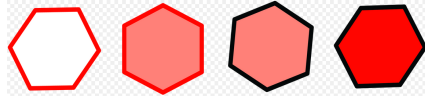


THEOS

THEORY AND SIMULATION  
OF MATERIALS

MARVEL



NATIONAL CENTRE OF COMPETENCE IN RESEARCH



QUANTUM ESPRESSO



ÉCOLE POLYTECHNIQUE  
FÉDÉRALE DE LAUSANNE

# Time-Dependent Density Functional Perturbation Theory: calculation of absorption spectra of molecules

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# Outline

1. **Exercise 1:** Calculation of absorption spectra in the Independent Particle Approximation
2. **Exercise 2:** Calculation of absorption spectra of interacting electrons using the **turboDavidson** program
3. **Exercise 3:** Calculation of absorption spectra of interacting electrons using the **turboLanczos** program
4. **Exercise 4:** Convergence of absorption spectra of Na<sub>2</sub>

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# Independent Particle Approximation

The simplest approximation: Independent Particle Approximation (IPA) which allows us to describe **single-particle excitations**.

## Fermi's golden rule

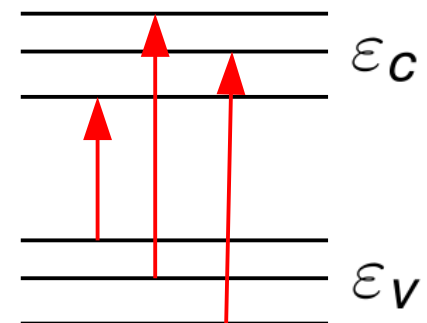
The transition probability per unit time from occupied states  $|\varphi_v\rangle$  to empty states  $|\varphi_c\rangle$  reads:

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

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

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

**Absorption coefficient:**  $\alpha(\omega) \propto \omega T(\omega)$



# Exercise 1: Calculation of absorption spectra in IPA

Go to the directory with the input files:

```
cd Hands-on_TDDFPT_ABS/exercise1
```

In this directory you will find:

- README – File describing how to do the exercise
- Benzene.scf.in – Input file for the SCF ground-state calculation
- Benzene.epsilon.in – Input file for a calculation of spectrum in IPA
- H.vbc.UPF – Pseudopotential of hydrogen
- C.vbc.UPF – Pseudopotential of carbon
- plot\_spectrum.gnu – Script to plot spectrum using **gnuplot**
- reference – Directory with the reference results
- out – Directory for temporary files

# Exercise 1: Calculation of absorption spectra in IPA

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

**Benzene.scf.in**

Input file for the SCF calculation

$C_6H_6$



**pw.x < Benzene.scf.in > Benzene.scf.out**

↑  
Input

↑  
Output

```
&CONTROL
  calculation = 'scf'
  restart_mode='from_scratch',
  pseudo_dir = './',
  outdir='./out',
  prefix='Benzene'
/
&SYSTEM
 ibrav = 6,
  celldm(1) = 32,
  celldm(3) = 0.83,
  nat = 12,
  ntyp = 2,
  ecutwfc = 40,
  nbnd = 20
/
&ELECTRONS
  diagonalization='david'
  mixing_mode = 'plain',
  mixing_beta = 0.6,
  conv_thr = 1.0d-8
/
ATOMIC_SPECIES
H 1.0 H.pz-vbc.UPF
C 12.01 C.pz-vbc.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}
```

# Exercise 1: Calculation of absorption spectra in IPA

The output SCF file `Benzene.scf.out` :

```
k = 0.0000 0.0000 0.0000 ( 58063 PWs)  bands (ev):  
-21.0314 -18.2544 -18.2527 -14.7154 -14.7145 -12.8536 -11.0182 -10.9287  
-10.1382 -10.1355 -9.1097 -8.1256 -8.1252 -6.3600 -6.3584 -1.2440  
-1.2428 -0.4093 0.1779 0.3011  
  
highest occupied, lowest unoccupied level (ev):  -6.3584  -1.2440
```

**HOMO**      **LUMO**

**HOMO** – Highest Occupied Molecular Orbital

**LUMO** – Lowest Unoccupied Molecular Orbital

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

# Exercise 1: Calculation of absorption spectra in IPA

**Step 2.** Perform a calculation of the absorption spectrum of benzene in the Independent Particle Approximation using the **epsilon.x** program.

## **Benzene.epsilon.in**

Input file for the calculation of spectrum

```
&INPUTPP
  calculation = 'eps'
  prefix = 'Benzene',
  outdir='./out'
/
&ENERGY_GRID
  smear_type = 'gaussian'
  intersmear = 0.1
  wmin = 0.0
  wmax = 15.0
  nw = 1000
/
```

- ← Type of the calculation
- ← The same prefix as in the SCF calculation
- ← Directory for temporary files
- ← Type of smearing of the spectrum
- ← The value of the smearing in eV
- ← Minimum value of frequencies for a plot in eV
- ← Maximum value of frequencies for a plot in eV
- ← Number of points between wmin and wmax

**epsilon.x < Benzene.epsilon.in > Benzene.epsilon.out**



# Exercise 1: Calculation of absorption spectra in IPA

The code `epsilon.x` produces 4 files:

- `epsr_Benzene.dat` – Real part of the response
- `epsi_Benzene.dat` – Imaginary part of the response (this is what we need)
- `eels_Benzene.dat` – Electron energy loss spectrum
- `ieps_Benzene.dat` – Response computed on the imaginary axis of frequency

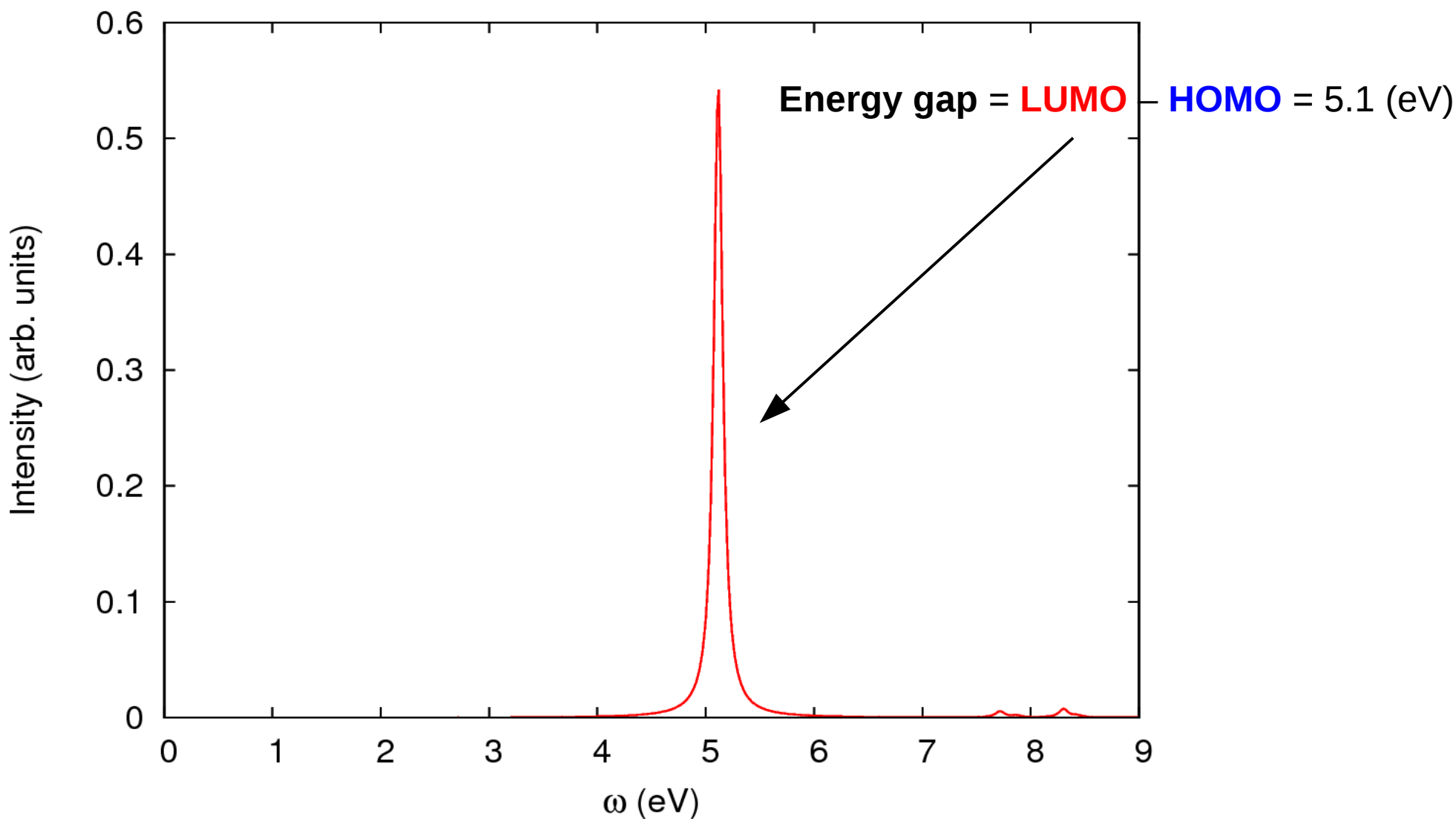
The content of `epsi_Benzene.dat` looks like this:

```
# energy grid [eV]      epsi_x      epsi_y      epsi_z
0.0000000000          0.0000000000  0.0000000000  0.0000000000
0.015015015          0.000000631  0.000000630  0.000000124
0.030030030          0.000001263  0.000001260  0.000000248
0.045045045          0.000001894  0.000001891  0.000000371
.....
```

Use `gnuplot` and the script `plot_spectrum.gnu` in order to plot the absorption spectrum of benzene `Benzene_spectrum.eps`

# Exercise 1: Calculation of absorption spectra in IPA

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



# Outline

1. **Exercise 1:** Calculation of absorption spectra in the Independent Particle Approximation
2. **Exercise 2:** Calculation of absorption spectra of interacting electrons using the **turboDavidson** program
3. **Exercise 3:** Calculation of absorption spectra of interacting electrons using the **turboLanczos** program
4. **Exercise 4:** Convergence of absorption spectra of Na<sub>2</sub>

# 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.
- 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.

**Theory:** *Xiaochuan Ge, PhD thesis "Seeing colors with TDDFT", SISSA (2013).*

# turboDavidson program for calculations of absorption spectra

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

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

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  $\hat{D} \rightarrow (\hat{H}^0 - \varepsilon_v)$  and  $\hat{K} \rightarrow \hat{P}_c \hat{V}'_{\text{HXC}} \varphi_v^0(\mathbf{r})$

**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.

# Exercise 2: Calculation of absorption spectra using the turboDavidson code

Go to the directory with the input files:

```
cd Hands-on_TDDFPT_ABS/exercise2
```

In this directory you will find:

- README – File describing how to do the exercise
- Benzene.scf.in – Input file for the SCF ground-state calculation
- Benzene.davidson.no\_int.in – Input file for a Davidson calculation of the eigenvalues (no interaction)
- Benzene.davidson.with\_int.in – Input file for a Davidson calculation of the eigenvalues (with interaction)
- Benzene.tddfpt\_pp.in – Input file for a post-processing calculation of a spectrum
- H.vbc.UPF – Pseudopotential of hydrogen
- C.vbc.UPF – Pseudopotential of carbon
- plot\_spectrum.gnu – Script to plot spectrum using **gnuplot**
- reference – Directory with the reference results
- out – Directory for temporary files

# Exercise 2: Calculation of absorption spectra using the turboDavidson code

**Step 1.** Perform a SCF ground-state calculation:

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

**Step 2.** Perform the turboDavidson calculation without the electronic interaction using the `turbo_davidson.x` program.

```
&lr_input
  prefix = 'Benzene',
  outdir='./out'
/
&lr_dav
  if_dft_spectrum = .true.
  p_nband_occ = 10
  p_nband_virt = 5
  num_init = 30
/
```

← The same prefix as in the SCF calculation  
← Directory for temporary files

← **Switch off the interaction**

← Number of highest occupied bands

← Number of lowest virtual (unoccupied) bands

← This parameter must be larger than or equal to  $p\_nband\_occ * p\_nband\_virt / 2$

```
turbo_davidson.x < Benzene.davidson.in > Benzene.davidson.out
```

## Exercise 2: Calculation of absorption spectra using the turboDavidson code

The code `turbo_davidson.x` produces a file `Benzene-dft.eigen` containing single-particle excitation eigenvalues:

```
# Energy(Ry) total X Y Z
0.37590598E+00 0.46112657E+00 0.70401836E-02 0.45408639E+00 0.47931192E-13
0.37599798E+00 0.46115096E+00 0.45411646E+00 0.70344976E-02 0.59956678E-12
0.37601265E+00 0.46120722E+00 0.45417084E+00 0.70363787E-02 0.51303634E-12
0.37610465E+00 0.46103177E+00 0.70436152E-02 0.45398816E+00 0.19716532E-10
0.43726351E+00 0.13192540E-10 0.32941403E-15 0.73689188E-13 0.13118521E-10
0.43737018E+00 0.13835614E-10 0.14625657E-13 0.60090840E-16 0.13820928E-10
0.48041706E+00 0.14768841E-01 0.95193281E-11 0.14676701E-08 0.14768839E-01
0.48052374E+00 0.12967454E-02 0.14330540E-08 0.88198051E-11 0.12967439E-02
.... .... .... .... ....
```

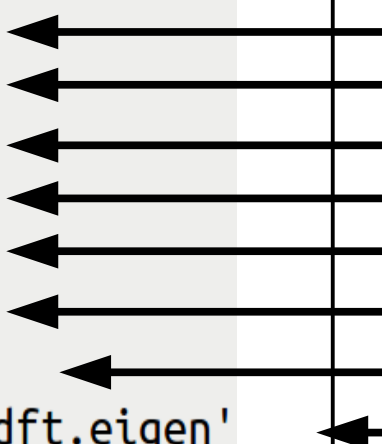


## Exercise 2: Calculation of absorption spectra using the turboDavidson code

**Step 3.** Perform a spectrum calculation using the `turbo_spectrum.x` program and using the eigenvalues computed in the previous step.

The input file `Benzene.tddfpt_pp.in` reads:

```
&lr_input
  prefix = 'Benzene',
  outdir = './out',
  td = 'davidson',
  start = 0.0,
  end   = 1.0,
  increment = 0.001,
  epsilon = 0.004,
  eign_file = 'Benzene-dft.eigen'
/
```



- ← The same prefix as in the SCF calculation
- ← Directory for temporary files
- ← Type of previous calculation
- ← Minimum value of frequencies for a plot in Ry
- ← Maximum value of frequencies for a plot in Ry
- ← Frequency step in Ry
- ← The value of Lorentzian smearing in Ry
- ← Frequency with Davidson eigenvalues

`turbo_spectrum.x < Benzene.tddfpt_pp.in > Benzene.tddfpt_pp.out`

# Exercise 2: Calculation of absorption spectra using the turboDavidson code

The `turbo_spectrum.x` program produces the file `Benzene.plot` which contains the absorption spectrum in a tabular format:

#	Energy(Ry)	total	Ry	X	Y	Z
#	Broadening is:	0.0040000				
	0.00000000E+00	0.00000000E+00		0.00000000E+00	0.00000000E+00	0.00000000E+00
	0.10000000E-02	0.54834907E-04		0.27093597E-04	0.27098657E-04	0.64265224E-06
	0.20000000E-02	0.11024611E-03		0.54473003E-04	0.54483060E-04	0.12900480E-05
	0.30000000E-02	0.16624050E-03		0.82141642E-04	0.82156630E-04	0.19422276E-05
	0.40000000E-02	0.22282506E-03		0.11010299E-03	0.11012284E-03	0.25992316E-05
	0.50000000E-02	0.28000688E-03		0.13836056E-03	0.13838522E-03	0.32611011E-05
	0.60000000E-02	0.33779314E-03		0.16691794E-03	0.16694732E-03	0.39278777E-05
	0.70000000E-02	0.39619114E-03		0.19577875E-03	0.19581279E-03	0.45996032E-05
	....	....		....	....	....

## Exercise 2: Calculation of absorption spectra using the turboDavidson code

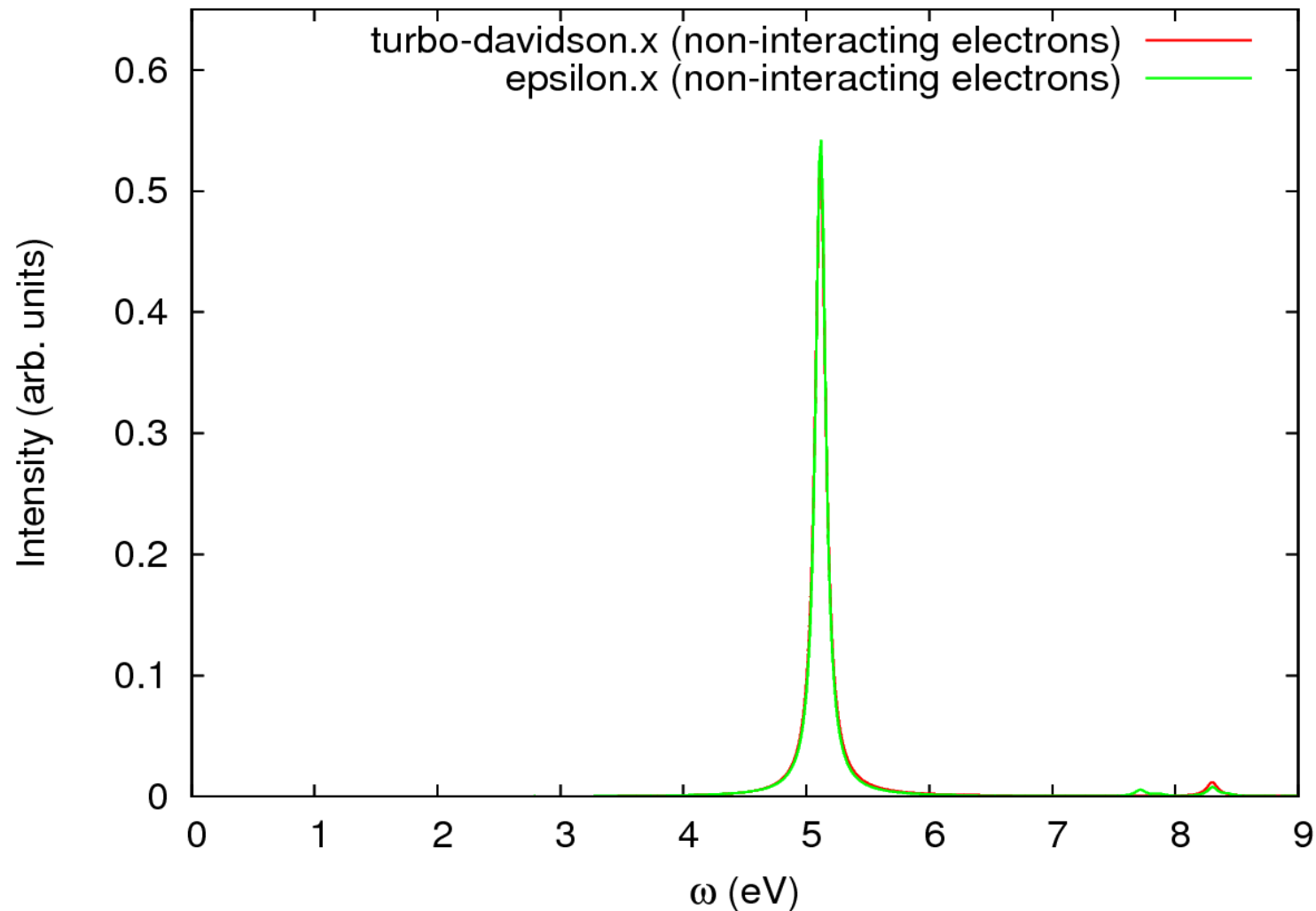
**Step 4.** Plot the spectrum using **gnuplot** and the script `plot_spectrum.gnu`

Since the interaction was switched off (`if_dft_spectrum=.true.`), you should obtain the same absorption spectrum as the one obtained using the **epsilon.x** program in the **exercise1**.

The script `plot_spectrum.gnu` will do such a comparison, and it will produce the file **Benzene\_spectrum.eps** which you can visualize.

## Exercise 2: Calculation of absorption spectra using the turboDavidson code

Comparison of the absorption spectrum of benzene computed in the Independent Particle Approximation using `turbo_davidson.x` and `epsilon.x` (file `Benzene_spectrum.eps`):



## Exercise 2: Calculation of absorption spectra using the turboDavidson code

### Now switch on the interaction!

Make the following modifications in the input files:

- Use the file `Benzene.davidson.with_int.in` where `if_dft_spectrum = .false.`
- In the file `Benzene.tddfpt_pp.in` set `eign_file = 'Benzene.eigen'`
- In `plot_spectrum.gnu` change the title to:  
`'turbo-davidson.x (interacting electrons)'`

**Note!** The calculation will be much longer: ~5-10 minutes using 4 cores.

Therefore, let us see the output files in the directory `'reference'`.

## Exercise 2: Calculation of absorption spectra using the turboDavidson code

Step 5. Perform the turboDavidson calculation with the electronic interaction

```
&lr_input
  prefix = 'Benzene',
  outdir='./out'
/
&lr_dav
  if_dft_spectrum = .false.
  p_nband_occ = 10
  p_nband_virt = 5
  num_init = 30
  num_eign = 15
  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
  poor_of_ram2 = .true.
/
```

← The same prefix as in the SCF calculation  
← Directory for temporary files

← **Switch on the interaction**  
← Number of highest occupied bands  
← Number of lowest virtual (unoccupied) bands  
← Number of initial vectors  
← Number of eigenvalues to be calculated  
← 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  
← Reduce RAM requirements

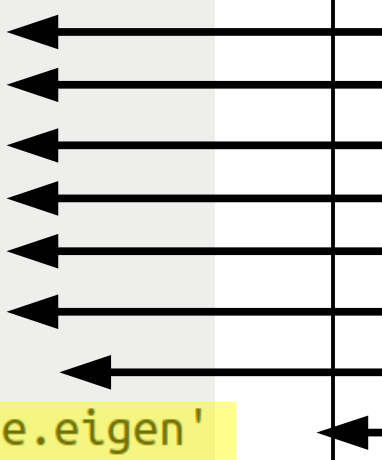
**turbo\_davidson.x < Benzene.davidson.in > Benzene.davidson.out**

## Exercise 2: Calculation of absorption spectra using the turboDavidson code

**Step 6 (optional).** Perform a spectrum calculation using the `turbo_spectrum.x` and using the eigenvalues computed in the previous step. The file `Benzene.plot` was already produced by turboDavidson.

The input file `Benzene.tddfpt_pp.in` reads:

```
&lr_input
  prefix = 'Benzene',
  outdir = './out',
  td = 'davidson',
  start = 0.0,
  end   = 1.0,
  increment = 0.001,
  epsil = 0.004,
  eign_file = 'Benzene.eigen'
/
```

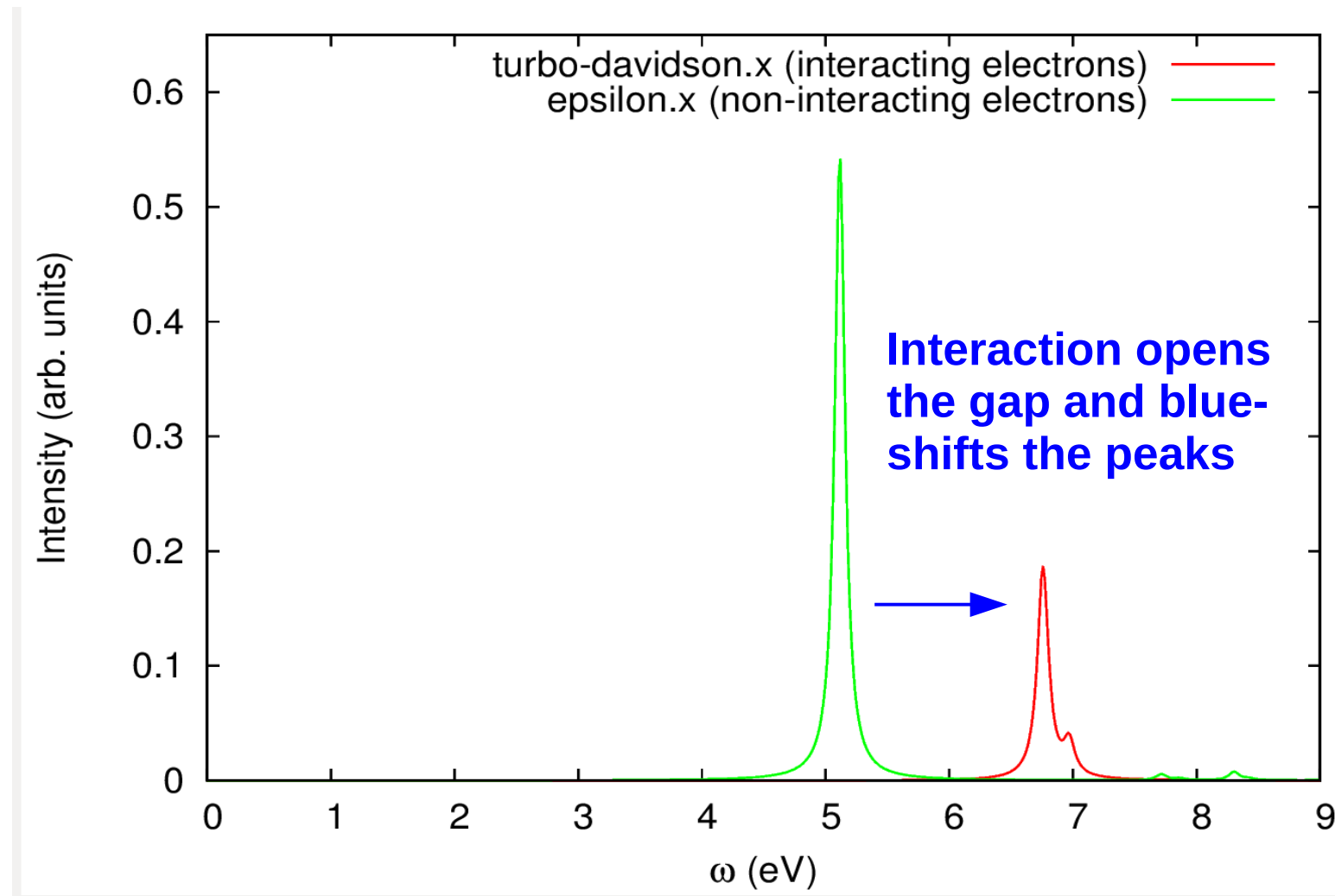


- ← The same prefix as in the SCF calculation
- ← Directory for temporary files
- ← Type of previous calculation
- ← Minimum value of frequencies for a plot in Ry
- ← Maximum value of frequencies for a plot in Ry
- ← Frequency step in Ry
- ← The value of Lorentzian smearing in Ry
- ← Frequency with Davidson eigenvalues

```
turbo_spectrum.x < Benzene.tddfpt_pp.in > Benzene.tddfpt_pp.out
```

## Exercise 2: Calculation of absorption spectra using the turboDavidson code

Comparison of the absorption spectrum of benzene computed using **turbo\_davidson.x** with interaction and using **epsilon.x** in the Independent Particle Approximation (file **Benzene\_spectrum.eps**):





# Outline

1. **Exercise 1:** Calculation of absorption spectra in the Independent Particle Approximation
2. **Exercise 2:** Calculation of absorption spectra of interacting electrons using the **turboDavidson** program
3. **Exercise 3:** Calculation of absorption spectra of interacting electrons using the **turboLanczos** program
4. **Exercise 4:** Convergence of absorption spectra of Na<sub>2</sub>

# 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!**

**Theory:** *Dario Rocca, PhD thesis "TDDFT: New algorithms with applications to molecular spectra", SISSA (2007).*

# turboLanczos program for calculation of absorption spectra

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

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

perturbation

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

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

interaction terms

**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.

# Exercise 3: Calculation of absorption spectra using the turboLanczos code

Go to the directory with the input files:

```
cd Hands-on_TDDFPT_ABS/exercise3
```

In this directory you will find:

- README – File describing how to do the exercise
- Benzene.scf.in – Input file for the SCF ground-state calculation
- Benzene.lanczos.in – Input file to perform Lanczos recursions
- Benzene.tddfpt\_pp.in – Input file for a postprocessing calculation of spectrum
- H.vbc.UPF – Pseudopotential of hydrogen
- C.vbc.UPF – Pseudopotential of carbon
- plot\_spectrum.gnu – Script to plot spectrum using **gnuplot**
- reference – Directory with the reference results
- out – Directory for temporary files

# Exercise 3: Calculation of absorption spectra using the turboLanczos code

**Step 1.** Perform a SCF ground-state calculation:

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

**Step 2.** Perform Lanczos recursions using the `turbo_lanczos.x` program  
The input file is `Benzene.lanczos.in` :

```
&lr_input  
  prefix = 'Benzene',  
  outdir='./out',  
  restart_step = 100,  
  restart = .false.  
/  
&lr_control  
  itermx = 1100,  
  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

← Response along the X axis (2: along Y, 3: along Z)

```
turbo_lanczos.x < Benzene.lanczos.in > Benzene.lanczos.out
```

# Exercise 3: Calculation of absorption spectra using the turboLanczos code

**Note!** The calculation will last ~5 minutes using 4 cores.

Therefore, let us see the output files in the directory **reference**.

In the output file **Benzene.lanczos.out** there is information about each Lanczos iteration :

```
Lanczos iteration:      2   Pol:1
lr_apply_liouvillian: applying interaction: normal
alpha(00000002)=  0.000000
beta (00000002)=  3.250639
gamma(00000002)=  3.250639
z1=          1  0.118716199800790E+01  0.0000000000000000E+00
```

In the directory **out**, which contains temporary files, there is a file **Benzene.beta\_term.1** which contains the information about beta Lanczos coefficients, which can be visualized for the analysis.

# Exercise 3: Calculation of absorption spectra using the turboLanczos code

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

The input file **Benzene.tddfpt\_pp.in** reads:

```
&lr_input
  prefix = 'Benzene',
  outdir = './out',
  itermax0 = 1100,
  itermax = 20000,
  extrapolation = 'osc',
  start = 0.0,
  end = 1.0,
  increment = 0.001,
  epsil = 0.004,
  ipol = 1
/
```

- ← The same prefix as in the SCF calculation
- ← Directory for temporary files
- ← Number of calculated Lanczos coefficient
- ← Number up to which the coefficients will be extrapolated
- ← Type of extrapolation (bi-constant)
- ← Minimum value of frequencies for a plot in Ry
- ← Maximum value of frequencies for a plot in Ry
- ← Frequency step in Ry
- ← The value of Lorentzian smearing in Ry
- ← Polarization direction (same as in turbo\_lanczos.x)

**turbo\_spectrum.x < Benzene.tddfpt\_pp.in > Benzene.tddfpt\_pp.out**

# Exercise 3: Calculation of absorption spectra using the turboLanczos code

The code `turbo_spectrum.x` produces a file `Benzene.plot_chi.dat` which can be used for plotting the absorption spectrum :

```
#          \omega (Ry)          Re(chi)          Im(chi)
chi_1_1=  0.0000000000000000E+00  0.428278391671114E+02  0.0000000000000000E+00
chi_1_1=  0.1000000000000000E-02  0.428279198751938E+02  0.645795138600257E-03
chi_1_1=  0.2000000000000000E-02  0.428281620024502E+02  0.129161436329857E-02
chi_1_1=  0.3000000000000000E-02  0.428285655579074E+02  0.193748176285888E-02
chi_1_1=  0.4000000000000000E-02  0.428291305566122E+02  0.258342143137753E-02
chi_1_1=  0.5000000000000000E-02  0.428298570196319E+02  0.322945747095084E-02
chi_1_1=  0.6000000000000000E-02  0.428307449740568E+02  0.387561399434450E-02
chi_1_1=  0.7000000000000000E-02  0.428317944530042E+02  0.452191512766540E-02
chi_1_1=  0.8000000000000000E-02  0.428330054956205E+02  0.516838501303605E-02
chi_1_1=  0.9000000000000000E-02  0.428343781470868E+02  0.581504781127286E-02
chi_1_1=  0.1000000000000000E-01  0.428359124586233E+02  0.646192770456826E-02
chi_1_1=  0.1100000000000000E-01  0.428376084874952E+02  0.710904889917749E-02
chi_1_1=  0.1200000000000000E-01  0.428394662970188E+02  0.775643562811093E-02
          . . . . .          . . . . .          . . . . .
```



## Exercise 3: Calculation of absorption spectra using the turboLanczos code

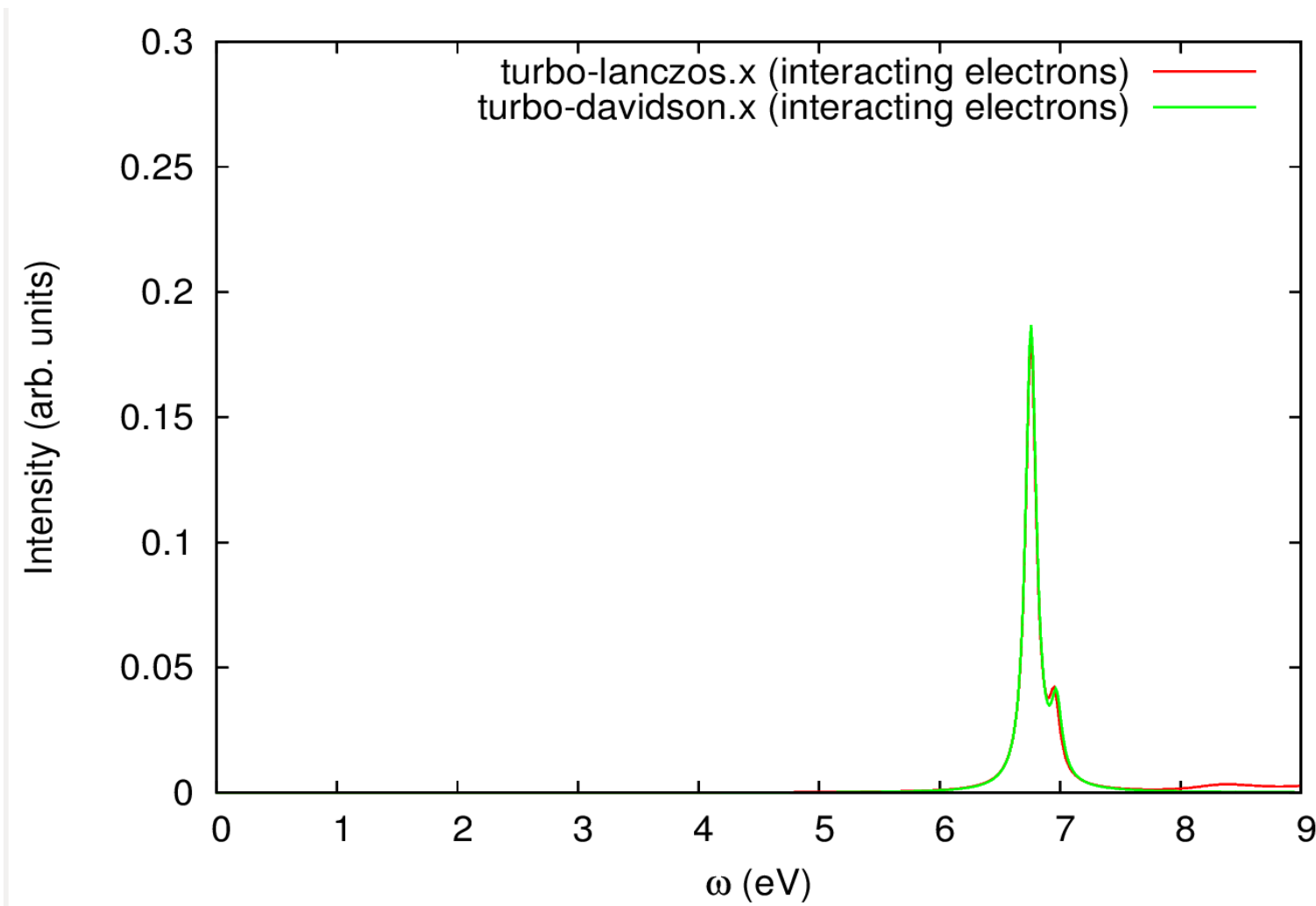
**Step 4.** Plot the spectrum using `gnuplot` and the script `plot_spectrum.gnu`

You should obtain the same excitation peak in the spectrum as was obtained using the code `turbo_davidson.x` in the **exercise2** including interaction.

The script `plot_spectrum.gnu` will do such a comparison, and it will produce the file `Benzene_spectrum.eps` which you can visualize.

# Exercise 3: Calculation of absorption spectra using the turboLanczos code

Comparison of the absorption spectrum of benzene computed using **turbo\_lanczos.x** and using **turbo\_davidson.x** both including the interaction (file **Benzene\_spectrum.eps**):



## Exercise 3: Calculation of absorption spectra using the turboLanczos code

`turbo_lanczos.x` allows us to obtain the absorption spectrum in a **wide frequency range** just by repeating a post-processing calculation using `turbo_spectrum.x` in a larger frequency range. This cannot be done with `turbo_davidson.x`

Make changes in `Benzene.tddfpt_pp.in`

```
&lr_input
  prefix = 'Benzene',
  outdir = './out',
  itermax0 = 1100,
  itermax = 20000,
  extrapolation = 'osc',
  start = 0.0,
  end = 3.0,
  increment = 0.001,
  epsil = 0.004,
  ipol = 1
/
```

← Increase the range of frequencies

```
turbo_spectrum.x < Benzene.tddfpt_pp.in > Benzene.tddfpt_pp.out
```

## Exercise 3: Calculation of absorption spectra using the turboLanczos code

`turbo_lanczos.x` allows us to obtain the absorption spectrum in a wide frequency range just by repeating a post-processing calculation using `turbo_spectrum.x` in a larger frequency range. This cannot be done with `turbo_davidson.x`

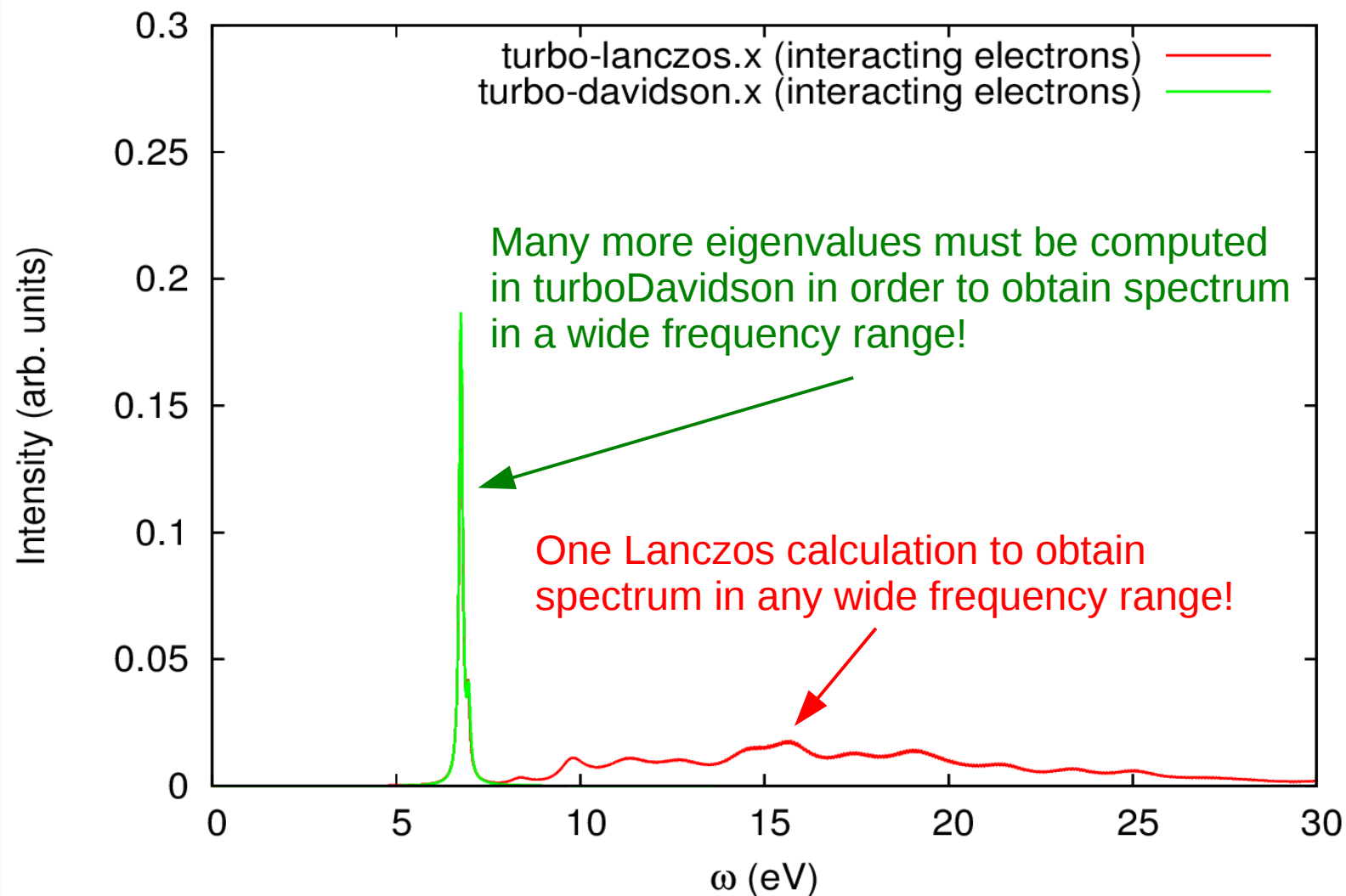
Make changes in the script `plot_spectrum.gnu`:

- `set xrange [0:30.0]`
- `set xtics 0.0, 5.0, 30.0`

Use `gnuplot` and the modified script `plot_spectrum.gnu` to produce the graph `Benzene_spectrum.eps`.

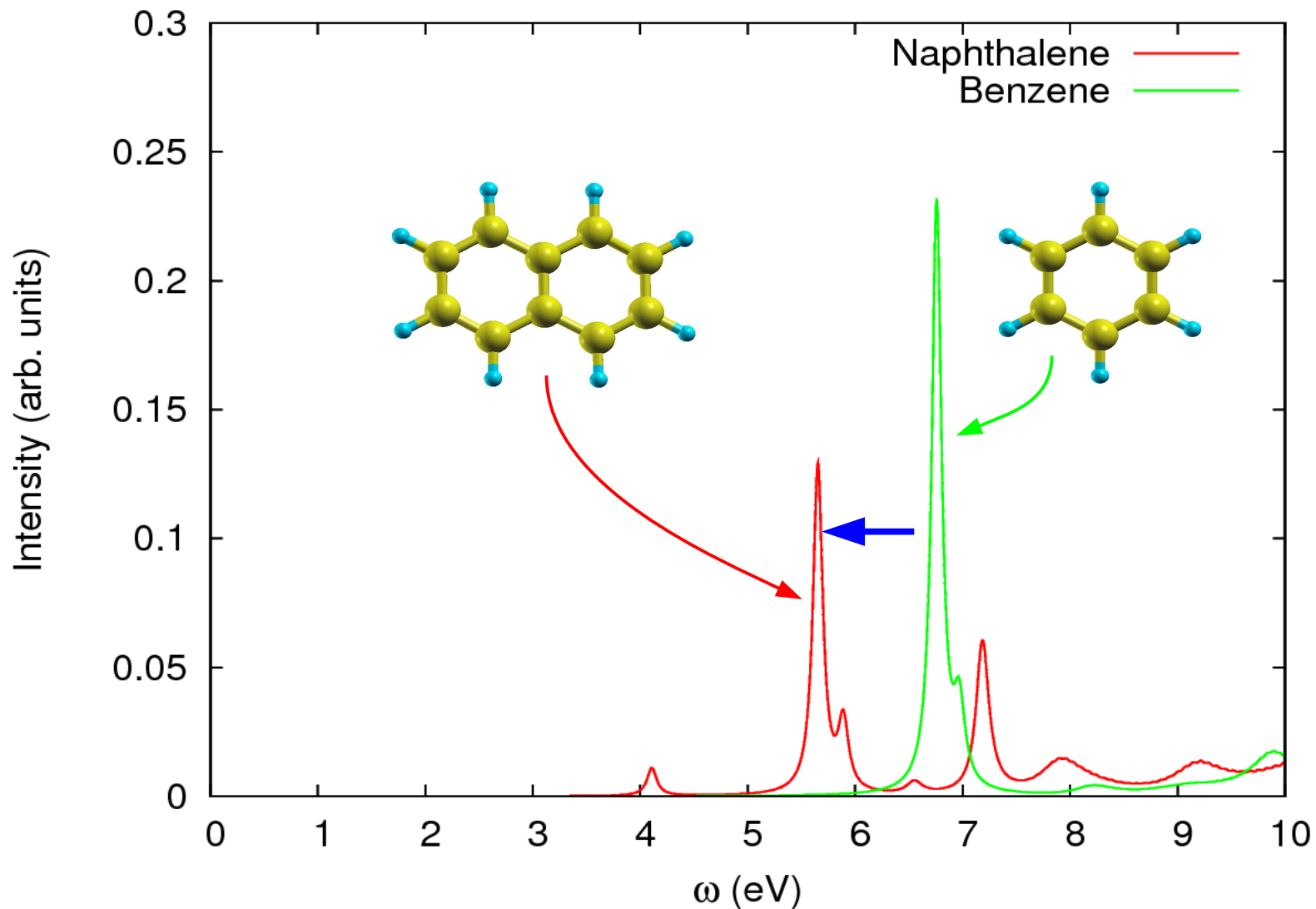
# Exercise 3: Calculation of absorption spectra using the turboLanczos code

Comparison of the absorption spectrum of benzene computed using **turbo\_lanczos.x** and using **turbo\_davidson.x** both including the interaction (file **Benzene\_spectrum.eps**):



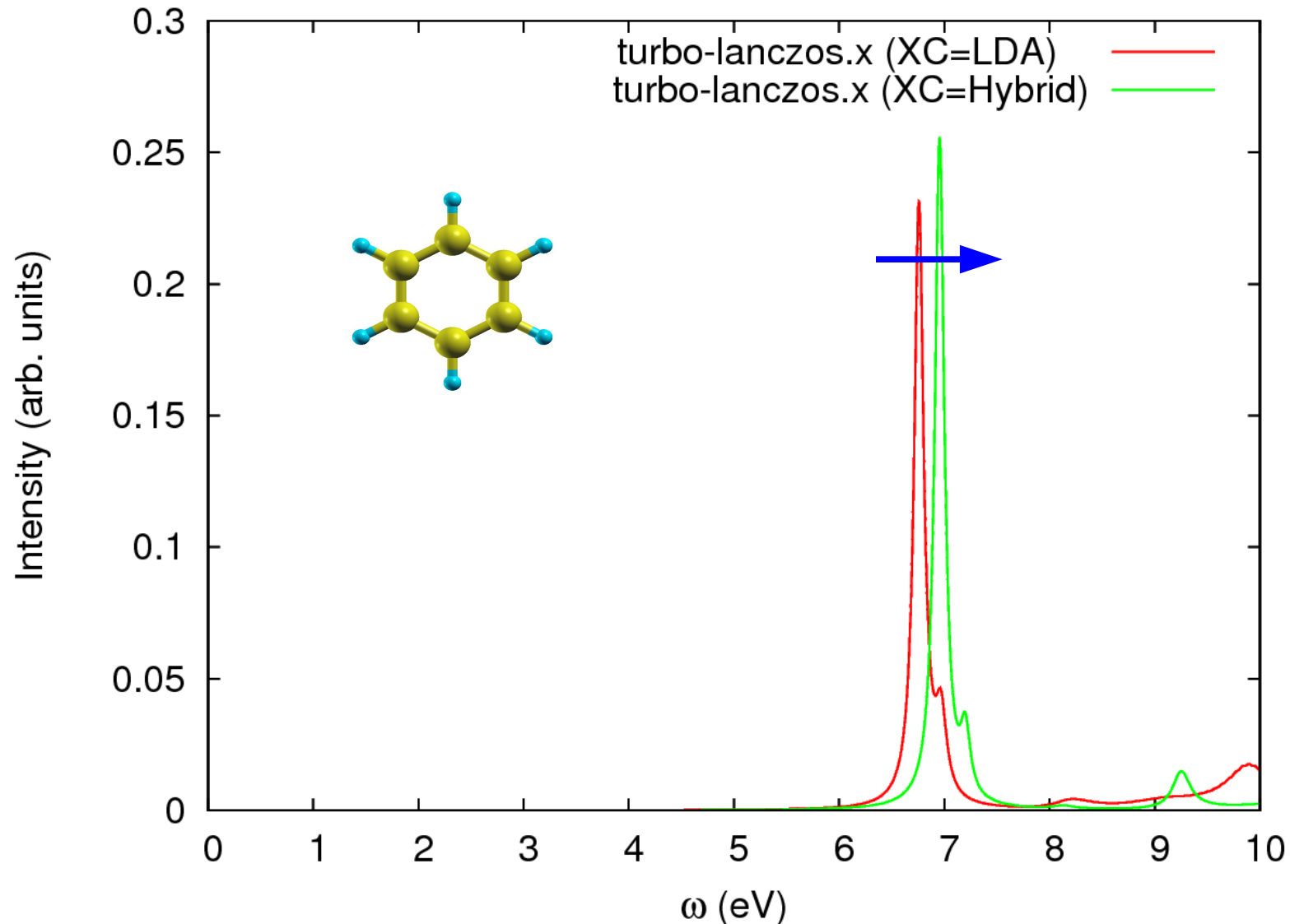
# Comparison of the absorption spectra of benzene and naphthalene

In naphthalene the pi-orbitals are more delocalized than in benzene, which leads to smaller energy gap, and which hence red-shifts the peaks.



# Comparison of the absorption spectra of benzene using local and non-local XC functionals

Hybrid exchange-correlation functionals open the energy gap and blue-shift the peaks (SCF: `input_dft='PBE0'`, Lanczos: `d0psi_rs=.true.`)



# Outline

1. **Exercise 1:** Calculation of absorption spectra in the Independent Particle Approximation
2. **Exercise 2:** Calculation of absorption spectra of interacting electrons using the **turboDavidson** program
3. **Exercise 3:** Calculation of absorption spectra of interacting electrons using the **turboLanczos** program
4. **Exercise 4:** Convergence of absorption spectra of Na<sub>2</sub>



# Exercise 4: Convergence of absorption spectra of Na2

Go to the directory with the input files:

```
cd Hands-on_TDDFPT_ABS/exercise4
```

Study the convergence of the absorption spectrum of Na2 with respect to:

- The number of Lanczos iterations `itermax = 50, 100, 150, ...` without using the extrapolation `extrapolation = 'no'`
- How many Lanczos iterations is needed to converge the spectrum when the extrapolation is used `extrapolation = 'osc'`?
- The size of the supercell `celldm(1) = 20, 30, 40, ...`

# Exercise 4: Convergence of absorption spectra of Na2

## No extrapolation of Lanczos coefficients

Na.lanczos.in

```
&lr_input
  prefix = 'Na2',
  outdir = './out',
  restart_step = 50,
  restart = .false.
/
&lr_control
  itermax = 50,
  ipol = 4
/
```

Na.tddfpt\_pp.in

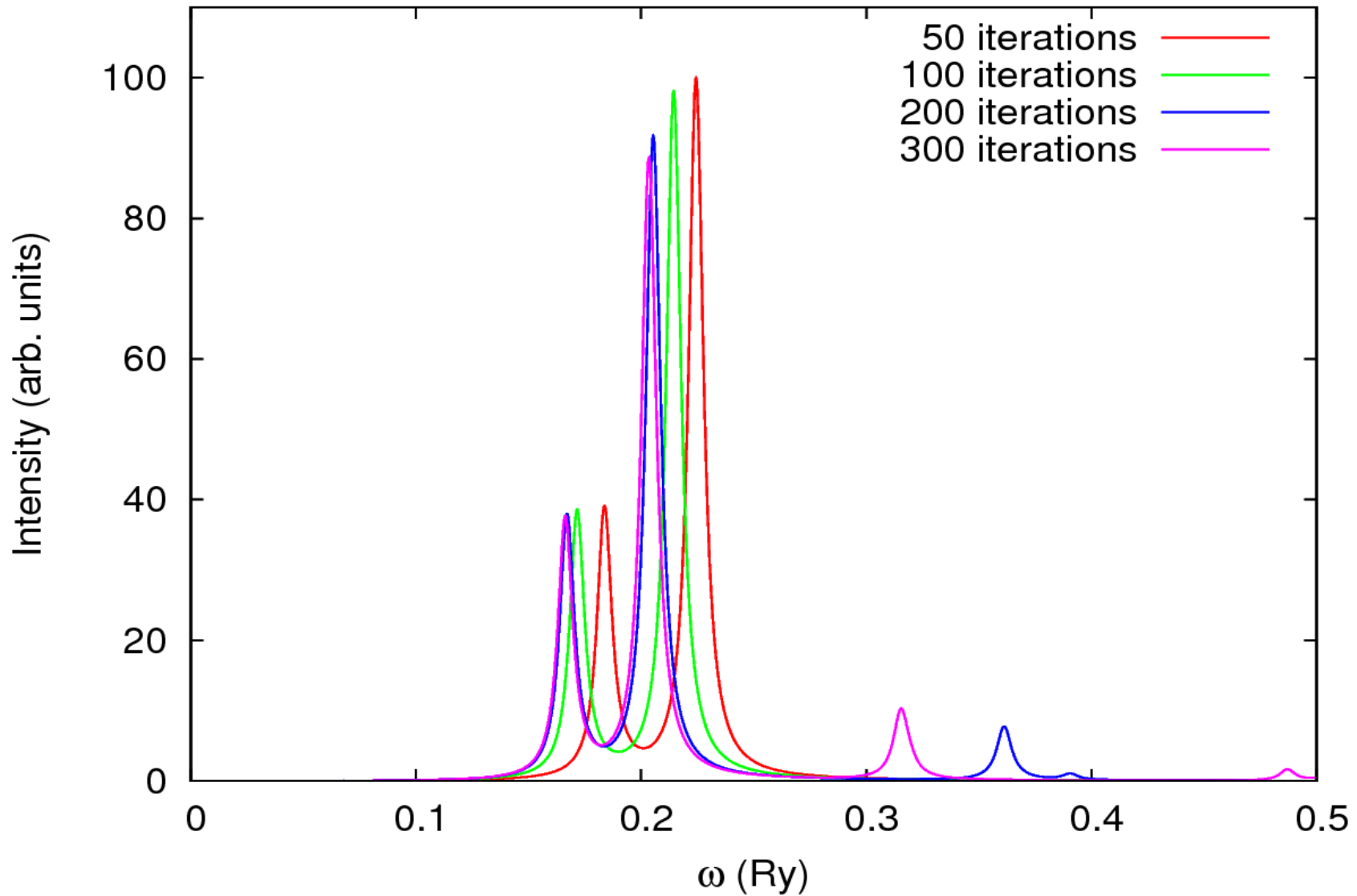
```
&lr_input
  prefix = 'Na2',
  outdir = './out',
  itermax0 = 50,
  itermax = 50,
  extrapolation = 'no',
  start = 0.0,
  end = 0.5,
  epsil = 0.004,
  increment = 0.001,
  ipol = 4
/
```

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.

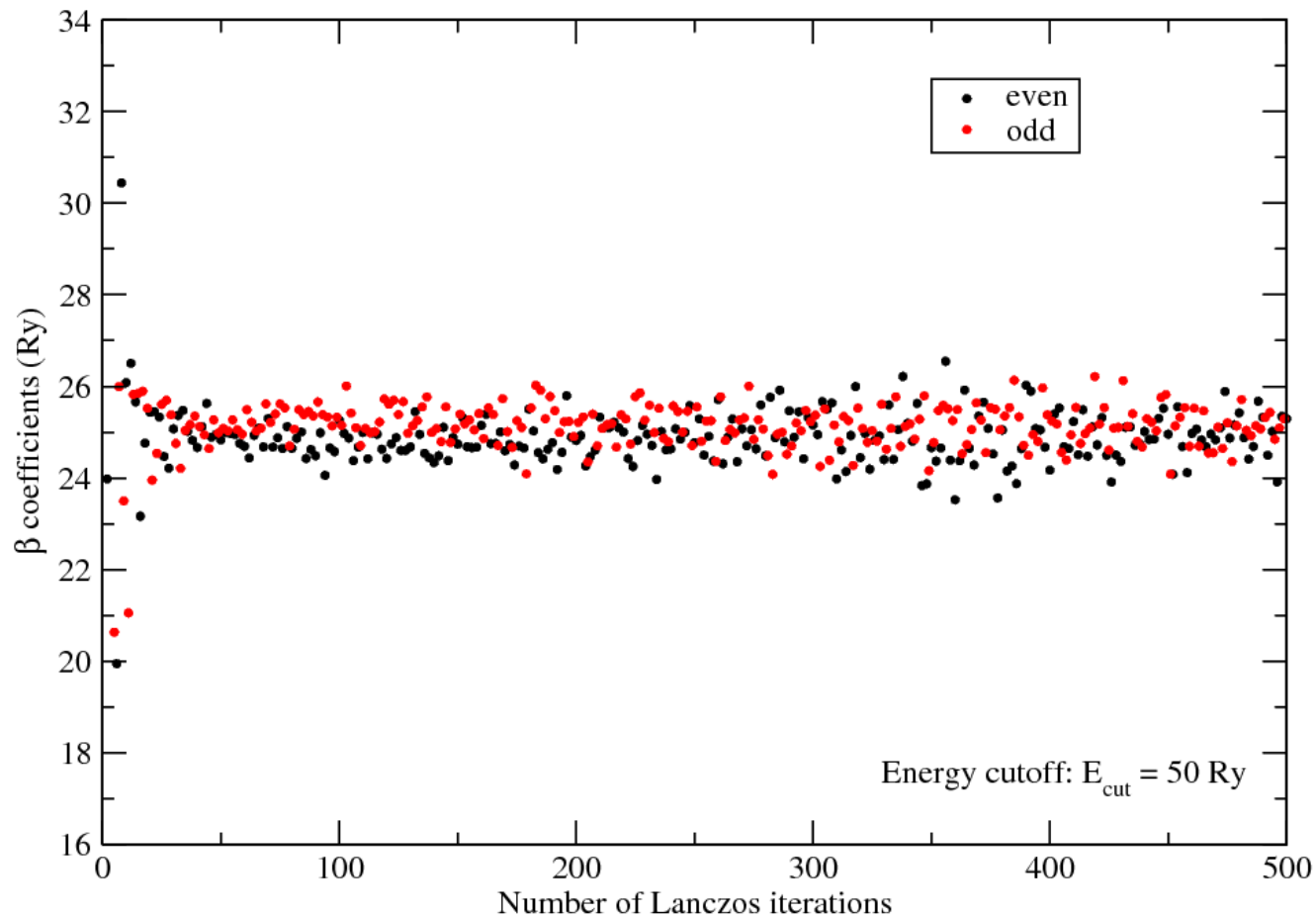
# Exercise 4: Convergence of absorption spectra of Na2

No extrapolation of Lanczos coefficients



# Exercise 4: Convergence of absorption spectra of Na2

Behaviour of  $\beta$  Lanczos coefficients



Lanczos coefficients oscillate around half of the kinetic-energy cutoff ( $50/2 = 25$  Ry in this case). Hence, we can extrapolate these coefficients.

# Exercise 4: Convergence of absorption spectra of Na2

## 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.

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

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

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

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

# Exercise 4: Convergence of absorption spectra of Na2

## Extrapolation of Lanczos coefficients

Na.lanczos.in

```
&lr_input
  prefix = 'Na2',
  outdir = './out',
  restart_step = 50,
  restart = .false.
/
&lr_control
  itermax = 170,
  ipol = 4
/
```

Na.tddfpt\_pp.in

```
&lr_input
  prefix = 'Na2',
  outdir = './out',
  itermax0 = 170,
  itermax = 5000,
  extrapolation = 'osc',
  start = 0.0,
  end = 0.5,
  epsil = 0.004,
  increment = 0.001,
  ipol = 4
/
```

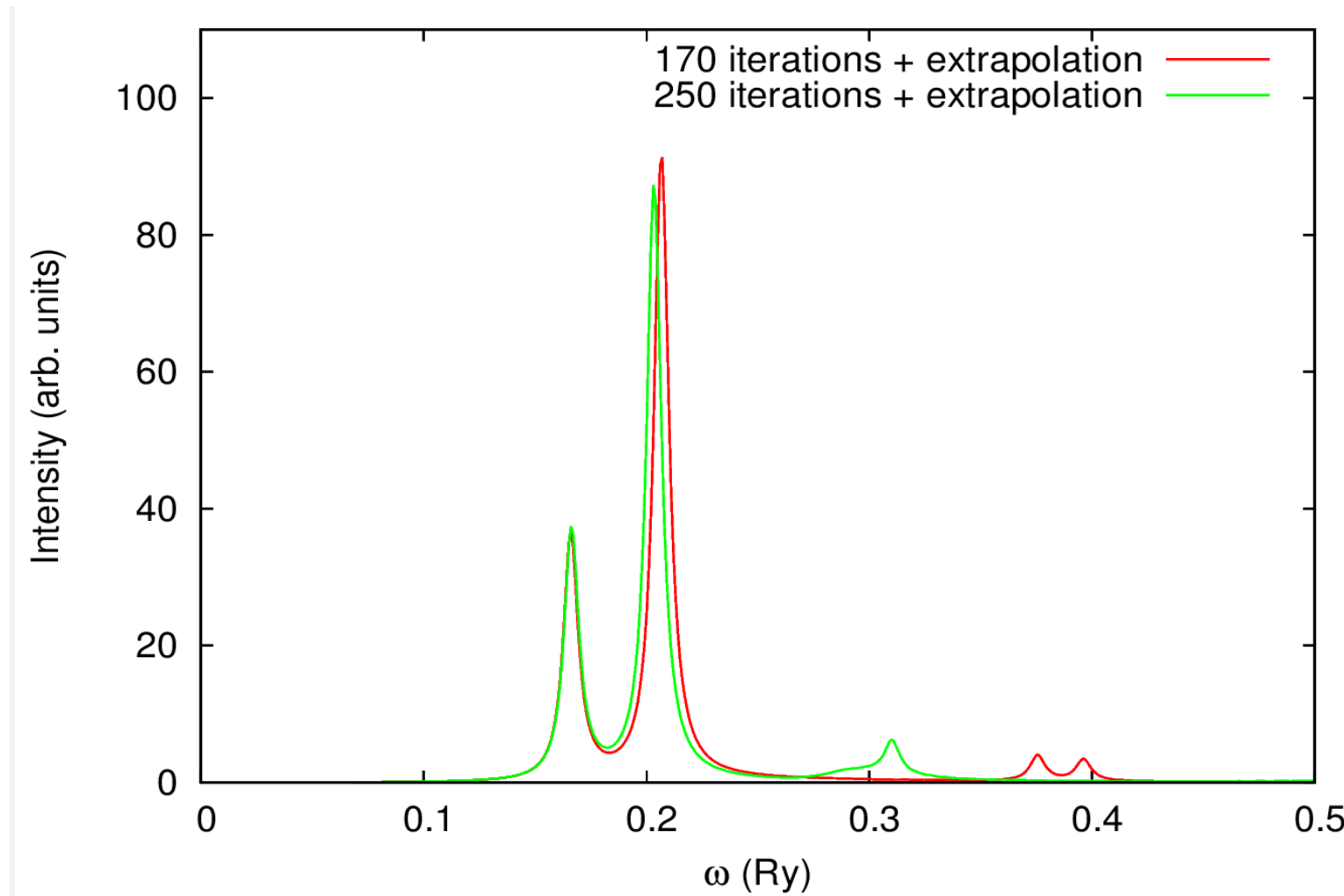
Must be equal !

Number up to which we extrapolate  
(can be very large, at negligible cost)

The extrapolation technique can be used if the number of Lanczos coefficients is larger than 150 (internal threshold in the **turbo\_spectrum.x** program).

# Exercise 4: Convergence of absorption spectra of Na2

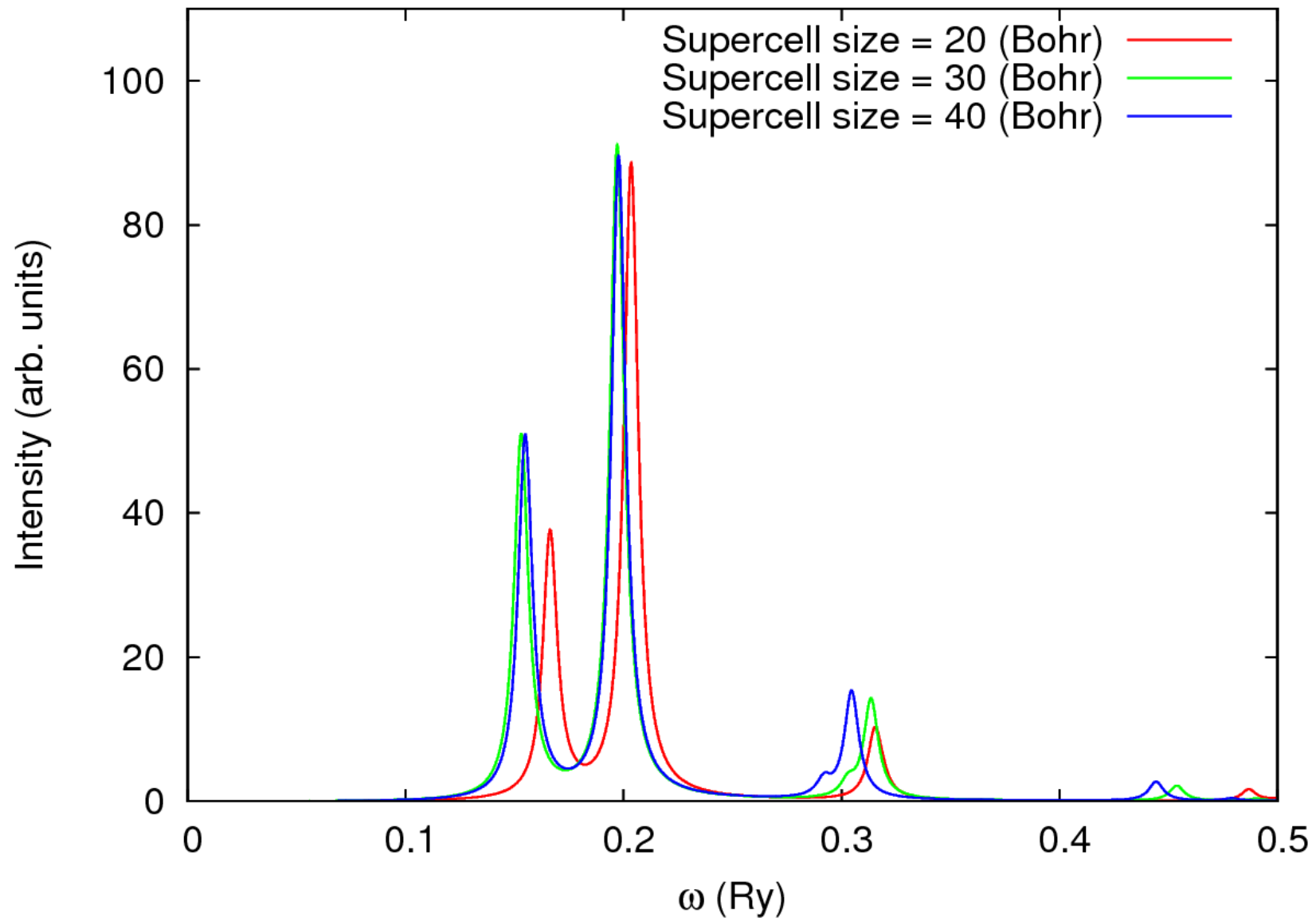
## Extrapolation of Lanczos coefficients



The convergence of the absorption spectrum is reached (much) faster if the extrapolation technique is used (especially for large systems)!

# Exercise 4: Convergence of absorption spectra of Na<sub>2</sub>

## Convergence with respect to the size of the supercell





# Bibliography

1. B. Walker, R. Gebauer,  
*Ultrasoft pseudopotentials in time-dependent density-functional theory*,  
J. Chem. Phys. **127**, 164106 (2007).
2. D. Rocca, R. Gebauer, Y. Saad, and S. Baroni,  
*Turbo charging time-dependent density-functional theory with Lanczos chains*,  
J. Chem. Phys. **128**, 154105 (2008).
3. O. Malcioglu, R. Gebauer, D. Rocca, and S. Baroni,  
*turboTDDFT – A code for the simulation of molecular spectra using the Liouville-Lanczos approach to TDDFPT*,  
Comp. Phys. Comm. **182**, 1744 (2011).
4. S. Baroni and R. Gebauer,  
*'The Liouville-Lanczos approach to TDDFPT' in 'Fundamentals of TDDFT'*,  
Springer, Berlin (2012).
5. X. Ge, S. Binnie, D. Rocca, R. Gebauer, and S. Baroni,  
*turboTDDFT 2.0 – Hybrid functionals and new algorithms within TDDFPT*,  
Comp. Phys. Comm. **185**, 2080 (2014).