QUANTUMESPRESSO

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

Iurii Timrov, Oscar Baseggip

Quantum ESPRESSO Summer School
Ljubljana, Slovenia
18 September 2019

Outline

1. **Example 4:** Calculation of absorption spectra in the Independent Particle Approximation

2. **Example 5:** Calculation of absorption spectra of interacting electrons using the **`turboDavidson`** program

3. **Example 6:** Calculation of absorption spectra of interacting electrons using the **`turboLanczos`** program

4. **Example 7:** Calculation of absorption spectra using B3LYP pseudo-potential

Outline

1. **Example 4:** Calculation of absorption spectra in the Independent Particle Approximation

2. **Example 5:** Calculation of absorption spectra of interacting electrons using the `turboDavidson` program

3. **Example 6:** Calculation of absorption spectra of interacting electrons using the `turboLanczos` program

4. **Example 7:** Calculation of absorption spectra using B3LYP pseudo-potential

Independent Particle Approximation

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

Fermi's golden rule

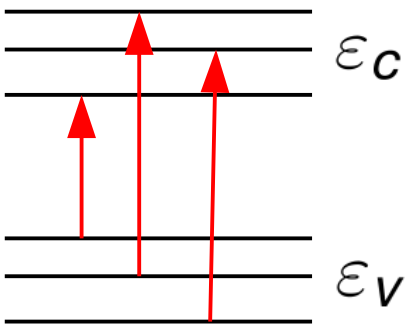
The transition probability per unit time from occupied states $|\varphi_v\rangle$ to empty states $|\varphi_c\rangle$ reads:

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

$V'_{ext} = -e\,\mathbf{E} \cdot \mathbf{r}$ 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

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



Example 4: Calculation of absorption spectra in IPA

Go to the directory with the input files:

```
cd  Day-3/example4
```

In this directory you will find:

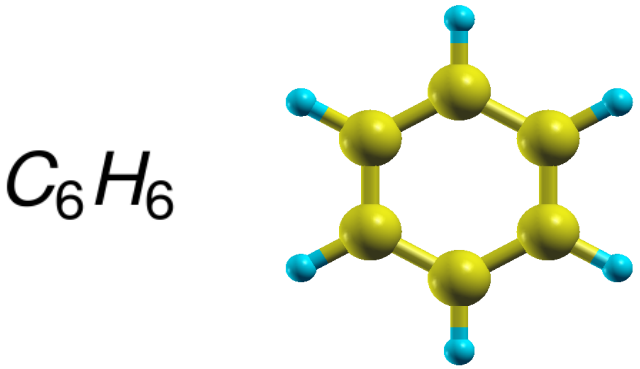
- `README.md` – File describing how to do the exercise
- `pw.benzene.in` – Input file for the SCF ground-state calculation
- `epsilon.benzene.in` – Input file for a calculation of spectrum in IPA
- `plot_spectrum.gp` – Script to plot spectrum using **`gnuplot`**
- `reference` – Directory with the reference results

Example 4: 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.

`pw.benzene.in`

Input file for the SCF calculation




```
&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 = 50,
    nbnd = 20
/
&ELECTRONS
    diagonalization='david'
    mixing_mode = 'plain',
    mixing_beta = 0.6,
    conv_thr =  1.0d-8
/
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}
```

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

Input

Output

Example 4: Calculation of absorption spectra in IPA

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

```
      k = 0.0000 0.0000 0.0000 ( 81088 PWs)   bands (ev):

-20.7330 -18.0168 -18.0149 -14.4574 -14.4563 -12.5195 -10.9200 -10.5656
 -9.9405  -9.9384  -8.5857  -8.0004  -8.0000  -5.8945  -5.8931  -0.8620
 -0.8615  -0.2970   0.2690   0.3613

  highest occupied, lowest unoccupied level (ev):    -5.8931    -0.8620
```

HOMO **LUMO**

HOMO – Highest Occupied Molecular Orbital

LUMO – Lowest Unoccupied Molecular Orbital

Energy gap = **LUMO** – **HOMO** = 5.0 (eV)

Example4: 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.

epsilon.benzene.in

Input file for the calculation of spectrum

```
&INPUTPP
  calculation = 'eps'
  prefix = 'Benzene',
  outdir='./out'
/
&ENERGY_GRID
  smeartype = '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 < epsilon.benzene.in > epsilon.benzene.out

Example 4: Calculation of absorption spectra in IPA

The code **epsilon.x** produces 4 files:

- **epsr.dat** – Real part of the response
- **epsi.dat** – Imaginary part of the response (this is what we need)
- **eels.dat** – Electron energy loss spectrum
- **ieps.dat** – Response computed on the imaginary axis of frequency

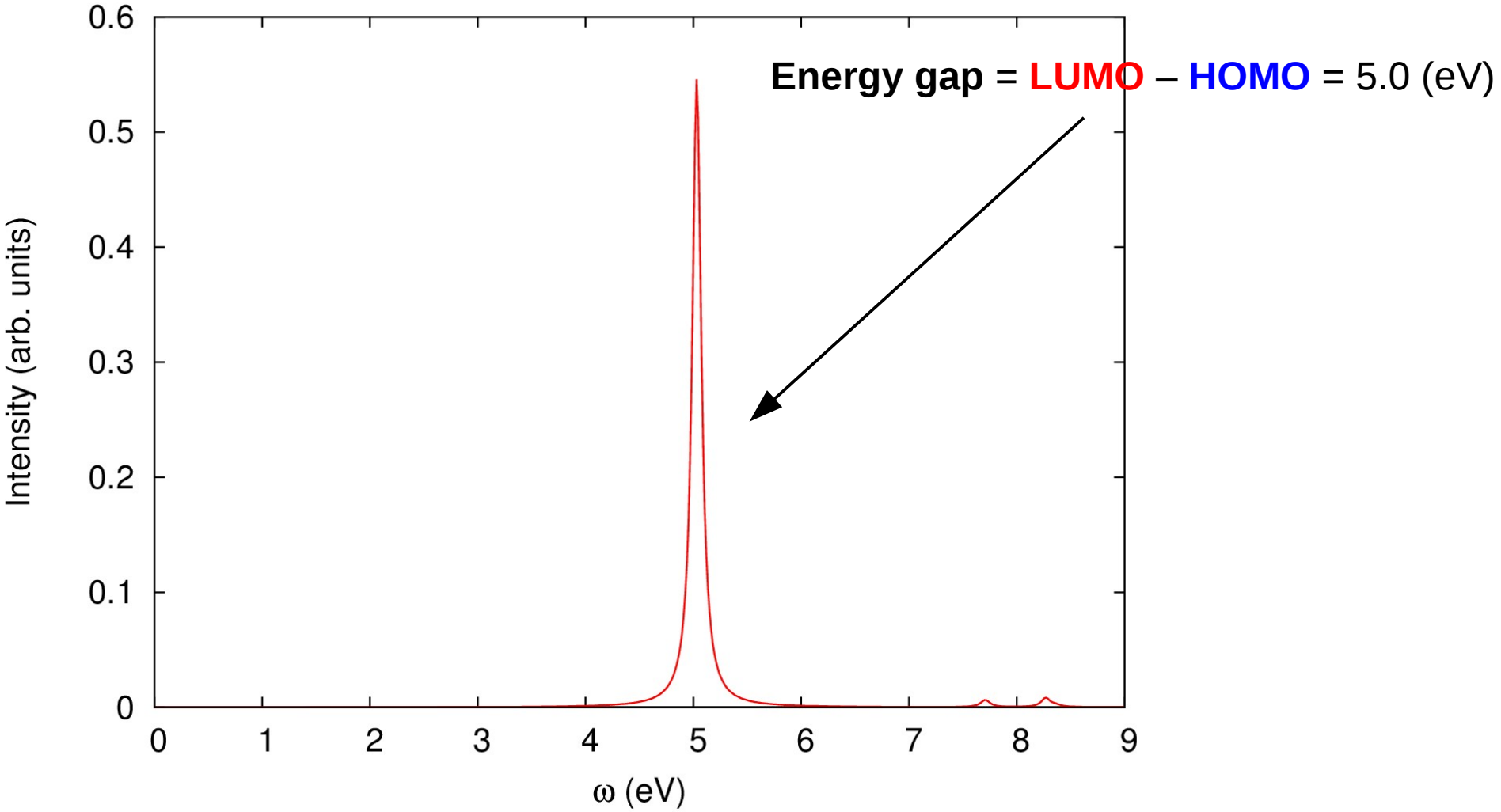
The content of **epsi.dat** looks like:

```
# energy grid [eV]   epsi_x          epsi_y          epsi_z
     0.015000       0.000001        0.000001        0.000000
     0.030000       0.000001        0.000001        0.000000
     0.045000       0.000002        0.000002        0.000000
     ...            ...             ...             ...
```

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

Example 4: Calculation of absorption spectra in IPA

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



Outline

1. **Example 4:** Calculation of absorption spectra in the Independent Particle Approximation

2. **Example 5:** Calculation of absorption spectra of interacting electrons using the **`turboDavidson`** program

3. **Example 6:** Calculation of absorption spectra of interacting electrons using the **`turboLanczos`** program

4. **Example 7:** Calculation of absorption spectra using B3LYP pseudo-potential

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):

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

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

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.

Example 5: Calculation of absorption spectra using turboDavidson

Go to the directory with the input files:

```
cd  Day-3/example5
```

In this directory you will find:

- `README.md` – File describing how to do the exercise
- `pw.benzene.in` – Input file for the SCF ground-state calculation
- `turbo_davidson.benzene.in` – Input file for a Davidson calculation of the eigenvalues
- `turbo_spectrum.benzene.in` – Input file for a post-processing calculation of the spectrum
- `plot_spectrum.gp` – Script to plot spectrum using **`gnuplot`**
- `reference` – Directory with the reference results

Example 5: Calculation of absorption spectra using turboDavidson

Step 1. Perform a SCF ground-state calculation:

```
pw.x < pw.benzene.in > pw.benzene.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.
  num_eign = 15
  num_init = 30
  num_basis_max = 90
  residue_conv_thr = 1.0E-6
  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 off the interaction
- 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 5: Calculation of absorption spectra using turboDavidson

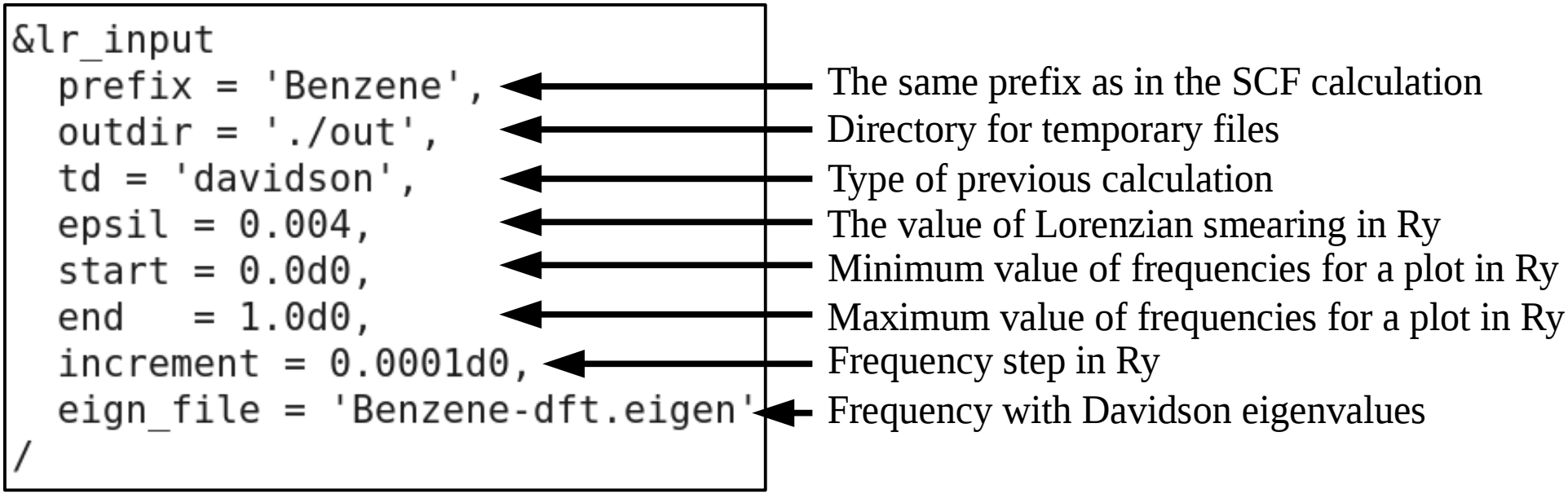
The code **`turbo_davidson.x`** produces a file **`Benzene-dft.eigen`** containing single-particle excitation eigenvalues:

# Energy(Ry)	total	X	Y	Z	
0.36978194E+00	0.46132988E+00	0.28464441E-01	0.43286544E+00	0.10578116E-13	
0.36981685E+00	0.46136936E+00	0.43291594E+00	0.28453416E-01	0.52375694E-11	
0.36988558E+00	0.46130314E+00	0.43284575E+00	0.28457396E-01	0.13942770E-14	
0.36992049E+00	0.46130546E+00	0.28462406E-01	0.43284306E+00	0.93824529E-10	
0.41130254E+00	0.15884862E-08	0.26872205E-10	0.33132431E-10	0.15284815E-08	
0.41140618E+00	0.46885002E-07	0.23355911E-09	0.11492550E-10	0.46639950E-07	
0.45290903E+00	0.16097314E-01	0.49157457E-10	0.10237851E-08	0.16097313E-01	
0.45301267E+00	0.26930724E-03	0.13406472E-08	0.68631445E-13	0.26930590E-03	
0.45968997E+00	0.65208744E-06	0.44228501E-12	0.28707171E-10	0.65205829E-06	
0.45979361E+00	0.32635301E-04	0.98902476E-11	0.22830130E-14	0.32635291E-04	
0.52463700E+00	0.22960254E-02	0.33713281E-15	0.46316775E-10	0.22960254E-02	
0.52466281E+00	0.28818920E-05	0.16753377E-11	0.36334017E-10	0.28818540E-05	
0.52467191E+00	0.28266195E-05	0.13895408E-11	0.14806708E-11	0.28266166E-05	
0.52469772E+00	0.22905249E-02	0.10021215E-09	0.48908868E-11	0.22905248E-02	
0.56615760E+00	0.21358413E-07	0.21185285E-07	0.17198848E-09	0.11394804E-11	
0.56618342E+00	0.48707756E-07	0.53966747E-08	0.43289556E-07	0.21525549E-10	
0.56768068E+00	0.65876871E-09	0.16762237E-10	0.62848990E-09	0.13516571E-10	

Example 5: Calculation of absorption spectra using turboDavidson

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

The input file **`turbo_spectrum.benzene.in`** reads:




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

Example 5: Calculation of absorption spectra using turboDavidson

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

# Energy(Ry)	Total	X	Y	Z
0.00000000E+00	0.00000000E+00	0.00000000E+00	0.00000000E+00	0.00000000E+00
0.10000000E-02	0.56616912E-04	0.27959778E-04	0.27977483E-04	0.67965106E-06
0.20000000E-02	0.11383935E-03	0.56219682E-04	0.56255103E-04	0.13645627E-05
0.30000000E-02	0.17167467E-03	0.84783371E-04	0.84836518E-04	0.20547819E-05
0.40000000E-02	0.23013035E-03	0.11365456E-03	0.11372544E-03	0.27503559E-05
0.50000000E-02	0.28921396E-03	0.14283700E-03	0.14292563E-03	0.34513327E-05
0.60000000E-02	0.34893320E-03	0.17233453E-03	0.17244091E-03	0.41577607E-05
0.70000000E-02	0.40929586E-03	0.20215101E-03	0.20227516E-03	0.48696889E-05
0.80000000E-02	0.47030986E-03	0.23229039E-03	0.23243230E-03	0.55871666E-05
0.90000000E-02	0.53198323E-03	0.26275665E-03	0.26291634E-03	0.63102441E-05
0.10000000E-01	0.59432413E-03	0.29355385E-03	0.29373132E-03	0.70389717E-05
0.11000000E-01	0.65734082E-03	0.32468608E-03	0.32488134E-03	0.77734008E-05
0.12000000E-01	0.72104170E-03	0.35615753E-03	0.35637059E-03	0.85135828E-05
0.13000000E-01	0.78543529E-03	0.38797243E-03	0.38820329E-03	0.92595701E-05
0.14000000E-01	0.85053022E-03	0.42013508E-03	0.42038374E-03	0.10011416E-04
0.15000000E-01	0.91633528E-03	0.45264983E-03	0.45291629E-03	0.10769172E-04
0.16000000E-01	0.98285938E-03	0.48552111E-03	0.48580538E-03	0.11532895E-04
0.17000000E-01	0.10501115E-02	0.51875341E-03	0.51905549E-03	0.12302637E-04
0.18000000E-01	0.11181009E-02	0.55235129E-03	0.55267120E-03	0.13078455E-04
0.19000000E-01	0.11868369E-02	0.58631939E-03	0.58665711E-03	0.13860404E-04

Example 5: Calculation of absorption spectra using turboDavidson

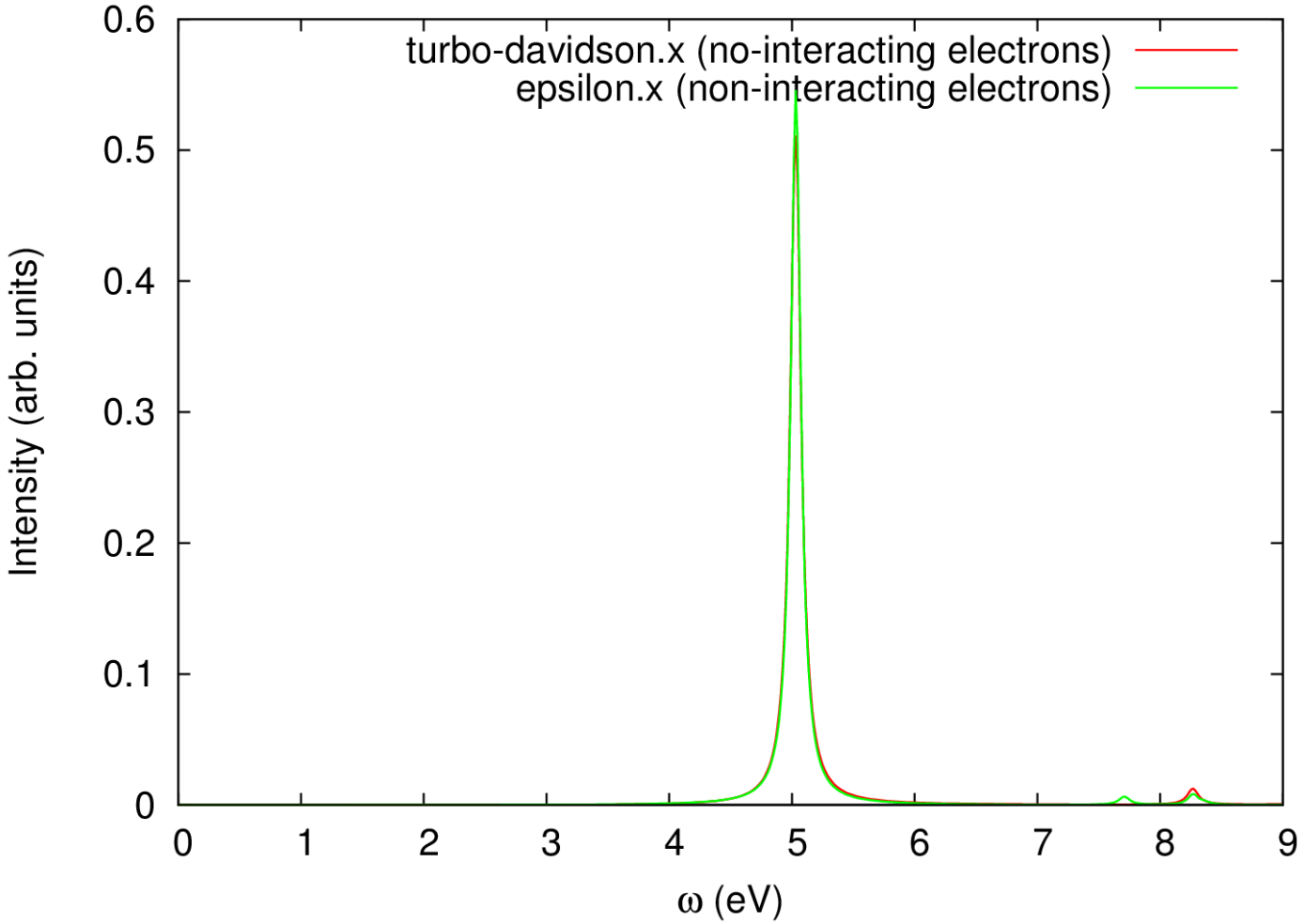
Step 4. Plot the spectrum using **`gnuplot`** and the script **`plot_spectrum.gp`**

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 **example4**.

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

Example 5: Calculation of absorption spectra using turboDavidson

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



Example 5: Calculation of absorption spectra using turboDavidson

Now switch on the interaction!

Make the following modifications in the input files:

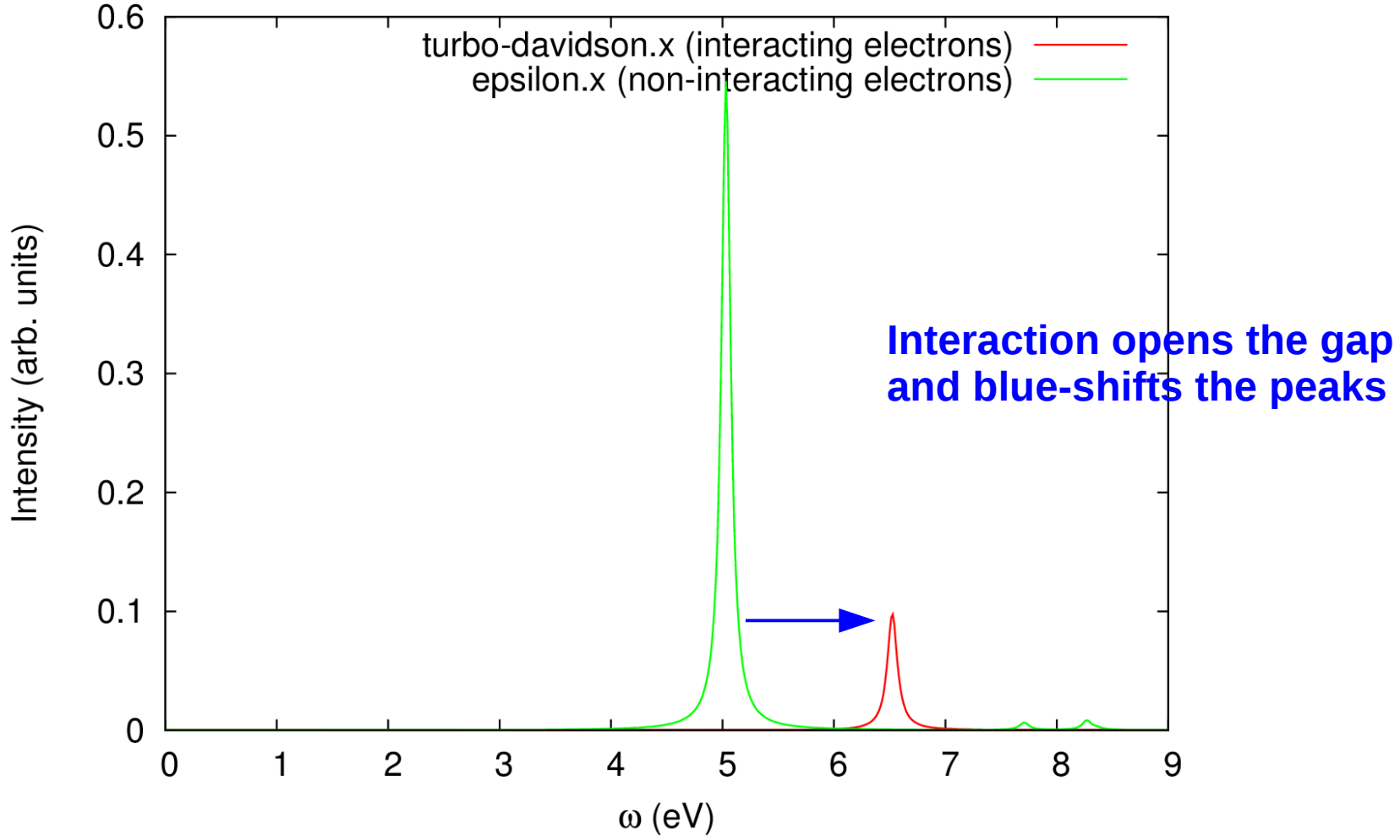
- In the file **`turbo_davidson.benzene.in`** set **`if_dft_spectrum = .false.`**
- In the file **`turbo_spectrum.benzene.in`** set **`eign_file = 'Benzene.eigen'`**
- In **`plot_spectrum.gp`** change the title to: **`'turbo-davidson.x (interacting electrons)'`**

Once these modifications are done, repeat steps 2, 3, and 4:

Note! The calculation will be a bit too long. Therefore, let us see the output files in the directory '**`reference`**'.

Example 5: Calculation of absorption spectra using turboDavidson

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. **Example 4:** Calculation of absorption spectra in the Independent Particle Approximation

2. **Example 5:** Calculation of absorption spectra of interacting electrons using the `turboDavidson` program

3. **Example 6:** Calculation of absorption spectra of interacting electrons using the `turboLanczos` program

4. **Example 7:** Calculation of absorption spectra using B3LYP pseudo-potential

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):

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 6: Calculation of absorption spectra using turboLanczos

Go to the directory with the input files:

```
cd  Day-3/example6
```

In this directory you will find:

- `README.md` – File describing how to do the exercise
- `pw.benzene.in` – Input file for the SCF ground-state calculation
- `turbo_lanczos.benzene.in` – Input file to perform Lanczos recursions
- `turbo_spectrum.benzene.in` – Input file for a postprocessing calculation of spectrum
- `plot_spectrum.gp` – Script to plot spectrum using **`gnuplot`**
- `reference` – Directory with the reference results

Example 6: Calculation of absorption spectra using turboLanczos

Step 1. Perform a SCF ground-state calculation:

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

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

```
&lr_input
  prefix = 'Benzene',
  outdir='./out',
  restart_step = 100,
  restart = .false.
/
&lr_control
  itermax = 1500,
  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 6: Calculation of absorption spectra using turboLanczos

Note! The calculation will be a bit too long. Therefore, let us see the output files in the directory **`reference`**.

In the output file **`turbo_lanczos.benzene.out`** there is information about each Lanczos iteration :

```
Lanczos iteration:        2   Pol:1
lr_apply_liouvillian: applying interaction: normal
alpha(00000002)= 0.000000000000000E+00
beta (00000002)= 0.325064551066342E+01
gamma(00000002)= 0.325064551066342E+01
z1=       1  0.118715821469858E+01  0.000000000000000E+00
```

In the directory **`out`**, which contains temporary files, there is a file **`Benzene.beta_gamma_z.1`** which contains the information about Lanczos coefficients:

```
          500
  3.85903052105713
  3.25064551066342
  3.25064551066342
(0.000000000000000E+000,0.000000000000000E+000)
  13.9284915055080
  13.9284915055080
(1.18715821469858,0.000000000000000E+000)
  ...
```

Example 6: Calculation of absorption spectra using turboLanczos

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 **`turbo_spectrum.benzene.in`** reads:

```
&lr_input
  prefix = 'Benzene',
  outdir = './out',
  itermax0 = 1500,
  itermax  = 20000,
  extrapolation = 'osc',
  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 (bi-constant)
- 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 6: Calculation of absorption spectra using turboLanczos

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

#	\hbar \omega(Ry)	Re(chi) (e^2*a_0^2/Ry)	Im(chi) (e^2*a_0^2/Ry)
chi_1_1=	0.000000000000000E+00	0.430317597214554E+02	0.000000000000000E+00
chi_1_1=	0.100000000000000E-03	0.430317605751854E+02	0.683128198125556E-04
chi_1_1=	0.200000000000000E-03	0.430317631363756E+02	0.136625666661881E-03
chi_1_1=	0.300000000000000E-03	0.430317674050269E+02	0.204938567584777E-03
chi_1_1=	0.400000000000000E-03	0.430317733811413E+02	0.273251549618109E-03
chi_1_1=	0.500000000000000E-03	0.430317810647211E+02	0.341564639798837E-03
chi_1_1=	0.600000000000000E-03	0.430317904557692E+02	0.409877865164046E-03
chi_1_1=	0.700000000000000E-03	0.430318015542892E+02	0.478191252750976E-03
chi_1_1=	0.800000000000000E-03	0.430318143602857E+02	0.546504829597058E-03
chi_1_1=	0.900000000000000E-03	0.430318288737639E+02	0.614818622739954E-03
chi_1_1=	0.100000000000000E-02	0.430318450947292E+02	0.683132659217564E-03
chi_1_1=	0.110000000000000E-02	0.430318630231883E+02	0.751446966068074E-03
chi_1_1=	0.120000000000000E-02	0.430318826591480E+02	0.819761570329994E-03
chi_1_1=	0.130000000000000E-02	0.430319040026164E+02	0.888076499042171E-03
chi_1_1=	0.140000000000000E-02	0.430319270536017E+02	0.956391779243841E-03
chi_1_1=	0.150000000000000E-02	0.430319518121132E+02	0.102470743797463E-02
chi_1_1=	0.160000000000000E-02	0.430319782781605E+02	0.109302350227465E-02
chi_1_1=	0.170000000000000E-02	0.430320064517541E+02	0.116133999918442E-02
chi_1_1=	0.180000000000000E-02	0.430320363329054E+02	0.122965695574502E-02
chi_1_1=	0.190000000000000E-02	0.430320679216258E+02	0.129797439899804E-02
chi_1_1=	0.200000000000000E-02	0.430321012179283E+02	0.136629235598565E-02
chi_1_1=	0.210000000000000E-02	0.430321362218257E+02	0.143461085375061E-02

Example 6: Calculation of absorption spectra using turboLanczos

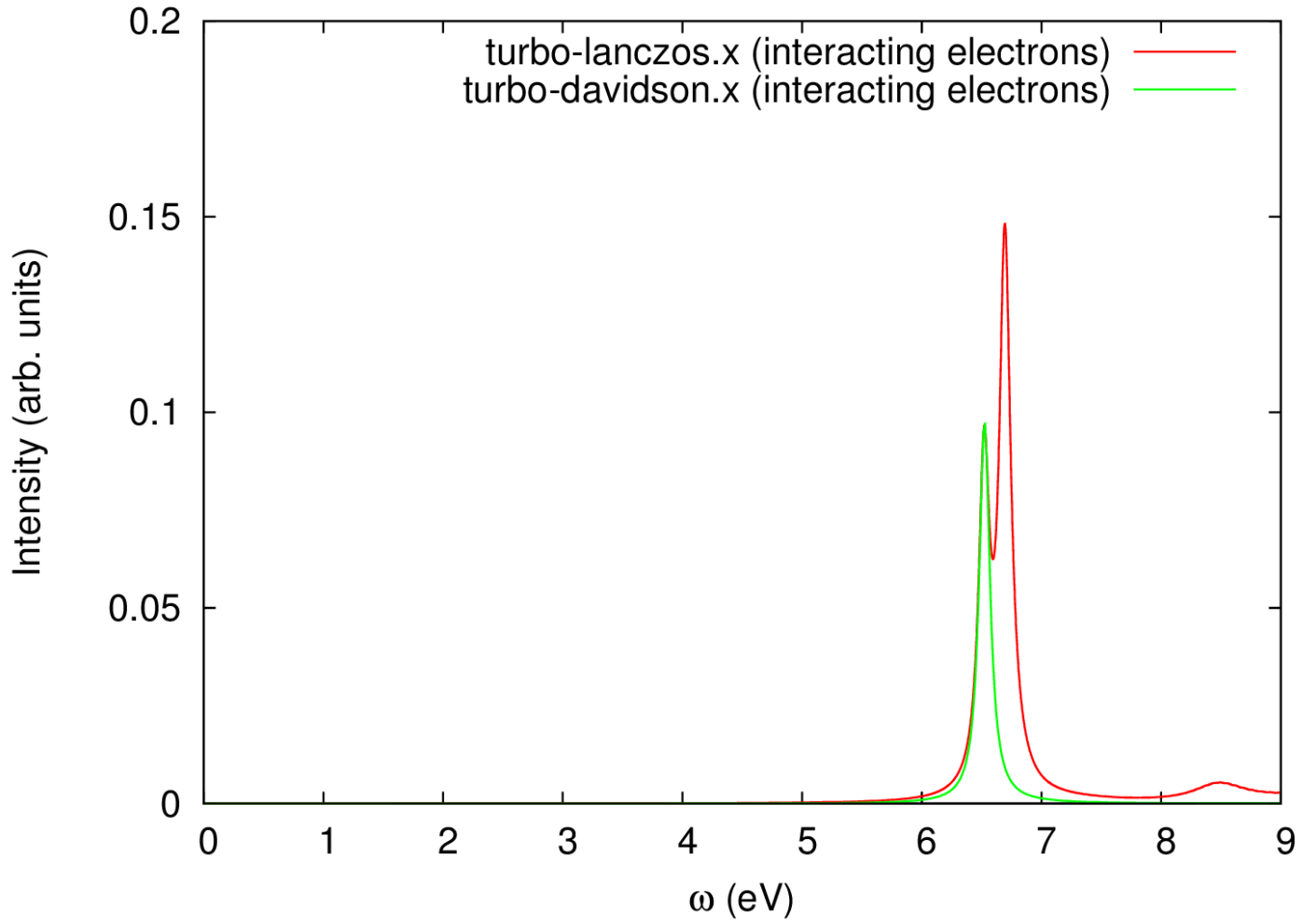
Step 4. Plot the spectrum using **`gnuplot`** and the script **`plot_spectrum.gp`**

You should obtain the same excitation peak in the spectrum as was obtained using the code **`turbo_davidson.x`** in the **example5** including interaction.

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

Example 6: Calculation of absorption spectra using turboLanczos

Comparison of the absorption spectrum of benzene computed using **`turbo_lanczos.x`** and using **`turbo_davidson.x`** both including the interation (file **`Benzene_spectrum.eps`**):



Example 6: Calculation of absorption spectra using turboLanczos

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 **turbo_spectrum.benzene.in**

```
&lr_input
  prefix = 'Benzene',
  outdir = './out',
  itermax0 = 1500,
  itermax  = 20000,
  extrapolation = 'osc',
  epsil = 0.004,
  start = 0.0d0,
  end   = 3.0d0,
  increment = 0.0001d0,
  ipol = 1
/
```

← Increase the range of frequencies

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

Example 6: Calculation of absorption spectra using turboLanczos

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**

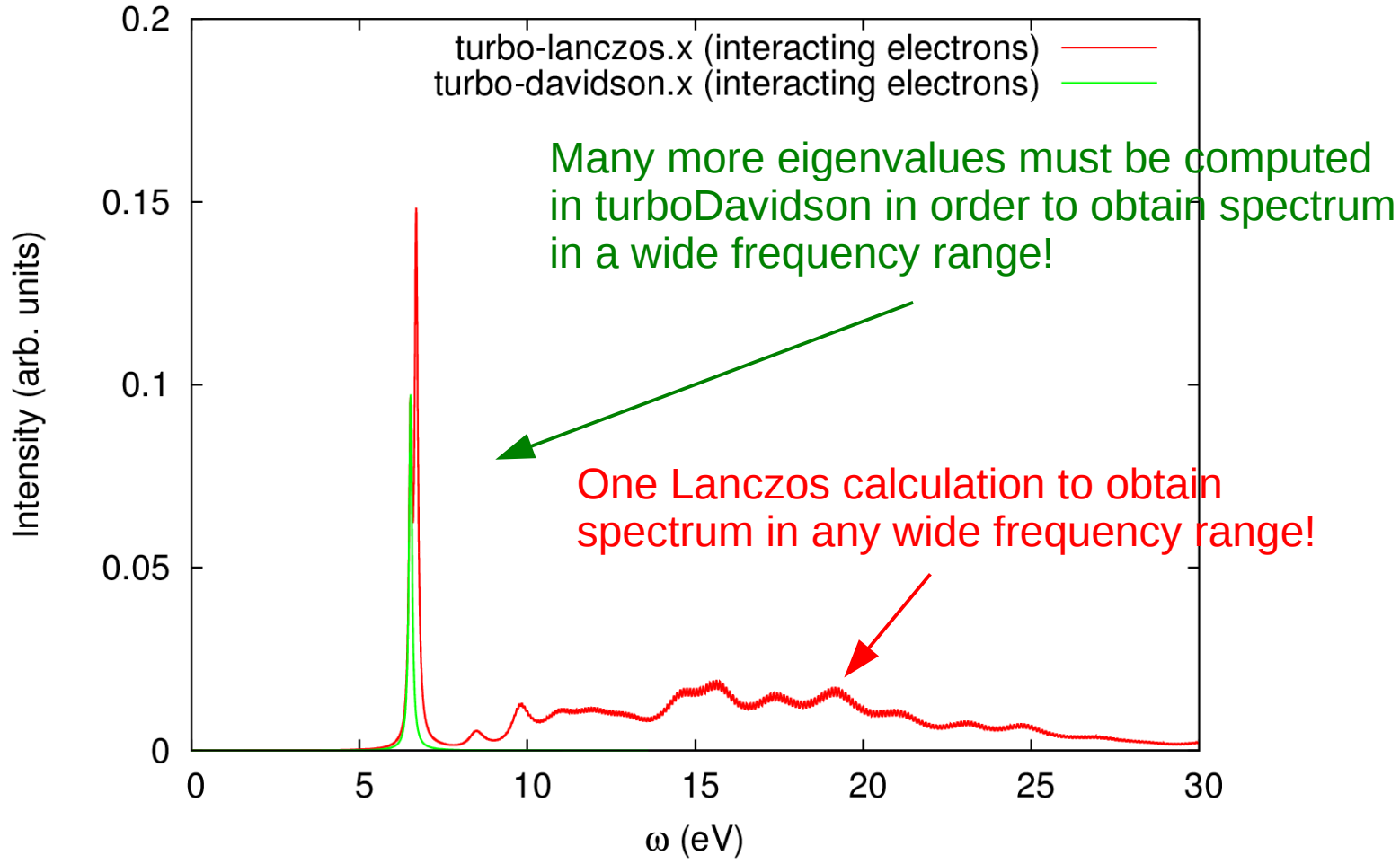
Make changes in the script **plot_spectrum.gp:**

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

Use **gnuplot** and the modified script **plot_spectrum.gp** to produce the graph **Benzene_spectrum.eps** .

Example 6: Calculation of absorption spectra using turboLanczos

Comparison of the absorption spectrum of benzene computed using **`turbo_lanczos.x`** and using **`turbo_davidson.x`** both including the interation (file **`Benzene_spectrum.eps`**):



Outline

1. **Example 4:** Calculation of absorption spectra in the Independent Particle Approximation

2. **Example 5:** Calculation of absorption spectra of interacting electrons using the `turboDavidson` program

3. **Example 6:** Calculation of absorption spectra of interacting electrons using the `turboLanczos` program

4. **Example 7:** Calculation of absorption spectra using B3LYP pseudo-potential

Example 7: Calculation of absorption spectra using B3LYP pseudo-potential

Go to the directory with the input files:

```
cd  Day-3/example7
```

In this directory you will find:

- `README.md` – File describing how to do the exercise
- `pw.methane.in` – Input file for the SCF ground-state calculation
- `turbo_davidson.methane.in` – Input file for a Davidson calculation of the eigenvalues
- `turbo_spectrum.methane.in` – Input file for a post-processing calculation of the spectrum
- `plot_spectrum_nohyb.gp` – Script to plot spectrum using **`gnuplot`**
- `plot_spectrum_hyb.gp` – Script to plot spectrum using **`gnuplot`**
- `reference` – Directory with the reference results

Example 7: Calculation of absorption spectra using B3LYP pseudo-potential

Step 1. Perform a SCF ground-state calculation:

```
pw.x < pw.methane.in > pw.methane.out
```

Step 2. Perform the turboDavidson calculation without B3LYP using the program.

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

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

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

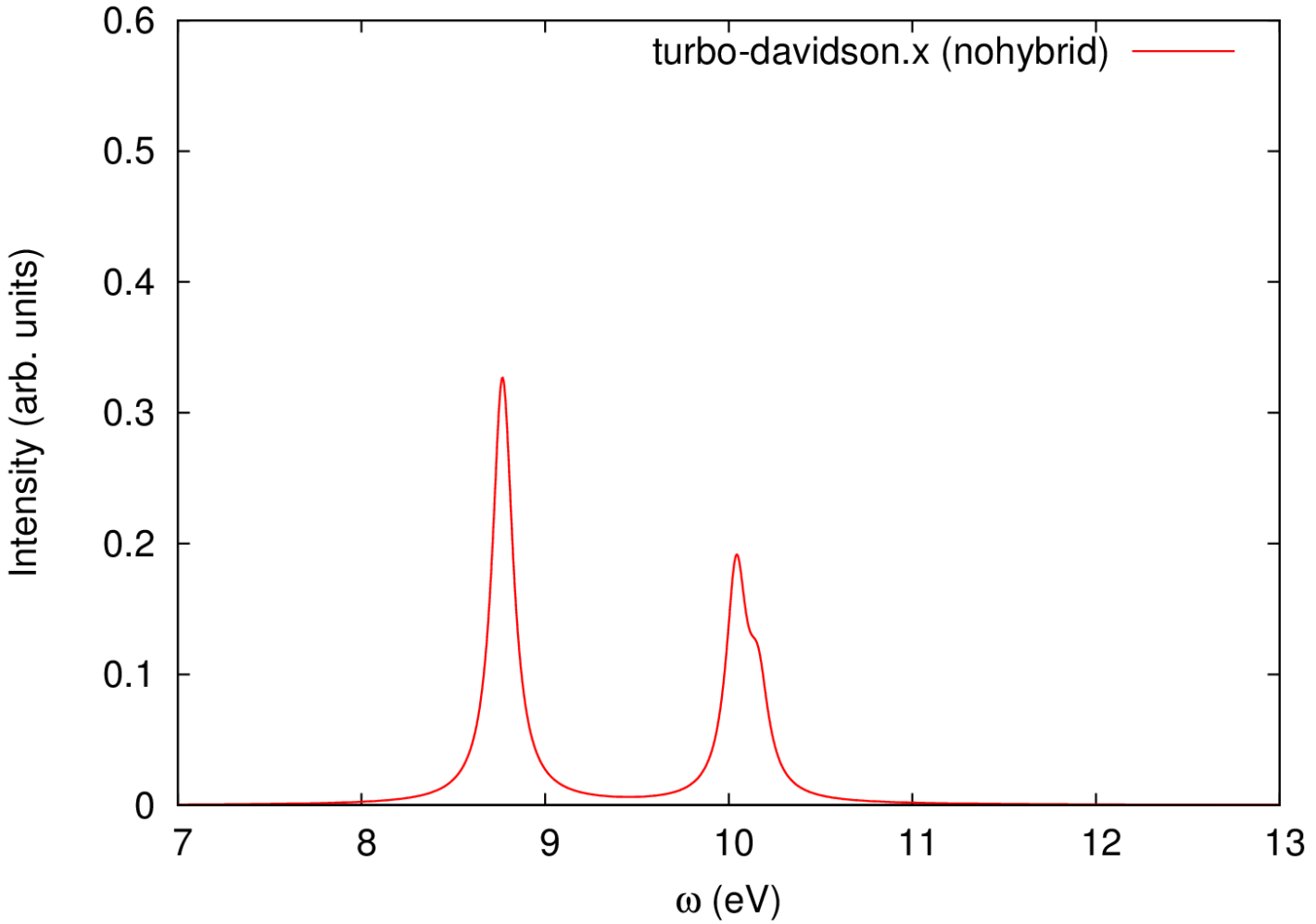
Step 4. Plot the spectrum using **gnuplot** and the script **plot_spectrum_nohyb.gp**

you should obtain the spectra without hybrid potential

The script **plot_spectrum_nohyb.gp** will produce the file **Methane_spectrum.eps** which you can visualize.

Example 7: Calculation of absorption spectra using B3LYP pseudo-potential

Absorption spectrum of methane using **`turbo_davidson.x`** (file **`Methane_spectrum.eps`**):



Example 7: Calculation of absorption spectra using B3LYP pseudo-potential

Now use B3LYP hybrid pseudo-potential!

Make the following modifications in the input files:

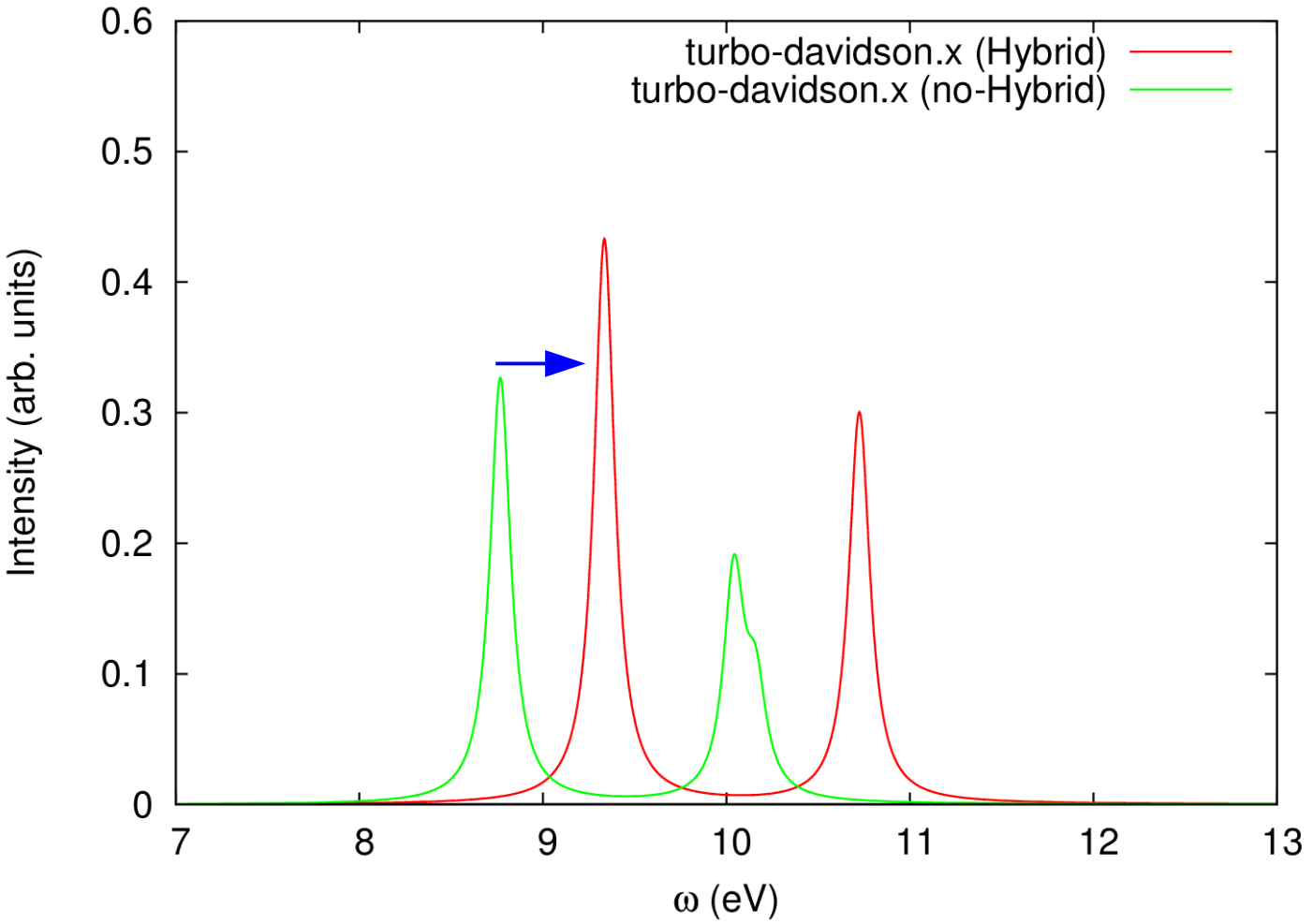
- In the file **`pw.methane.in`** add **`input_dft = 'B3LYP'`**
- In the file **`turbo_davidson.methane.in`** set **`d0psi_rs = .true.`**
- Use **`plot_spectrum_hyb.gp`**

Once these modifications are done, repeat all steps:

Note! The calculation will be a bit too long. Therefore, let us see the output files in the directory '**`reference`**'.

Example 7: Calculation of absorption spectra using B3LYP pseudo-potential

Hybrid exchange-correlation functionals open the energy gap and blue-shift the peaks:



Bibliography

1. B. Walker, R. Gebauer,
Ultrasoft pseudopotentials in time-depepndent 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).