

# Linear Response Time-Dependent Density Functional Theory

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## Problem Statement

- Compute the optical absorption spectrum of a  $2 \times 2$  unit cell of  $\alpha$  – *Tellurene* based on Linear response time dependent density functional theory.
- Objective is to perform the above the task with and without long-range exact-exchange correction.

$$\text{Absorption spectrum, } \alpha(\omega) = \sum_I \frac{f_I}{\omega - \omega_I},$$

$\omega_I$  is the I-th excitation energy, with  $|I\rangle$  is the I-th excited-state wave function with  $|0\rangle$  being the ground state





## Outline of the solution

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- Obtain the ground state information corresponding to  $\alpha$  – *Tellurence*.
- Use the ground state information to estimate the excited behavior using time dependent density functional theory without long-range exact-exchange correction.
- Similarly estimate the excited behavior employing linear response to TD-DFT with the long-range exact-exchange correction.



# Hands-on: Examine Input File

```

*start(on/off)
(how of it)                :
.false.                    : (lstart)
*end                        :

*linear-response TDFT
(how of it)                :
.false.                    : (lrtddft)
                           :
(whether to specify states)  :
.true.                     :

(long-range exchange scheme) :
.false.                    : (llcexchange) long-range correction for exchange
*molecular dynamics
(how of it)                :
0                           : (ifmd) = 0:non, 1:CG, 2:NVE-MD, 3:NVT-MD
(time step)                :
0.1d0  50                  : (dtmd, nstop) time step, total step (dtmd = 120.d0)

```

# Hands-on: Examine Input File

```
*start(on/off)
(how of it)      :
.false.          : (lstart)
*end              :

*linear-response TDFT
(how of it)      :
.false.          : (lrtdfft)

(long-range exchange scheme) :
.false.          : (llcexchange) long-range correction for exchange
```

- **lstart** determines if the simulation runs from  $t=0$  or subsequent steps.
- **lrtdfft** determines calculation of the Casida coupling matrix.
- **llcexchange** determines whether or not we want to incorporate long range correction for exchange functional.



# Hands-on: Examine Input File



**\*molecular dynamics**

(how of it)

0

(time step)

0.1d0 50

:

:

: (ifmd) = 0:non, 1:CG, 2:NVE-MD, 3:NVT-MD

:

: (dtmd, nstop) time step, total step (dtmd = 120.d0)

**time step:** Time step in [a.u.] for numerically integrating TDDFT equations

**how of it: 0** to run non adiabatic MD for 50 time steps at 300K



# Zero point energy calculation



- Check your current directory

*ls /yourWorkspace/QXMD-Repo/examples/06-LRTDDFT/Te*

- Ensure you have the following in the directory

*0.lrtddft=F 1.lrtddft=T 6.llcexchange=T*

- Go to 0.lrtddft=F to submit the zero point energy calculation which will be used subsequently to estimate the excited state information and compute the absorption spectrum.

- Before submitting, please ensure the following in your control folder

*ls 0.lrtddft=F/control*

*Opt.Te12-beta\_GGA.ion PAW filename input.config input.file*



# TDDFT calculation without long-range exact-exchange correction



- After estimating the ground state energies and information proceed to next step.
- Go to **1.lrtddft=T** folder in */yourWorkSpace/QXMD-Repo/examples/06-LRTDDFT/Te*
- Ensure you have following in your **control** folder  
*Opt.Te12-alpha\_GGA.ion Opt.Te12-beta\_GGA.ion PAW filename input.config input.file*
- Ensure you have **lstart** and **lrtddft** flags turned on. Here, **llexchange** will be turned off
- Also, make sure you have **band index of hole** as **31** and **band index of particle** as **38**.
- Copy the contents of *0.lrtddft=F/data* to *2.lrtddft=T/data*
- Submit the job





# TDDFT calculation without long-range exact-exchange correction



- After estimating the ground state energies and information proceed to next step.
- Go to **6.llexchange=T** folder in */yourWorkSpace/QXMD-Repo/examples/06-LRTDDFT/Te*
- Ensure you have following in your **control** folder  
*Opt.Te12-beta\_GGA.ion PAW filename input.config input.file*
- Ensure you have **lstart,lrtdfft, llexchange** flags turned on.
- Also, make sure you have **band index of hole** as **31** and **band index of particle** as **38**.
- Copy the contents of *0.lrtdfft=F/data* to *6.llexchange=T/data*
- Submit the job





# Analysis of absorption spectrum

- Corresponding to  $1.lrtddft=T$  and  $6.llexchange=T$  check for *Oscillator\_strength* folder.
- Edit the *oscillator\_strength.f90* file to locate the relative position of your corresponding *data* folder.
- If everything went fine, you should see an output file *Oscillator\_strength.dat*.
- The content of this file should look similar to following output.

```
# Optical absorption spectra represented as oscillator strengths
# Gaussian filter = 0.050000 [eV]
# E (eV) f_x f_y f_z ave
0.000000E+00 0.000000E+00 0.000000E+00 0.000000E+00 0.000000E+00
1.000000E-02 0.000000E+00 0.000000E+00 0.000000E+00 0.000000E+00
2.000000E-02 0.000000E+00 0.000000E+00 0.000000E+00 0.000000E+00
3.000000E-02 0.000000E+00 0.000000E+00 0.000000E+00 0.000000E+00
4.000000E-02 0.000000E+00 0.000000E+00 0.000000E+00 0.000000E+00
5.000000E-02 0.000000E+00 0.000000E+00 0.000000E+00 0.000000E+00
6.000000E-02 0.000000E+00 0.000000E+00 0.000000E+00 0.000000E+00
...
....
```



## Analysis of absorption spectrum (contd.)

- Once you have obtained *Oscillator\_strength.dat* with and without exact exchange correction, plot the average corresponding to 5<sup>th</sup> column w.r.t energies in the first column.

