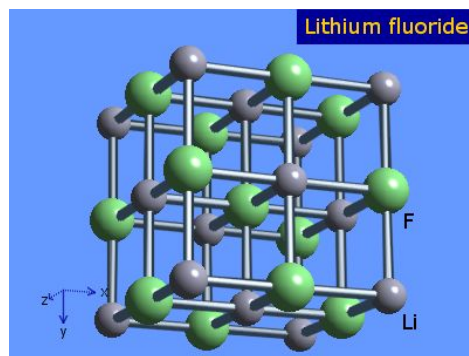




## Solid LiF: excitons at work

[Shortcut to examples [01](#) [02](#) [03](#) [04](#) [05](#) [06](#) [07](#) and [exercises](#) ]  
by Andrea Marini

[Tutorial [pdf](#) document]



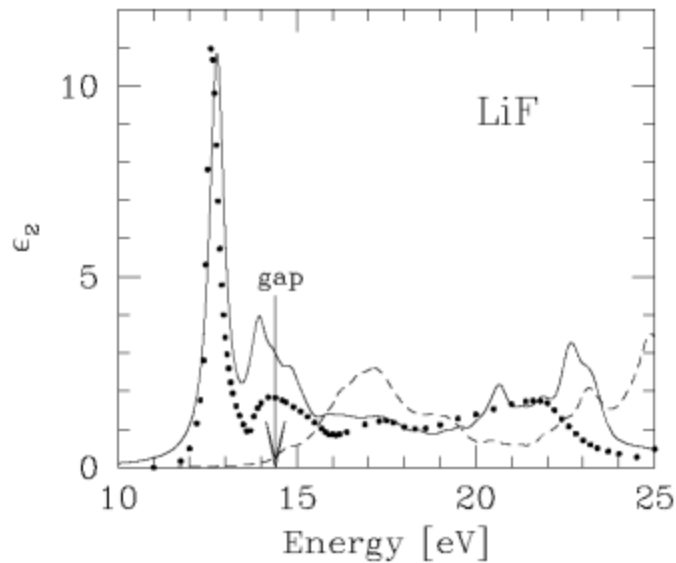
*LiF structure.*

### The material

- FCC lattice
- Two atoms per cell, Li and F (8 electrons)
- Lattice constant 7.61 [a.u.]
- Plane waves cutoff 40 Hartree (1800 RL vectors)

### Introduction

We will start the TDDFT tutorial exactly where standard local approximations for  $f_{xc}$  (like ALDA) do not work at all. The optical spectrum of solid LiF[[1](#)] is dominated by a strongly bound exciton (3 eV binding energy)[[2](#)] and will immediately see that any independent particle approximation drastically fail to describe the complex structures that are observed experimentally.



Optical absorption of solid LiF. Dots: experiment. Continuous line: BSE. Dashed line: RPA-QP. See [2] for details.

In the following we will describe in detail the different TDDFT related calculations. For each example you can find a link to the Input file with a brief explanation of the variables meaning.

We will also use this first system to explain in detail some of the most relevant technical aspects of yambo.

### **[01] Initialization: [01\\_init](#) (yambo -i -V 1)**

This section describes the standard [initialization](#) procedure. As this initialization is common to all yambo runs it will be described extensively only in this case.

To run this example enter the *YAMBO* directory (where you have previously created the *SAVE* folder) and type:

```
localhost:>yambo -F Inputs/01_init -J 01_init
```

and you will see

```
<---> [01] Game Summary
<---> [02] Input variables setup
<---> RL-shells | | [000%] --(E) --(X)
<---> RL-shells |#####| [100%] --(E) --(X)
<---> [02.01] K-grid lattice
<---> [02.02] Input (E)nergies[ev] & Occupations
<---> [03] Transferred momenta grid: Indexes
<---> [04] Game Over & Game summary
```

If now you edit the *r-01\_setup* you will find a lot of useless (



) informations about your system like, the Fermi level

```
[02.02] Input (E)nergies[ev] & Occupations
=====
```

```
Fermi Energy[ev] - T[ev/K] :-0.241627  0.000100  1.160400
Bands summary           : Full      Empty
                        0001-0004  0005-0050
Indirect Gap [ev][min-max]:  9.11330  14.79631
```

confirming that, yes, our bulk LiF is a **wide** gap insulator. Then you can see the effect of using

```
MaxGvecs= 800          RL # [INI] Max number of G-vectors planned to use
```

in the *Inputs/01\_init* file. In the report file we notice that

```
G-vectors           [RL space]: 1807
                    [wavefunctions]: 1807
```

whereas the Reciprocal Space shells found by yambo are

```
G-vector (S)hells. Format: [Snn] G`s
[S0030]:  773 [S0029]:  749 [S0028]:  725 [S0027]:  701 [S0026]:  645
[S0025]:  609 [S0024]:  561 [S0023]:  537 [S0022]:  531 [S0021]:  459
[S0020]:  411 [S0019]:  387 [S0018]:  339 [S0017]:  331 [S0016]:  307
[S0015]:  283 [S0014]:  259 [S0013]:  229 [S0012]:  181 [S0011]:  169
[S0010]:  137 [S0009]:  113 [S0008]:   89 [S0007]:   65 [S0006]:   59
[S0005]:   51 [S0004]:   27 [S0003]:   15 [S0002]:    9 [S0001]:    1
```

so that the highest number of RL vectors we can use is 773, lower than the charge number given by Abinit and different from the value for *MaxGvecs* we provided. This happens because yambo has calculated the Reciprocal Space shells up to 800 to find that the highest closed shell corresponds to 773 RL vectors. Note that, independently of the value you set for any variable that defines a dimension in the RL space, yambo redefines it, in order to match it to the nearest closed shell.

**[02-03] Random-Phase approximation: [02\\_RPA\\_no\\_LF](#) (yambo -o c) [03\\_RPA\\_LF](#)(yambo -o c) [03\\_RPA\\_LF\\_QP](#)(yambo -o c -V 1)**

The easiest way of calculating the absorption spectrum of LiF is the [Random Phase Approximation](#) (RPA). In *Inputs/02\_RPA\_no\_LF* a simple RPA calculation is done with

```
NGsBlkXd=1      RL      #      (Xd)      Response block size
```

or, equivalently, neglecting Local Fields Effects (LFE). To run this example type

```
localhost:>yambo -F Inputs/02_RPA_no_LF -J 02_RPA_no_LF
```

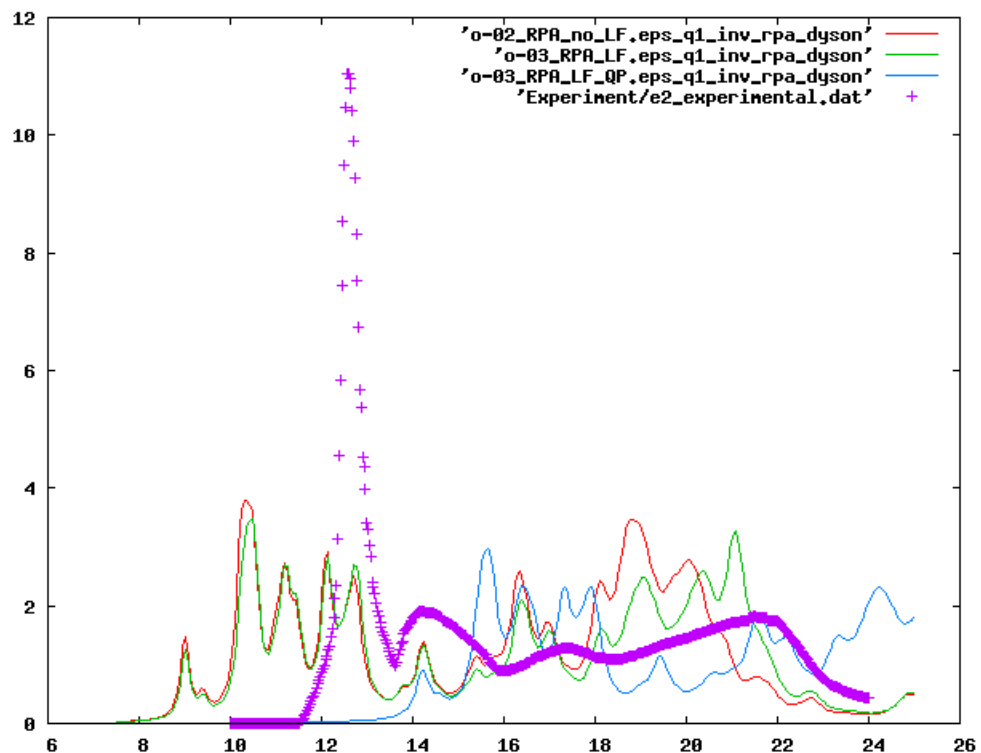
The optional `-J` flag is used to label the output/report/log files (see [here](#) for the command line synopsis).

In `Inputs/03_RPA_LF` the response function size is changed to 51 RL. This means including Local Field Effects corresponding to charge oscillations expanded up to the 51<sup>st</sup> RL component. The converged value for `NGsBlkXd` shall be determined by doing several calculations with different values and checking the effect on the final physical result (the absorption spectrum, in this case).

After having run

```
localhost:>yambo -F Inputs/03_RPA_LF -J 03_RPA_LF
```

we can compare the result of our calculations with the experimental curve (that you find in the `Experiment` folder).

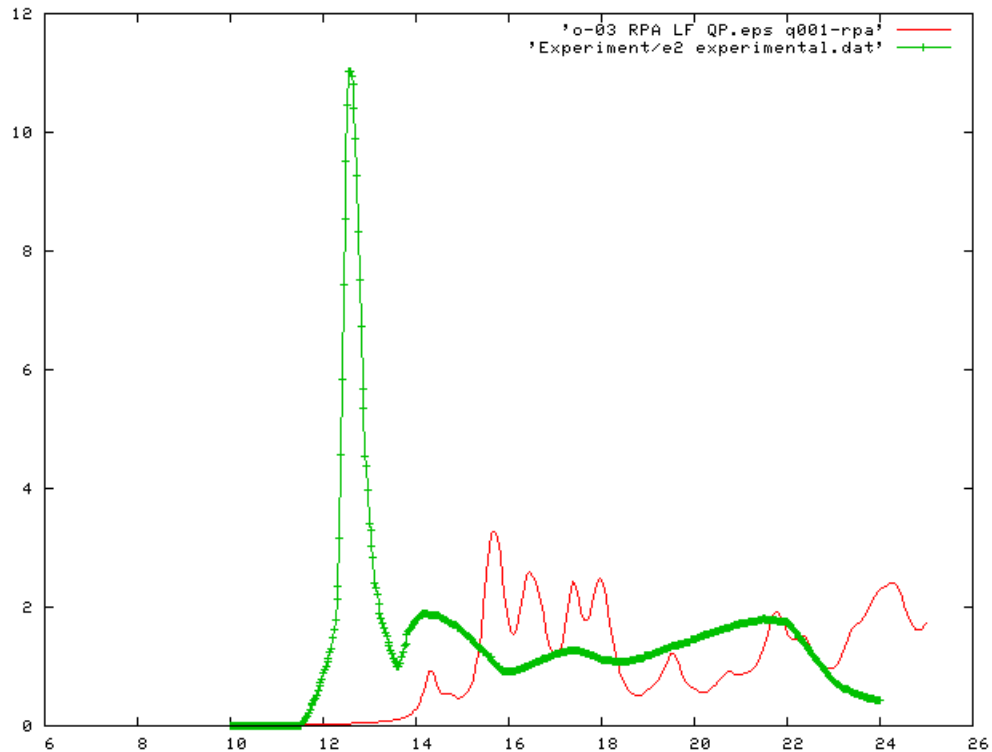


The comparison with the experiment clearly show that the RPA is not at all adequate in the case of LiF. We notice two main discrepancies between theory and experiment: the RPA absorption onset is too low and the shape lacks the sharp peak observed experimentally at around 12 eV. The onset position can be artificially corrected using a scissor operator

(representing the QP gap correction) of 5.19 eV that simply opens rigidly the LDA gap. This is shown in *Inputs/03\_RPA\_LF\_QP* with the line

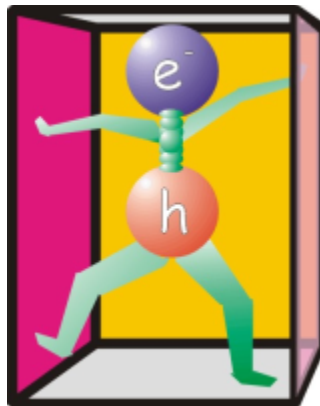
```
% XfnQP_E  
5.190000 | 1.000000 | 1.000000 | # [EXTQP Xd] E parameters (c/v)  
%
```

The resulting spectrum fits better with the experiment but now there seems to be an even more serious problem:



there is an experimental peak well below the QP absorption onset:

an **EXCITON!**



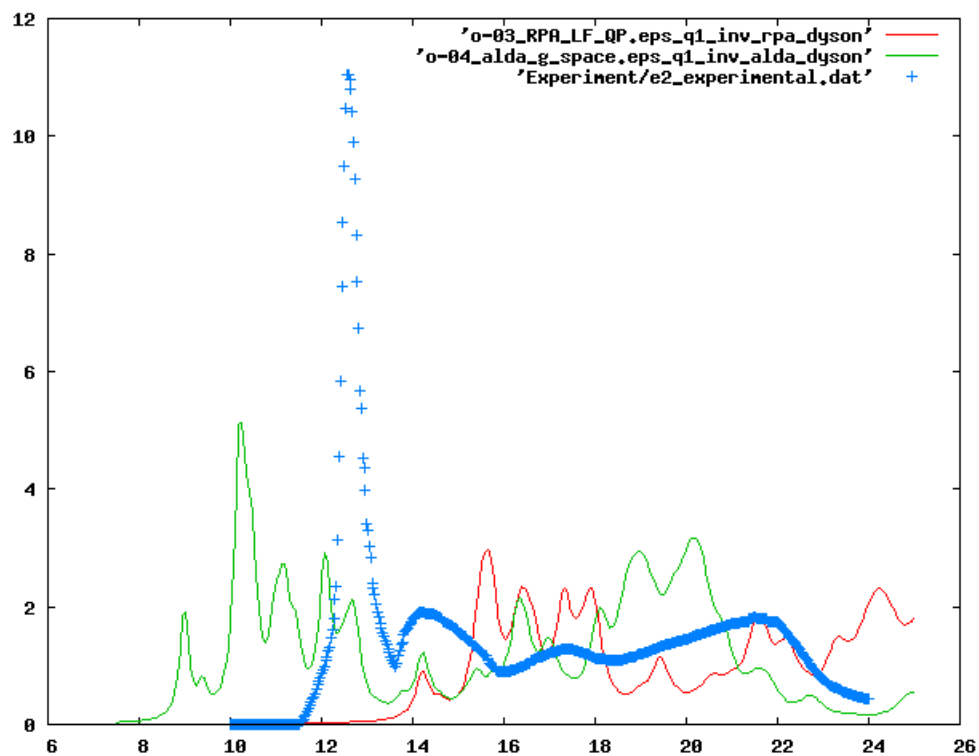
#### [04] ALDA: [04\\_ALDA\\_g\\_space](#)(yambo -o c -t a)

Our first attempt to go beyond RPA is using [TDDFT](#) in the Adiabatic LDA approximation. Depending on the exchange-correlation(xc) functional used in the ground state calculation yambo will produce a corresponding xc-kernel. In this case, as reported by the `a2y` command we are using a Perdew Wang parametrization.

Running

```
localhost:>yambo -F Inputs/04_alda_g_space -J 04_alda_g_space
```

we get



Unfortunately ALDA only slightly changes the RPA result. The situation will change in more isolated system (reduced dimensionality).

#### [05] The Statically screened Electron-electron interaction: [05\\_W](#)(yambo -b)

As simple RPA and ALDA approximations have not described correctly the experimental spectrum we have to move towards more elaborate techniques like the Bethe-Salpeter (BS) equation.

A key ingredient in the [BS kernel](#) is the electron-electron interaction commonly evaluated in the [static](#) approximation. The input file *Inputs/05\_W* describes how to calculate it. The variables used in this input file have the same physical meaning of those used in the optical absorption calculation. The only difference is that, in general, the response function dimension obtained in the examples (03-04), gives an upper bound to the number of RL vectors needed here. This is because the size of response matrix in an RPA calculation defines also the size of the Hartree potential, whose short-range components are not screened. In the present case, instead, the electron-electron interaction is screened and, for this reason, the RL vectors needed are considerably smaller than in the RPA case. So let's type (no *-j* option here)

...

```
localhost:>yambo -F Inputs/05_W
```

... and after waiting for some minutes the result, that is the [database](#) *SAVE/ndb.em1s*. Here it is better to skip the *-j* option as we will need to read this database in the next examples.

## **[06] The Bethe-Salpeter equation, Excitons: [06\\_BSE](#)(yambo -o b -y h)**

The input file *Inputs/06\_BSE* describes how to calculate an excitonic absorption spectrum, using as a solver of the BS equation the [recursive Haydock Method](#). Before running *yambo* we must have a closer look at the input file:

The line

```
% KfnQP_E
 5.80000 | 1.000000 | 1.000000 |      # [EXTQP BSK BSS] E parameters (c/v)
%
```

applies a 5.8 eV scissor in order to open the LDA gap.

```
BSresKmod= "xc"          # [BSK] Resonant Kernel mode. (`x`; `c`; `d`)
```

Here we are doing a BSE calculation including both exchange and correlation terms in the the [resonant part](#) only of the kernel as the coupling part generally induces a small effect in semiconductors and insulators. We will see the effect of the coupling term in the H<sub>2</sub> molecule.

```
% BSEBands
 2 | 7 |          # [BSK] Bands range
%
BSENGBlk= 51      RL # [BSK] Screened interaction block size
BSENGexx= 773    RL # [BSK] Exchange components
```

Here we specify the range of bands to be used and the RL components for the screened interaction (51) (read from the `ndb.em1s` file) and for the Hartree term (773, the maximal available). **Remember** that the BS kernel is written in Bloch space and its size is given by

BS kernel size = Valence Bands × Conduction Bands × K-points in the whole BZ

In our case the size is 2304. The BS bands range must be converged with care trying to keep as a few bands as possible.

### Running

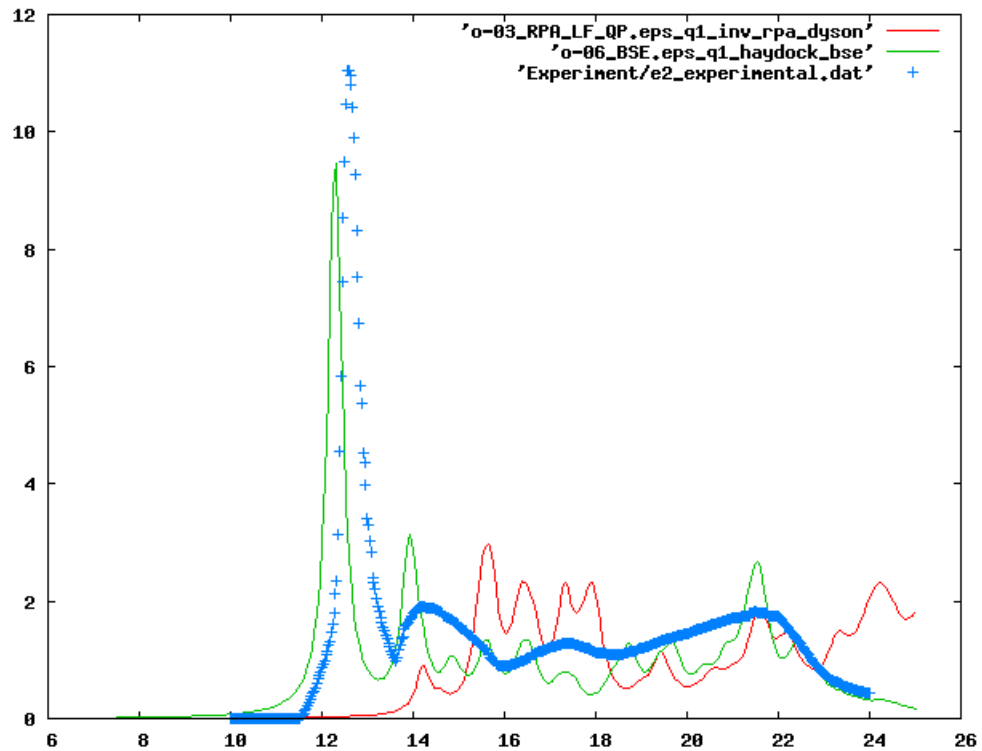
```
localhost:>yambo -F Inputs/06_BSE -J 06_BSE
```

will calculate the BS kernel and store in in the `06_BSE` folder. Before analyzing the BS absorption spectrum we can edit the log file `I-06_BSE_optics_bse_bss` to observe the on-the-fly live timing feature of yambo:

```
[...]
<---> BSK |                               | [000%] --(E) --(X)
<05s> BSK |#                               | [007%] 05s(E) 01m-07s(X)
<11s> BSK |###                             | [015%] 10s(E) 01m-06s(X)
[...]
<01m-02s> BSK |#####                       | [093%] 01m-01s(E) 01m-06s(X)
<01m-07s> BSK |#####                       | [100%] 01m-06s(E) 01m-06s(X)
[...]
```

The two numbers at the end of each line represents the elapsed time(E) and the expected time(X). The latter estimates the time needed to complete that particular section (the BS kernel construction in this case).

Finally we can compare the resulting BS optical absorption with the experimental result. We see how strong is the excitonic effect, if compared to the RPA calculation. The BS equation is, then, able to describe the bound electron-hole state responsible for the peak observed experimentally below the QP gap.

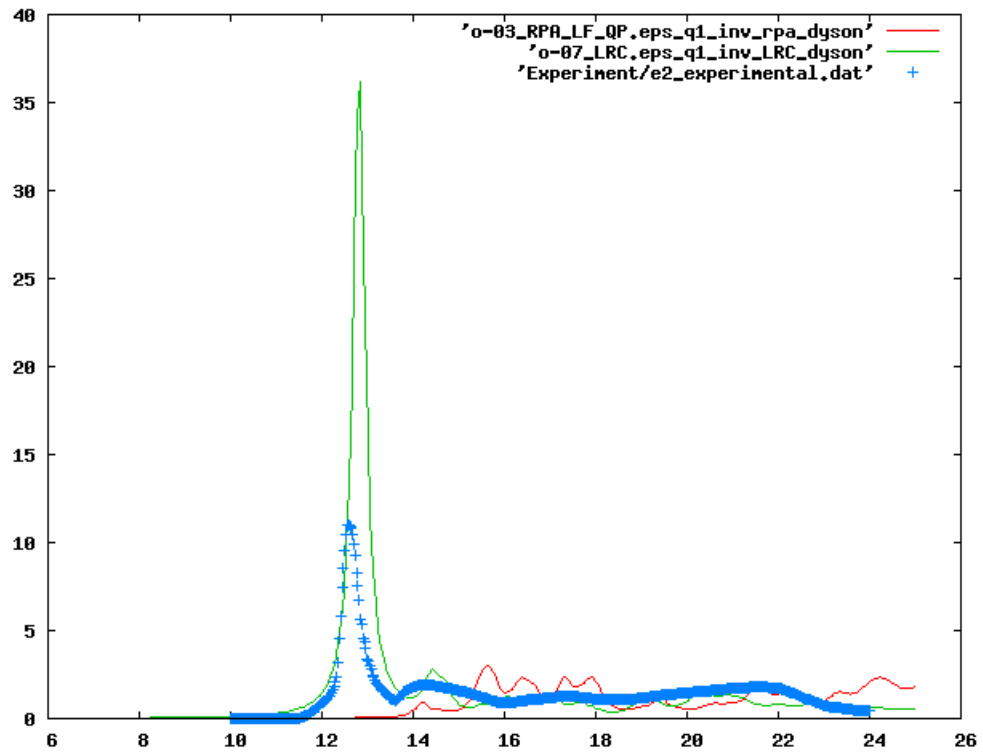


**[07] A Bethe-Salpeter based  $F_{xc}$ : [07\\_LRC](#)(yambo -o c -t l)**

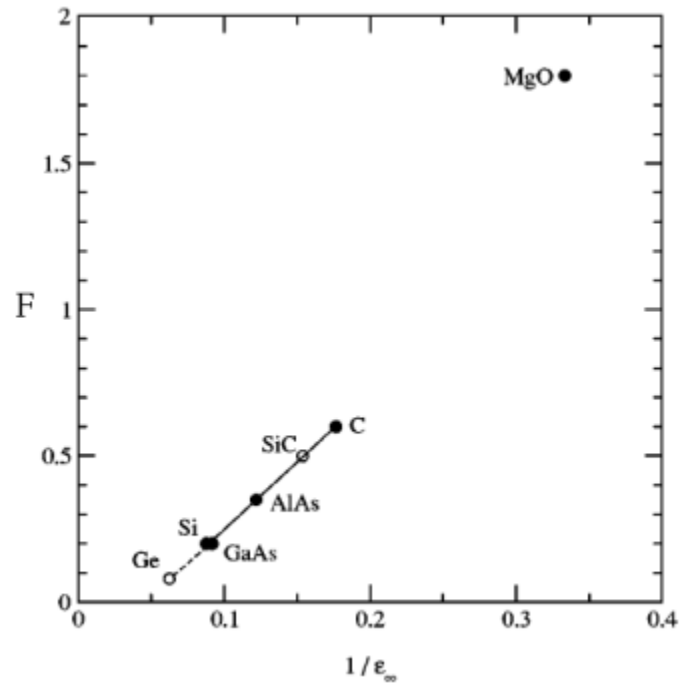
As the subject of this tutorial is TDDFT we might be a little bit disappointed at this stage as the only method that yields a reasonable absorption spectrum for LiF is based on MBPT. It is possible, however, to extract from the BS kernel a possible approximation for the xc-kernel, as described [here](#). This approach is efficient, but is far too complicated, and requires the prior computation of the BS kernel. An alternative possibility is to use a simple [Long Range Component](#) model, as introduced in [Reining](#). In this model, the yambo input file *Inputs/07\_LRC* describes a model where

$$f_{xc}(\mathbf{r}, \mathbf{r}') \equiv \frac{F_0}{|\mathbf{r} - \mathbf{r}'|}$$

with  $F_0 = LRC\_alpha = -8.7$ .



We see from the previous figure that the agreement with the BS calculation is not very good. Nevertheless this simple model captures the presence of an exciton and works quite well for a large number of simple semiconductors, as shown in [Botti](#):



For a more detailed and careful discussion of the LRC kernel, have a look at the [Hydrogen chain tutorial](#).

### Additional Exercises

1. Calculate the absorption spectra like in section [02-03](#) increasing the polarization RL size, the polarization bands to find the converged values.
2. Plot the EELS spectrum obtained in section [02-03](#) and check the effect of increasing the polarization bands. Do a resonant only calculation (using the -V option) to see that the EELS cannot be described using only the resonant part of the response function.
3. See the effect of using a denser BZ sampling grid running Abinit with, for example  

```
ngkpt2 6 6 6
```
4. Repeat the [BSE](#) calculation increasing the bands.
5. Calculate the [BSE](#) spectrum using a diagonal only interaction (see [here](#)).

### References

1. [LiF on wikipedia](#).
2. M. Rohlfing, S. Louie, Phys. Rev. Lett. **81**, 2312 (2000).
3. A. Marini, R. Del Sole, and A. Rubio, Phys. Rev. Lett., **91**, 256402 (2003), G. Adragna, R. Del Sole, and A. Marini, Phys. Rev. B **68**, 165108 (2003), F. Sottile, V. Olevano, and L. Reining, Phys. Rev. Lett. **91**, 056402 (2003).
4. Reining, V. Olevano, A. Rubio, and G. Onida, Phys. Rev. Lett. **88**, 066404 (2002).
5. S. Botti, Phys. Rev. B **69**, 155112 (2004).