Linear Response Time-Dependent Density Functional Theory
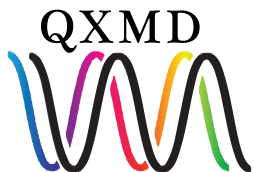
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Problem Statement

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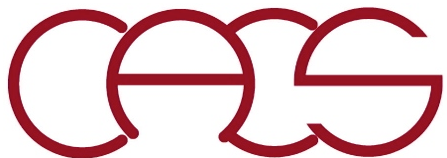
- Objective is to perform the above the task with and without long-range exact-exchange correction.

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

ω_I is the I-th excitation energy, with $|I\rangle$ is the I-th excited-state wave function with $|O\rangle$ *being the ground state*

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Outline of the solution

- **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.**

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```
*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)
```

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

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

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

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

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*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)

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

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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** *ic/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,lrtddft, 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.lrtddft=F/data to 6.llexchange=T/data*
- **Submit the job**

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Analysis of absorption spectrum

- **Corresponding to 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
 …
 ….
```

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- Once you have obtained *Oscillator_strength.dat.* with and without exact exchange correction, plot the average corresponding to 5th column w.r.t energies in the first column.