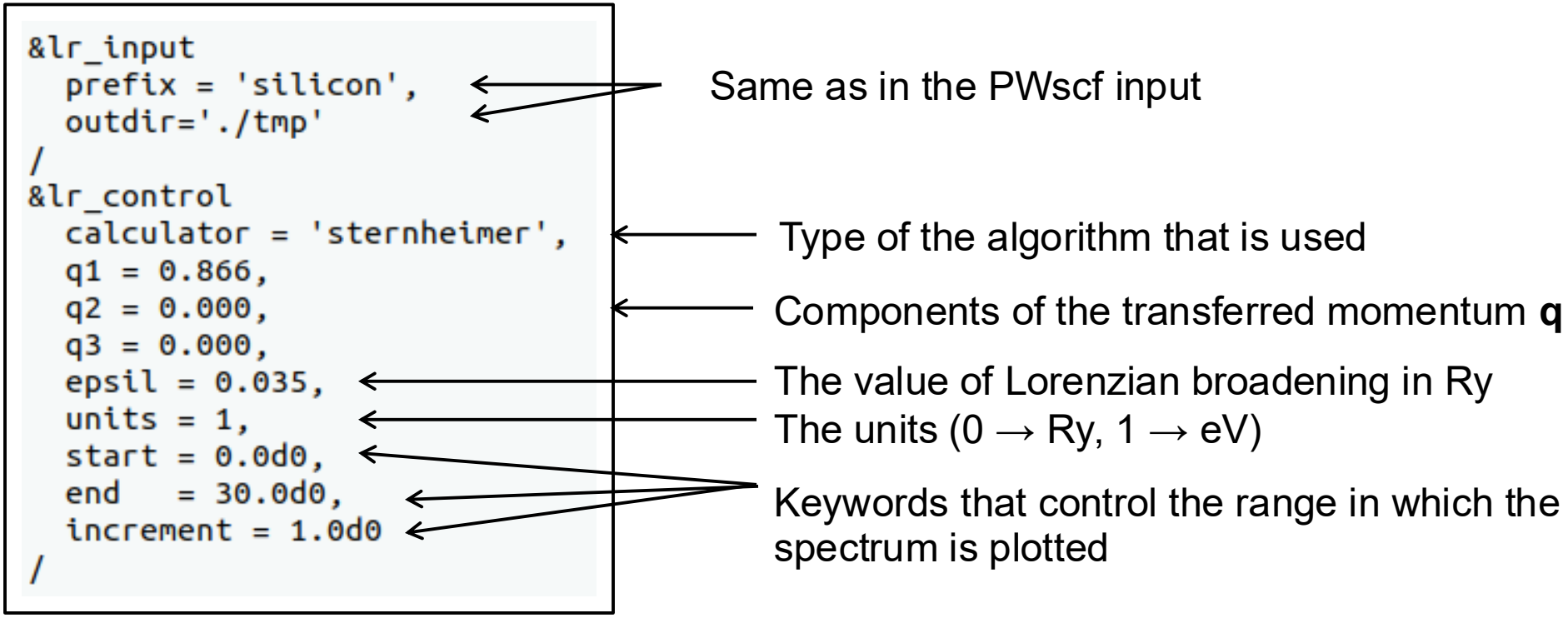
Moreover, the disc space must be large enough, because the code writes quite large files on disc and it may fail if there is not enough space (will be improved in the future version of QE).

Use the parallelization over **k** point pools to speed up the calculation.

exercise2: Input file for turboEELS

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

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

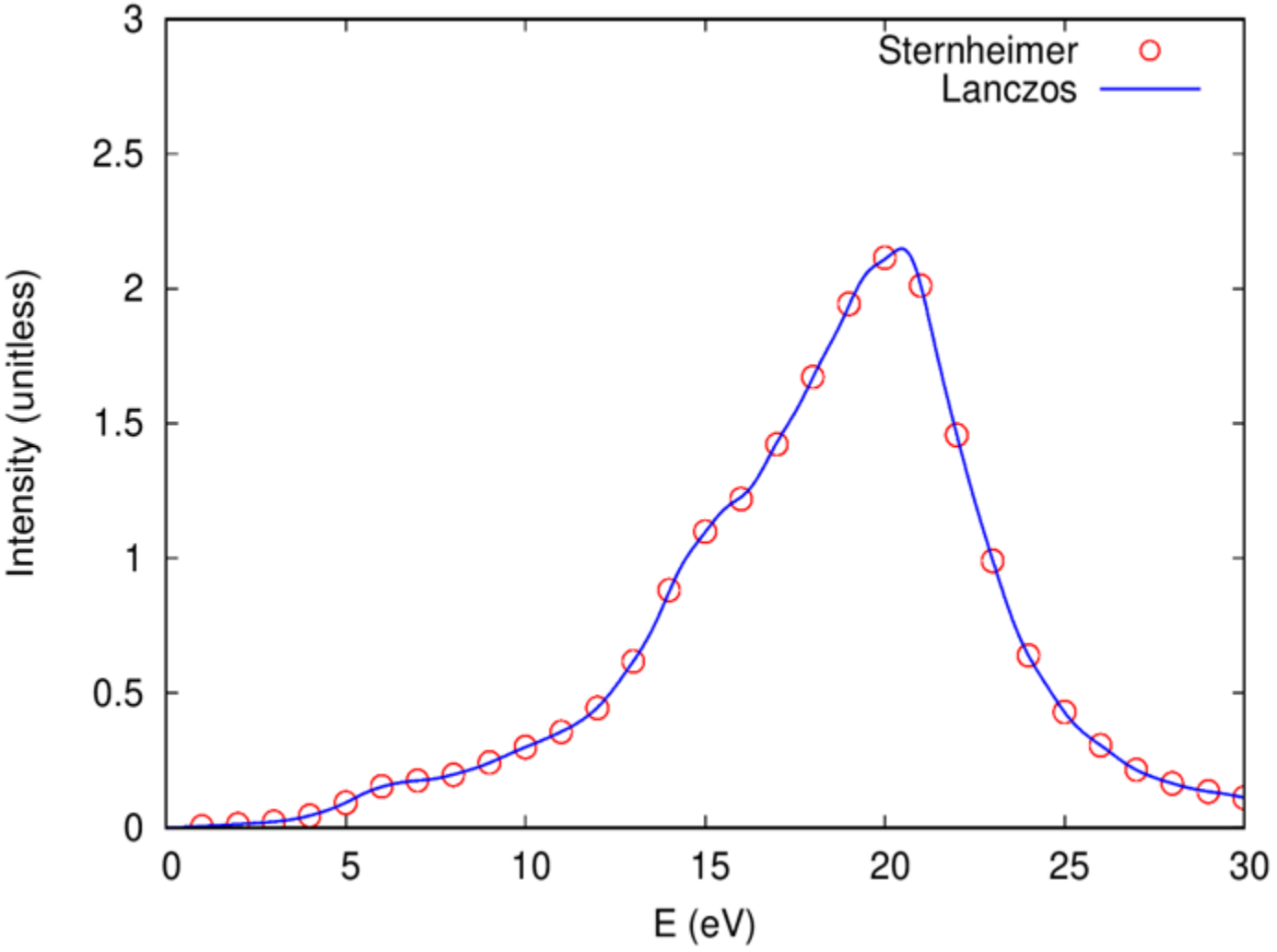


turbo_eels.x < turbo_eels.si.sternheimer.in > turbo_eels.si.sternheimer.out

exercise2: The computed EELS

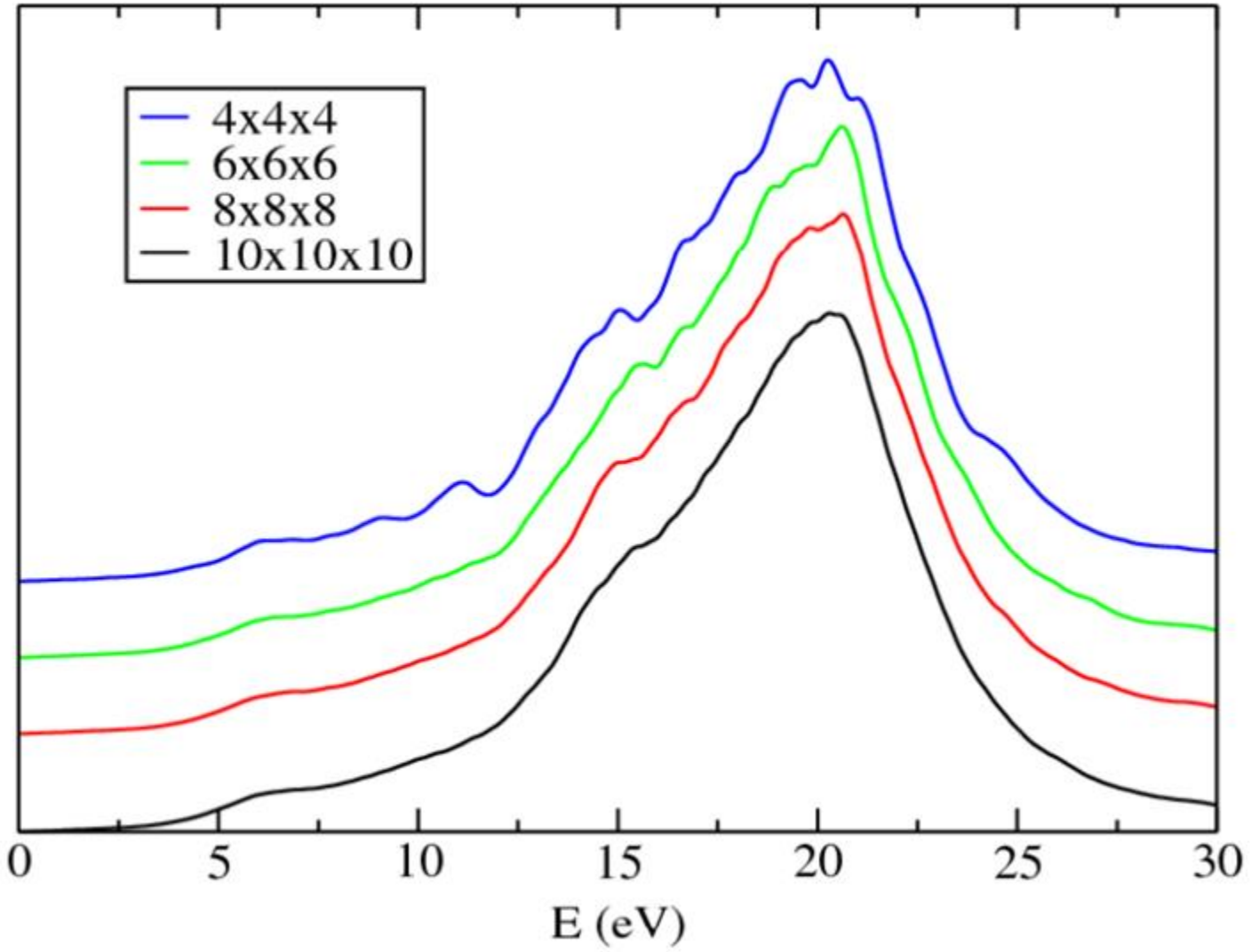
The Sternheimer and Lanczos algorithms give exactly the same spectrum.

Sternheimer is much slower than Lanczos!



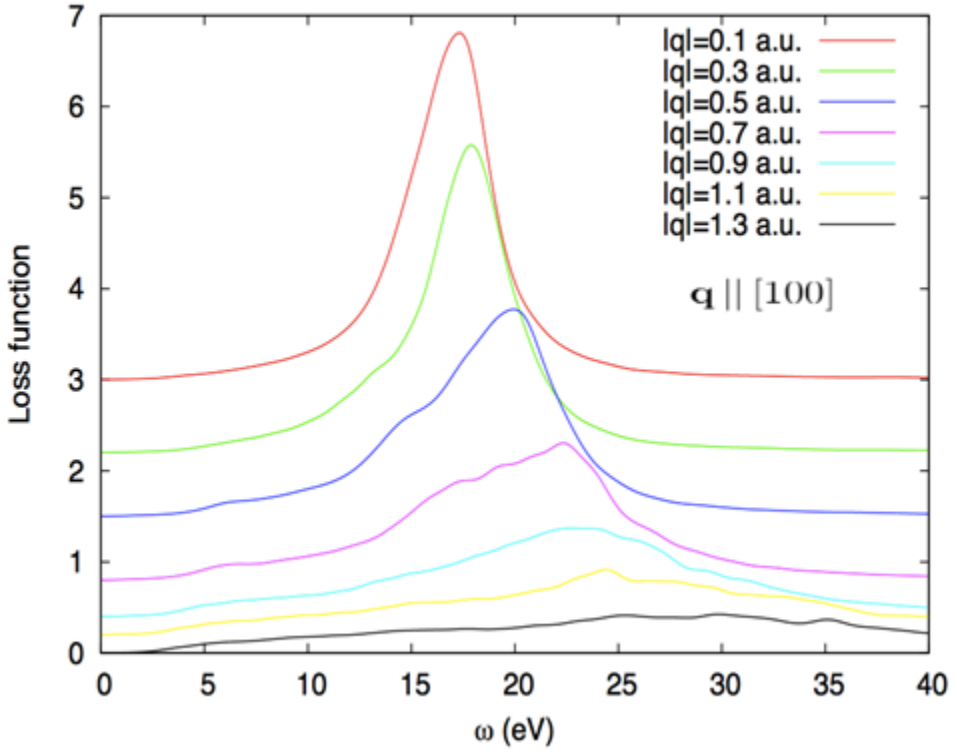
Convergence w.r.t. **k** mesh

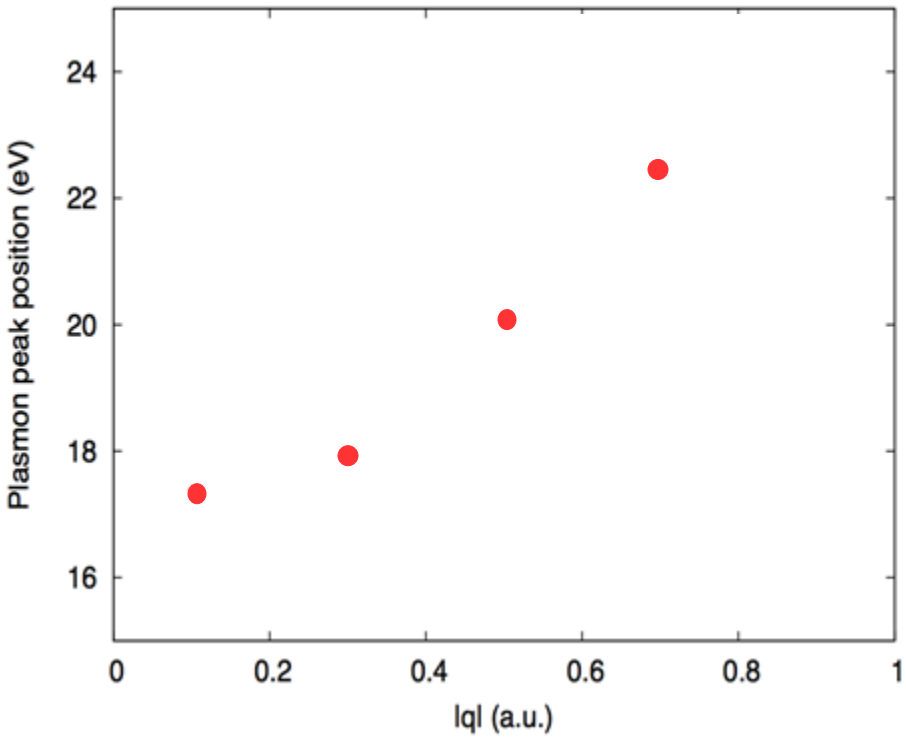
Convergence of EELS with respect to the size of the **k** points mesh



Plasmon dispersion

Plasmon dispersion in bulk silicon

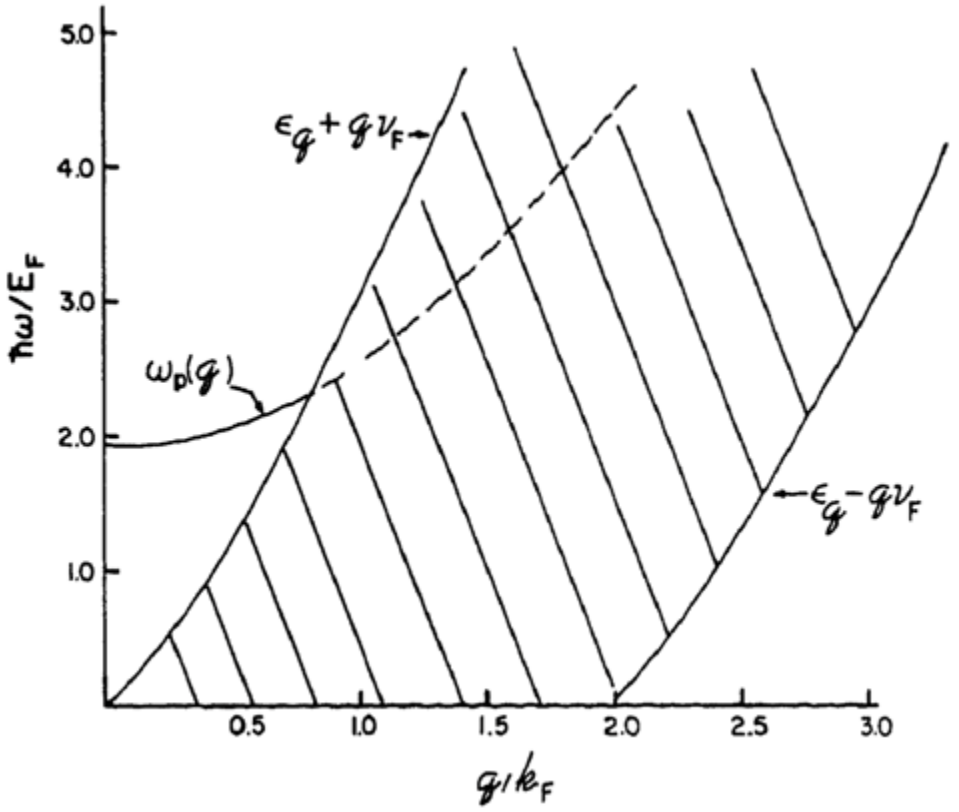




By increasing **q**, the plasmon peak blue-shifts and broadens, because it enters in the electron-hole continuum.

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)