



Fun with a Hydrogen chain: the obscure(?) reasons for the failure of the ALDA

by Andrea Marini

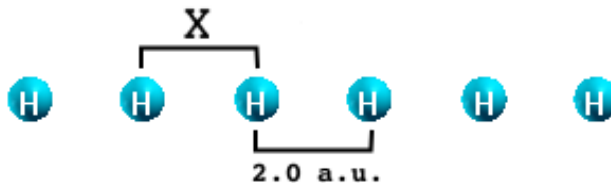
[Tutorial [pdf](#) document]

In the first TDDFT [tutorial](#) we learned how to calculate the response function in the TDDFT scheme.

You should have noticed that the performance of the ALDA gradually worsens moving from 0 to 3 dimensions. This means that the drawbacks of the approximation are somehow due to possibility that the electrons move in "wider" regions of space.

The subject of this tutorial is to show how yambo can be used to pin down the reasons for the failure of the ALDA in a simple system. The conclusions of this tutorial do not mean to be general, but they should convince you that there is a link between the local assumption of the ALDA and the polarization of electrons in extended directions.

The system used in this tutorial is an infinite H_2 molecular chain. This is a very simple physical system consisting of H atoms that are distributed in sets of two atoms placed at a variable distance X from each other.



The physical properties of the chain are functions of the distance X . When $X=2$. a.u. the system is metallic. By increasing X the chain becomes semiconducting with increasing gap.

First of all, after having downloaded the zip files of the [tutorial yambo databases](#) you should have six folders corresponding to the six values of X (2.05, 2.1, 2.2., 2.3, 2.4 and 2.5).

The ALDA failure

The first step of this tutorial is to run the calculation of the dynamical absorption in the TDLDA approximation.

We will describe here only the case of $X=2.05$ a.u.. You are invited to repeat the calculation for $X=2.5$ and, if you wish, for all the other cases.

Enter the 2.05 directory and run the setup launching yambo

```
localhost> cd 2.05
localhost> ls
BSE/ SAVE/
localhost> yambo
```

Editing the `r_setup` file we notice that the system has a small (0.27 eV) gap.

Now we can directly run the TDLDA calculation by typing

```
localhost> yambo -o b -t a -y d -V qp
```

You are now redirected to the editing of the `yambo.in` input file.

```
optics                # [R OPT] Optics
bse                   # [R BSK] Bethe Salpeter Equation.
alda_fxc              # [R TDDFT] The ALDA TDDFT kernel
bss                   # [R BSS] Bethe Salpeter Equation solver
KfnQPdb= "none"      # [EXTQP BSK BSS] Database
KfnQP_N= 1           # [EXTQP BSK BSS] Interpolation neighbours
% KfnQP_E
  0.000000 | 1.000000 | 1.000000 |      # [EXTQP BSK BSS] E parameters (c/v)
%
% KfnQP_W
  0.000    | 0.000    | 0.000    | 0.000    |      # [EXTQP BSK BSS] W parameters (c/v)
%
KfnQP_Z= ( 1.000000 , 0.000000 )      # [EXTQP BSK BSS] Z factor (c/v)
BSresKmod= "x"                        # [BSK] Resonant Kernel mode. (`x`; `c`; `d`)
% BSEBands
  1 | 20 |                                # [BSK] Bands range
%
BSENGexx= 7659          RL             # [BSK] Exchange components
BSSmod= "d"            # [BSS] Solvers `h/d/i/t`
% BEnRange
  0.000000 | 10.000000 | eV           # [BSS] Energy range
%
% BDmRange
  0.100000 | 0.100000 | eV           # [BSS] Damping range
%
BEnSteps= 100          # [BSS] Energy steps
% BLongDir
  1.000000 | 0.000000 | 0.000000 |      # [BSS] [cc] Electric Field
%
```

Please change the highlighted values to ...

```
% KfnQP_E
  3.500000 | 1.000000 | 1.000000 |      # [EXTQP BSK BSS] E parameters (c/v)
%
...
% BSEBands
  1 | 2 |
```

```
%
...
BEnSteps= 1000          # [BSS] Energy steps
...
```

Now use the *resp* verbosity to activate the flag needed to dump to file the eigenvectors of the BS Hamiltonian:

```
localhost> yambo -o b -t a -y d -V resp
```

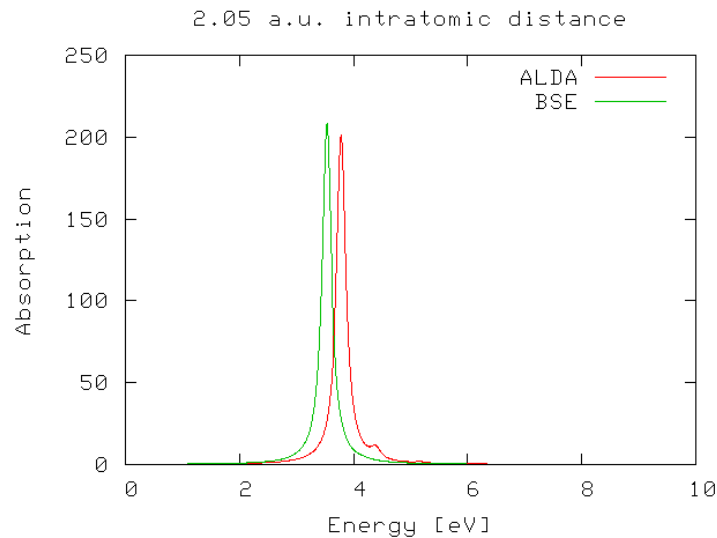
and remove the # to the flag

```
#WRbsWF          # [BSS] Write to disk excitonic the FWs
```

Now run yambo. In the folder *./BSE* you will find the absorption spectra (*o-BSE.eps_q001-bd*) calculated using the Many-Body based Bethe-Salpeter(BS) equation. If you wish you can find [here](#) a dedicated section about the BS calculation.

For the moment we will keep the results of the Bethe-Salpeter equation as a reference for our calculations. The BS equation leads indeed a proper and accurate description of the optical properties of the H₂ molecular chains.

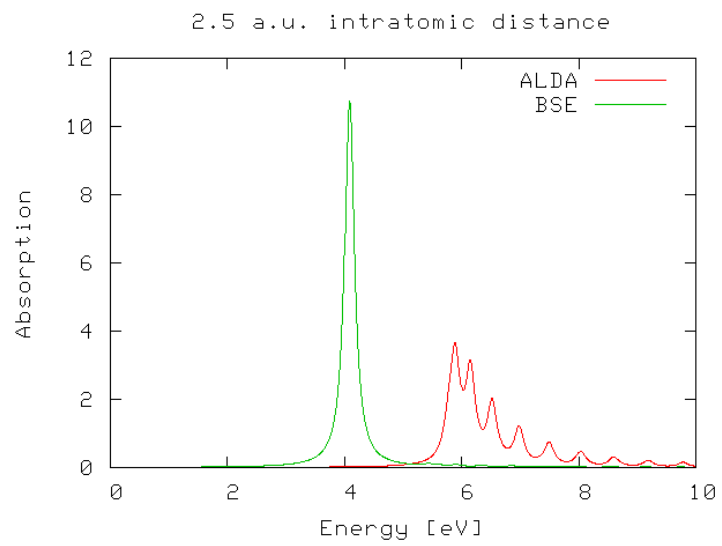
If you plot the ALDA result against the BS one you will find that there is a reasonable agreement between the two curves.



Now, please, repeat the same procedure in the 2.5 folder

```
localhost> cd ../2.5
localhost> yambo
localhost> yambo -o b -t a -y d -V 2
...
```

If you plot again the ALDA result against the BS one you will find that in this case the performance of the ALDA is much worse.



The question now is ...



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```

density                # [R] Density
electrons              # [R] Electrons (and holes)
Format= "g"           # Output format [(g)nuplot/(x)crysden]
Direction= "1"        # [rlu] [1/2/3] for 1d or [12/13/23] for 2d [123] for 3D
FFTGvecs= 7659        RL # [FFT] Plane-waves

```

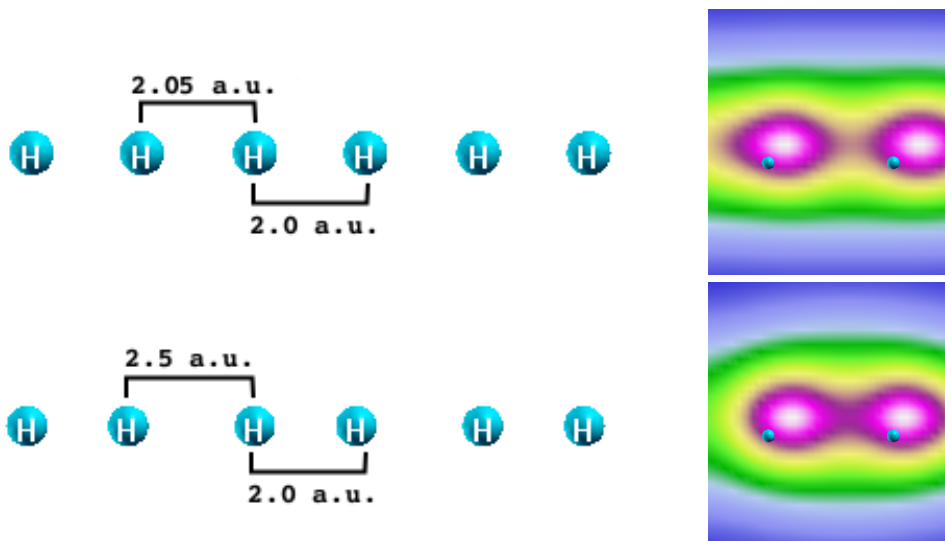
As our system is one-dimensional and it is lying parallel to the z axis we need to change the *Direction*="12" so to perform a contour plot on the "XY" plane. To use [Xcrysden](#) switch to "x" the value of the *Format* variable.

Now you can launch ypp.

At the end of the quick calculation you will find in your directory the file *o.density_2d.xsf* that you can plot using Xcrysden. We have provided a script to automatically view this file in the *../bin* folder. To use it type

```
localhost>../bin/launch_xcrysden.sh o.density_2d.xsf
```

Follow the same procedure for the other distance and compare the two densities. You should see something like



We see that the smaller the gap (@ 2.05 a.u.) the more delocalized the electronic density. The consequence is that electrons can move more freely in the 2.05 case. At the same time, however, the polarization will be more "metallic-like" where the ALDA is expected to work better.

The TDLDA excitations wavefunction

Using YPP we can do something more. We can plot the wavefunction corresponding to the most intense peak in the dielectric function. The excitation wavefunction is a two-coordinate (r_1 , and r_2) function and represents the probability amplitude of finding the electron at position r_1 when the hole is in r_2 . The larger this probability the

more delocalized is the perturbation induced by the external field. A mean large distance between the electron and hole also reflects the poor correlation felt by the two bodies. YPP can plot either the case where the electron and the hole are forced to be in the same space point, or the case where the hole's position is fixed somewhere and the electron is left free to move. This second case is more appropriate here.

We need first to identify the index of the corresponding eigenstate. Running

```
localhost>ypp -e s
```

YPP will create a file named *o.exc_l_sorted* that contains the list of peaks in the dielectric function ordered with increasing peak intensity.

```
#
# E [ev]      Strength  Index
#
  3.783688   1.000000   1.000000
   4.38457   0.03179    3.000000
   5.171     0.3731E-2  5.000
```

We see that the peak with energy 3.78 dominates the spectra and it corresponds to the index 1. If we type now

```
localhost>ypp -e w
```

to get the input file

```
exc_wf          # [R] Excitonic Wavefunction
exc_p           # [R] Excitonic Properties
plot           # [R] Plot
Format= "x"    # Output format [(g)nuplot/(x)crysden]
Direction= "12" # [rlu] [1/2/3] for 1d or [12/13/23] for 2d [123] for 3D
FFTGvecs= 7659 RL # [FFT] Plane-waves
States= "1 - 1" # Index of the BS state(s)
Degen_Step= 0.0100 eV # Maximum energy separation of two degenerate states
% Cells
  1 | 1 | 1 | # Number of cell repetitions (even or 1)
%
% Hole
  0.000 | 0.000 | 0.000 | # [cc] Hole position in unit cell
%
```

It is interesting to do a 3D plot. To this end we set *Direction*="123" and replace 1 with 16 in Cells (this value will expand the unit cell along the X direction). The *States* variable is already set to the peak number 1.

We put the hole in the middle of the chain by setting

```
% Hole
  1.02500 | 12.50000 | 12.50000 | # [cc] Hole position in unit ce
%
```

remember that the first field must be set to the interatomic distance divided by two. In the case of 2.5 a.u. the first field will

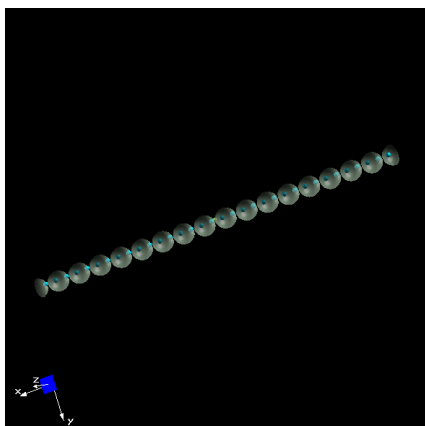
be 1.25.

If we run now ypp it will create the file *o.exc_3d_1.xsf* that you can plot by using

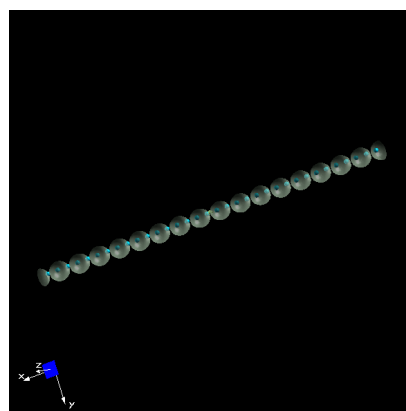
```
localhost>../bin/launch_xcrysden.sh o.density_2d.xsf
```

If we compare the plot with the one obtained by solving the BS equation we should see

Excitation wavefunctions for 2.05 a.u. distance

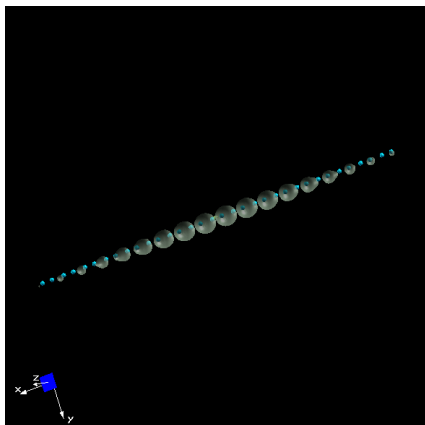


BS equation

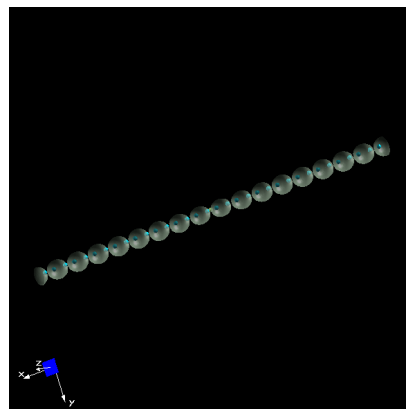


TDLDA

Excitation wavefunctions for 2.5 a.u. distance



BS equation



TDLDA

We immediately see that, while the ALDA excitation is always spread all over the chain, in the 2.5 distance case the "true" wavefunction acquires a tail that decreases the probability of finding the electron and the hole very far from each other.

This saturation of the excitation wavefunction is the physical reason for the poor performance of the ALDA. As it is a local approximation it cannot take into account a long-range correlation between the electron and the hole.

A long-range kernel beyond the TDLDA

So, we realized that a simple plot of the excitation wavefunction can pin down the possible reasons for the breakdown of the ALDA. In general if you know the problem, you should be half way through the quest for a solution. Is it true?

We have seen the failure of the ALDA in the case of the H₂ chain when the intra-molecular distance increases. We also have seen how the excitation wave function differs from the one obtained by solving the Bethe Salpeter equation in the case of 2.5 a.u. intermolecular distance. Such discrepancy has been traced back to the long-range correlation between the electron and hole, that cannot be captured by the simple local approximation.

Now, we use yambo to check whether simple approximations for the f_{xc} kernel can cure the ALDA drawbacks. To this end we use the [Reciprocal space Dyson equation for the response function](#) (-o c option).

The key point is to realize that, indeed, the f_{xc} kernel acts like a self-energy in the Dyson equation for χ . As in the case of quasiparticles, the most optimal self-energy can be chosen by looking at the structure of the bare propagator, X_0 in this case.

If you look [here](#) you will see that in the long wavelength limit X_0 behaves like q^2 . As a naive consequence the self-energy must cancel this power dependence to ensure that the product $f_{xc}X_0$ remains finite in the optical limit.

This simple argument is enough to introduce the long-range TDDFT kernel

$$f_{xc}(\mathbf{r}, \mathbf{r}', \omega) \sim \frac{\alpha(\omega)}{|\mathbf{r} - \mathbf{r}'|}$$

Now we will use this kernel with a static approximation for the parameter alpha, first for the chain of intermolecular distance 2.5 a.u..

Enter the 2.5 directory

```
localhost> cd 2.5
```

and generate the input file for a tddft calculation in reciprocal space, specifying you want the long-range kernel:

```
localhost> yambo -o c -t l
```

You are now redirected to the editing of the yambo.in input file.

```

optics                # [R OPT] Optics
chi                   # [R CHI] Dyson equation for Chi.
lrc_fxc               # [R TDDFT] The LRC TDDFT kernel
XfnQPdb= "none"      # [EXTQP Xd] Database
XfnQP_N= 1           # [EXTQP Xd] Interpolation neighbours
% XfnQP_E
  0.000000 | 1.000000 | 1.000000 |      # [EXTQP Xd] E parameters (c/v)
%
% XfnQP_W
  0.000    | 0.000    | 0.000    | 0.000    |      # [EXTQP Xd] W parameters (c/v)
%
XfnQP_Z= ( 1.000000 , 0.000000 )      # [EXTQP Xd] Z factor (c/v)
% QpntsRXd
  1 | 41 |      # [Xd] Transferred momenta
%
% BndsRnXd
  1 | 20 |      # [Xd] Polarization function bands
%
NGsBlkXd= 1          RL # [Xd] Response block size
% EnRngeXd
  0.00000 | 10.00000 | eV # [Xd] Energy range
%
% DmRngeXd
  0.10000 | 0.10000 | eV # [Xd] Damping range
%
ETStpsXd= 100        # [Xd] Total Energy steps
% LongDrXd
  1.000000 | 0.000000 | 0.000000 |      # [Xd] [cc] Electric Field
%
LRC_alpha= 0.000000 # [TDDFT] LRC alpha factor

```

Please change the yellow values ...

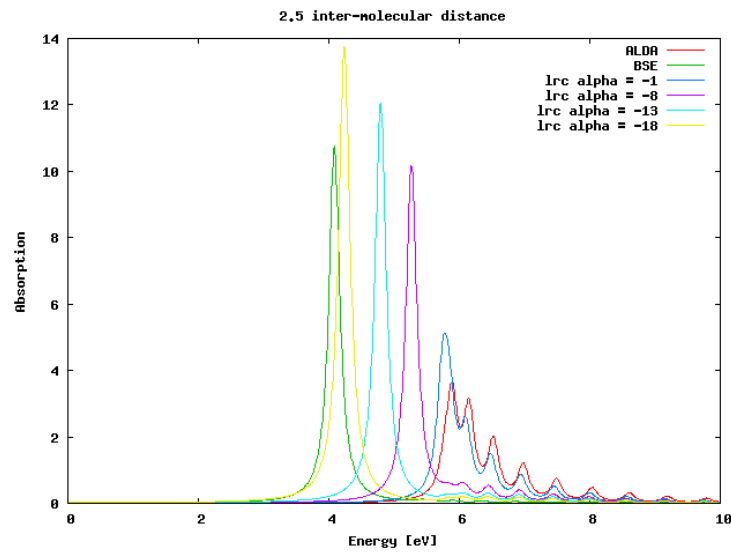
```

% XfnQP_E
  3.5000000 | 1.000000 | 1.000000 |      # [EXTQP Xd] E parameters (c/v)
%
% QpntsRXd
  1 | 1 |      # [Xd] Transferred momenta (We want only q=0 response)
%
% BndsRnXd
  1 | 2 |      # [Xd] Polarization function bands
%
NGsBlkXd= 100        RL # [Xd] Response block size (Put some local fields, not too
...
ETStpsXd= 1000      # [Xd] Total Energy steps
...

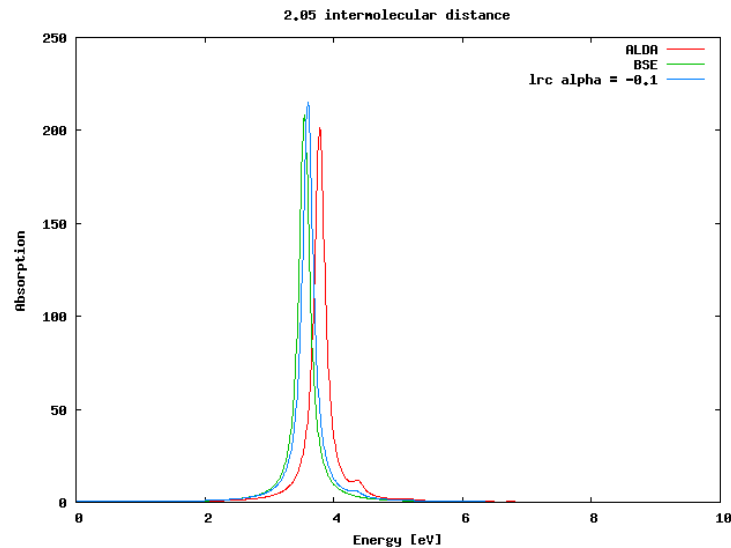
```

... and run yambo.

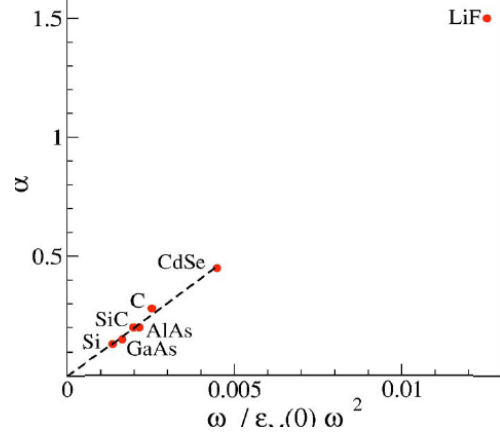
Now we can perform different calculations assigning different values to the variable LRC_alpha. This value is a static approximation to $\alpha(\omega)$ in the long-range expression for f_{xc} . This must be negative (the interaction between electron and hole is attractive). Try different numbers in the range 0 to -20. You will see that around LRC_alpha=-19 we obtain the same excitation energy of the BSE spectrum.



Now you can repeat the same calculations for the chain with 2.05 intermolecular distance. Once you will find the optimal value of %alpha, you will realize that as expected, it is one order of magnitude smaller than the one needed for the previous, more inhomogeneous system.



To conclude this tutorial note that the value of α you found is much larger than in any solid, as showed in this picture. Can you understand why ?



The Bethe-Salpeter equation

The H₂ Hydrogen chain constitutes an example of a perfectly one-dimensional system. This property causes some tricky numerical problems that are, however, related to a precise physical process: the extreme confinement of 3D electrons in a small region of space. So we start using yambo to perform a BS calculation, and you will immediately see where the problem is !

We start by generating the input file. At the command line we have to tell yambo to construct the [BSE](#) (-o b) , to calculate the [static screened interaction](#) (-b), and to [diagonalize](#) the BS matrix (yambo -y d). The input line will be:

```
localhost> yambo -o b -b -y d -V qp
```

The generated input file describes our first attempt to calculate the excitonic polarization spectrum of the H chain:

```
optics                # [R OPT] Optics
bse                   # [R BSK] Bethe Salpeter Equation.
emls                  # [R Xs] Static Inverse Dielectric Matrix
bss                   # [R BSS] Bethe Salpeter Equation solver
KfnQPdb= "none"      # [EXTQP BSK BSS] Database
KfnQP_N= 1           # [EXTQP BSK BSS] Interpolation neighbours
% KfnQP_E
  0.000000 | 1.000000 | 1.000000 |          # [EXTQP BSK BSS] E parameters (c/v)
%
% KfnQP_W
  0.000    | 0.000    | 0.000    | 0.000    |          # [EXTQP BSK BSS] W parameters (c/v)
%
KfnQP_Z= ( 1.000000 , 0.000000 )          # [EXTQP BSK BSS] Z factor (c/v)
BSresKmod= "xc"                          # [BSK] Resonant Kernel mode. (`x`; `c`; `d`)
% BSEBands
  1 | 2 |                                  # [BSK] Bands range
%
BSENGBlk= 1 RL # [BSK] Screened interaction block size
BSENGexx= 7659 RL # [BSK] Exchange components
XfnQPdb= "none" # [EXTQP Xd] Database
XfnQP_N= 1 # [EXTQP Xd] Interpolation neighbours
% XfnQP_E
  0.000000 | 1.000000 | 1.000000 |          # [EXTQP Xd] E parameters (c/v)
%
% XfnQP_W
  0.000    | 0.000    | 0.000    | 0.000    |          # [EXTQP Xd] W parameters (c/v)
%
XfnQP_Z= ( 1.000000 , 0.000000 )          # [EXTQP Xd] Z factor (c/v)
% QpntsRXs
  1 | 41 |                                  # [Xs] Transferred momenta
%
% BndsRnXs
  1 | 20 |                                  # [BSK] Bands range
%
NGsBlkXs= 1 RL # [Xs] Response block size
% LongDrXs
  1.000000 | 0.000000 | 0.000000 |          # [Xs] [cc] Electric Field
%
BSSmod= "d" # [BSS] Solvers `h/d/i/t`
```

```
% BEnRange
0.00000 | 10.00000 | eV # [BSS] Energy range
%
% BDmRange
0.10000 | 0.10000 | eV # [BSS] Damping range
%
BEnSteps= 100 # [BSS] Energy steps
% BLongDir
1.000000 | 0.000000 | 0.000000 | # [BSS] [cc] Electric Field
%
```

Remember to change the highlighted values. The first change is to include a QP gap correction of 3.5 eV

```
% KfnQP_E
3.50000 | 1.000000 | 1.000000 | # [EXTQP BSK BSS] E parameters (c/v)
%
```

Then we decide some reasonable size of the inverse dielectric function that defines the statically screened interaction.

```
NGsBlkXs= 111
BSENGexx= 111
```

Finally you should change

```
% BSEBands
1 | 2 | # [BSK] Bands range
%
```

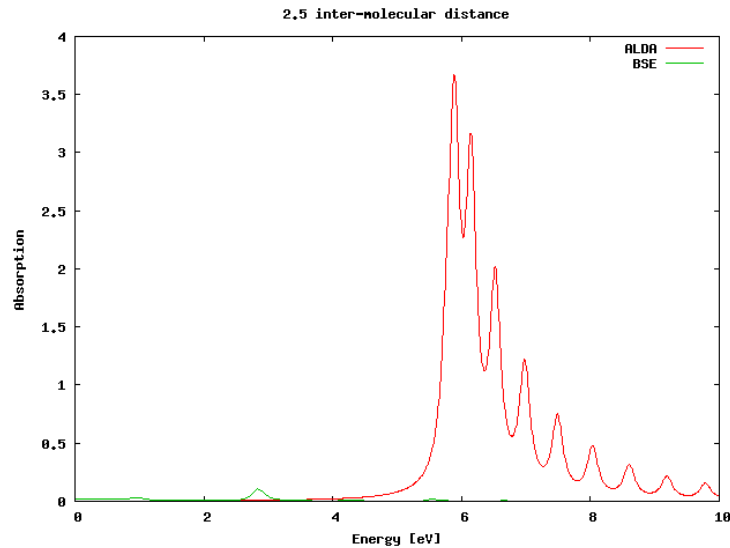
2 bands are enough to get reasonable results.

Remember also to uncomment the variable WRbsWF if you want to plot the excitonic wave function afterwards

so we run

```
localhost> yambo
```

To our great surprise the polarization spectrum we obtain is completely wrong, with just a poor signal around 3eV which is nonsense.



The reason of this serious failure of the BS calculation is due to the peculiar geometry of the H chain, and of corresponding BZ sampling that is strictly one dimensional, This is readily detected in any report file, like *r_setup*

```
[...]
[02.01] K-grid lattice
=====

Compatible Grid might be 1D
Bl [rlu]= -0.01250  0.00000  0.00000
Grid dimensions      : 80
K lattice UC volume [au]:  0.0011
```

As a consequence the *region* of space assigned to each k-point is strongly compressed in one of the dimensions, like the thin slices of this picture



The drastic consequence of this compression is that each region receives a piece of the electron-electron interaction that is multiplied by a *form factor* of the region, that, in general **is assumed spatially constant**. With such a severe sampling of the BZ this assumption is no longer valid and the screened interaction is anomalously enhanced.

To avoid this anomalous electron-electron interaction we use the Random Integration Method (-c option) described [here](#):

```
localhost> yambo -c -o b -b -y d
```

and use for the [RandOpts](#) and for the [RandGvec](#):

```
RandQpts= 1000000          # [RIM] Number of random q-points in the BZ
RandGvec= 1                RL # [RIM] Coulomb interaction RS components
```

RandQpts specifies the number of random points to use and *RandGvec* the number of RL components to evaluate.

After typing

```
localhost:>yambo
```

we notice a new section in the report file *r_optics_bse_emls_bss_rim_cut*:

```
[04] Coulomb potential Random Integration (RIM)
=====

[RD./SAVE/ndb.RIM]-----
Brillouin Zone Q/K grids (IBZ/BZ): 41 80 41 80
Coulombian RL components      : 1
Coulombian diagonal components :yes
RIM random points             : 1000000
RIM RL volume                 [a.u.]: 0.08864
Real RL volume                 [a.u.]: 0.08820
Eps^-1 reference component    :0
Eps^-1 components             : 0.00000 0.00000 0.00000
RIM anisotropy factor         : 0.00000
- S/N 003292 ----- v.02.09.09 -
```

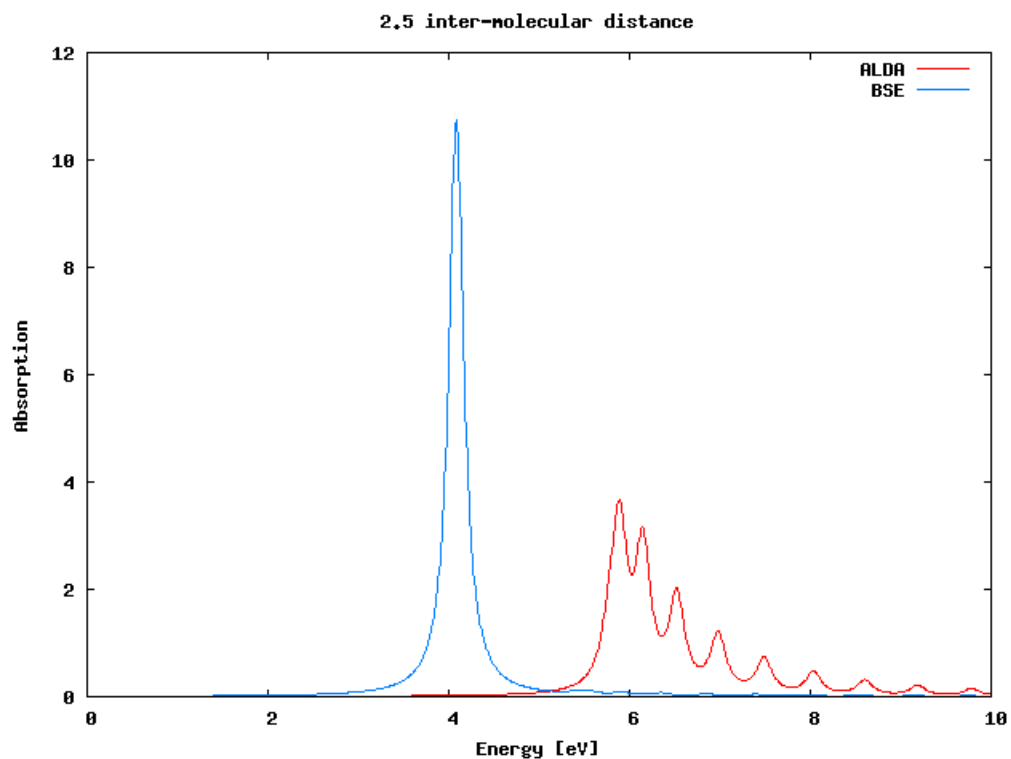
Summary of Coulomb integrals for non-metallic bands |Q|[au] RIM/Bare:

```
Q [1]:0.1000E-4 0.7653 * Q [2]: 0.01745 0.06494
Q [3]: 0.03491 0.17408 * Q [4]: 0.05236 0.28906
Q [5]: 0.06981 0.39545 * Q [6]: 0.08727 0.48820
Q [7]: 0.104720 0.566608 * Q [8]: 0.122173 0.631844
Q [9]: 0.139626 0.685750 * Q [10]: 0.157080 0.730229
Q [11]: 0.174533 0.767000 * Q [12]: 0.191986 0.797519
Q [13]: 0.209440 0.822983 * Q [14]: 0.226893 0.844352
Q [15]: 0.244346 0.862396 * Q [16]: 0.261799 0.877727
Q [17]: 0.279253 0.890832 * Q [18]: 0.296706 0.902101
Q [19]: 0.314159 0.911847 * Q [20]: 0.331613 0.920320
Q [21]: 0.349066 0.927727 * Q [22]: 0.366519 0.934233
Q [23]: 0.383972 0.939973 * Q [24]: 0.401426 0.945061
Q [25]: 0.418879 0.949588 * Q [26]: 0.436332 0.953633
Q [27]: 0.453786 0.957260 * Q [28]: 0.471239 0.960523
Q [29]: 0.488692 0.963470 * Q [30]: 0.506145 0.966138
Q [31]: 0.523599 0.968561 * Q [32]: 0.541052 0.970768
Q [33]: 0.558505 0.972783 * Q [34]: 0.575959 0.974629
Q [35]: 0.593412 0.976322 * Q [36]: 0.610865 0.977879
Q [37]: 0.628319 0.979314 * Q [38]: 0.645772 0.980640
Q [39]: 0.663225 0.981867 * Q [40]: 0.680678 0.983004
Q [41]: 0.698132 0.984061
```

The interesting result is that 2nd and the 4th column of numbers reflects the effect of the BZ compression: 1 means little effect, small numbers mean large effect. We see that the effect is huge for points in the BZ with small modulus (1st and 3rd columns).

The final BS polarizability is, now, physically correct and

substantially different from ALDA.



Additional Exercises

1. The H chain is a one dimensional system, and, consequently it should not absorb when the light is polarized perpendicularly to the chain axis (the x direction).

Repeat the [RPA](#), [ALDA](#), [BSE](#) calculations for light polarized perpendicular to the chain axis to verify that the polarization is much smaller than in the parallel case.

2. Use `ypp` to plot the excitonic wave function.
3. Repeat the whole tutorial for the other intratomic distances, whose databases are provided in the tutorial zip file.