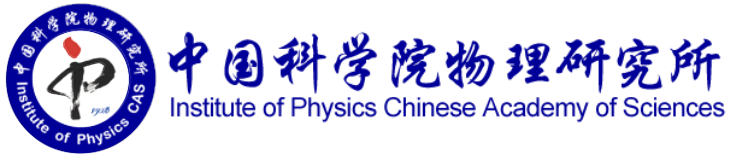


Time Dependent ab initio Package (TDAP) Introduction

Reporter: Daqiang Chen

Supervisor: Sheng Meng

December 2, 2020

Contents

Ab Initio Molecular Dynamics

Born-Oppenheimer approximation

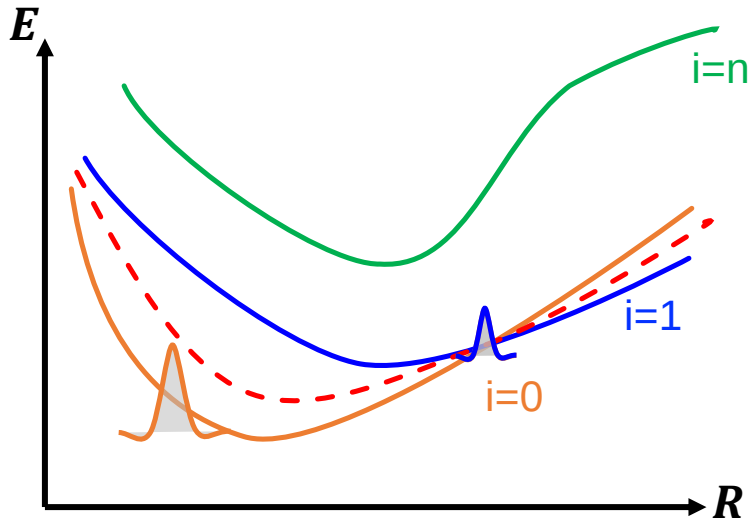
$$H = T_n + H_e = T_n + T_e + V_{ee} + V_{en}$$

$$H_e(\boldsymbol{r},\boldsymbol{R})\phi_i^a(\boldsymbol{r},\boldsymbol{R}) = E_i(\boldsymbol{R})\phi_i^a(\boldsymbol{r},\boldsymbol{R})$$

$$\Psi(\boldsymbol{R},\boldsymbol{r},t) = \sum_i \chi_i(\boldsymbol{R},t)\phi_i^a(\boldsymbol{r},\boldsymbol{R})$$

$$i\hbar\frac{d}{dt}\chi_i(\boldsymbol{R},t) = \{-\frac{\hbar}{2M}\sum_j(G_{ij} + 2\boldsymbol{F}_{ij}\cdot\nabla_{\boldsymbol{R}}) - \frac{\hbar}{2M}\nabla_{\boldsymbol{R}}^2 + E_i(\boldsymbol{R})\}\chi_i(\boldsymbol{R},t)$$

$$M\dot{\boldsymbol{R}} = -\nabla_R E_i(\boldsymbol{R}) = -\nabla_R\langle\phi_i^a|H_e|\phi_i^a\rangle$$



adiabatic potential energy surface

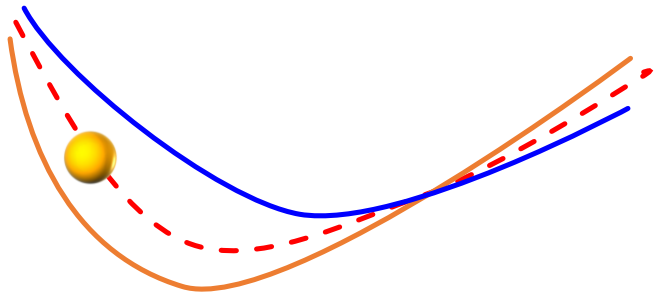
Born M, Huang K. Dynamical theory of crystal lattices[M]. Clarendon press, 1954.
Domcke W, Yarkony D, Köppel H. Conical intersections: electronic structure, dynamics & spectroscopy[M]. World Scientific, 2004.
Hunter G. Conditional probability amplitudes in wave mechanics[J]. International Journal of Quantum Chemistry, 1975, 9(2): 237-242.

Mixed quantum–classical dynamics

Ehrenfest MD

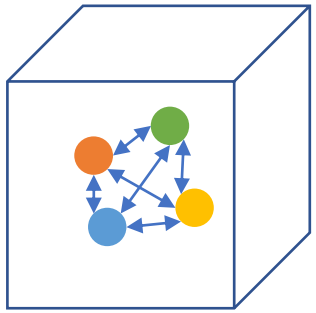
$$M\dot{\boldsymbol{R}} = -\nabla_R E_i(\boldsymbol{R}) = -\nabla_R \langle \Phi | H_e | \Phi \rangle$$

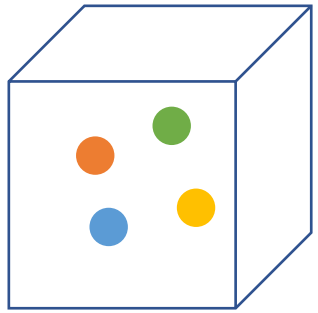
$$i\hbar \frac{\partial}{\partial t} \Phi(\boldsymbol{r}, \boldsymbol{R}, t) = H_e(\boldsymbol{r}, \boldsymbol{R}) \Phi(\boldsymbol{r}, \boldsymbol{R}, t)$$



SolutionMethod evolve

Real-time time dependent density functional theory (RT-TDDFT)





$$i\hbar \frac{\partial}{\partial t} \psi_i(\boldsymbol{r}, \boldsymbol{R}, t) = H_e^{KS}\left(n^{\mathrm{KS}}(\boldsymbol{r}, \mathrm{t})\right) \psi_i(\boldsymbol{r}, \boldsymbol{R}, t)$$

$$H_e^{KS}\left(n^{\mathrm{KS}}(\boldsymbol{r}, \mathrm{t})\right) = -\frac{\hat{p}^2}{2m_e} + V^{KS}\left(n^{\mathrm{KS}}(\boldsymbol{r}, \mathrm{t})\right)$$

$$V^{KS}(n^{KS}) = V^{en}\left(n^{\mathrm{KS}}, \boldsymbol{R}\right) + V^{H}\left(n^{\mathrm{KS}}\right) + V_0^{XC}(n^{\mathrm{KS}})$$

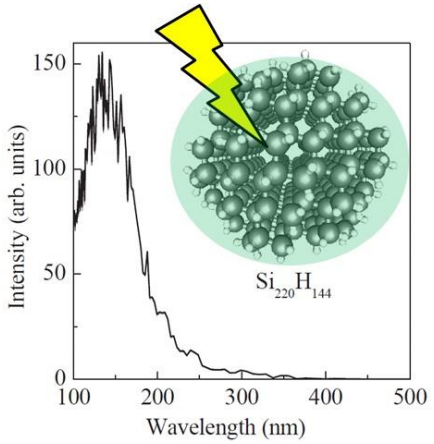
$$n(r,t) = \Phi^*(\boldsymbol{r}, \boldsymbol{R}, t)\ \Phi(\boldsymbol{r}, \boldsymbol{R}, t) \quad \Longleftrightarrow \quad n^{KS}(\boldsymbol{r}, \mathrm{t}) = \sum_i \ \psi_i^*(\boldsymbol{r}, \boldsymbol{R}, t) \psi_i(\boldsymbol{r}, \boldsymbol{R}, t)$$

XC.functional GGA/LDA

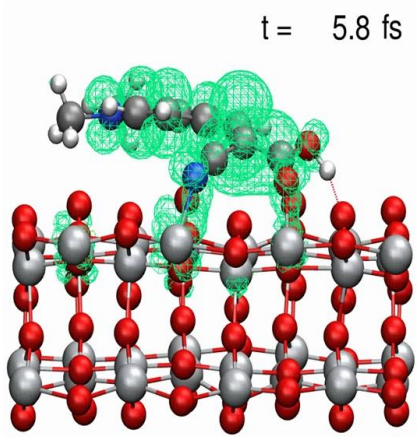
Craig I R et al. The Journal of chemical physics, 2004, 121(8): 3368-3373.
You P et al. Electronic Structure, 2019, 1(4): 044005.

Time Dependent ab initio Package (TDAP)

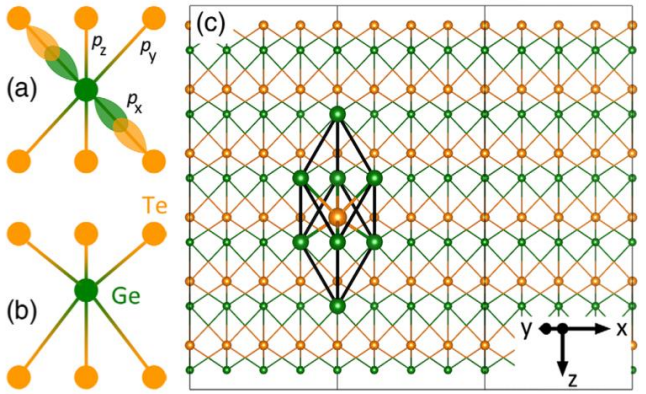
TDAP is a real-time ab initio approach for nonadiabatic excited state molecular dynamic simulations, which follows the Ehrenfest dynamics & RT-TDDFT.



Photoexcitation of a Si cluster



Ultrafast electron injection in solar cells



Ultrafast laser-induced phase transition

J. Ren, et al. Molecular Physics 108, 1829 (2010).
L.Y. Wei, et al. J. Phys. Chem. C 121, 5905 (2017).
Chen N K,, et al.. Physical review letters, 2018, 120(18): 185701.

Time Dependent ab initio Package (TDAP)

Some software based on rt-TDDFT and their main features.

	TDAP	**TDAPW**	OCTOPUS	ELK	GPAW	YAMBO	NWCHEM	SALMON
Dipole Field	√	√	√	●	√	●	√	√
Vector Field	√	√	√	√	×	√	×	√
Berry Phase	√	×	×	√	×	√	×	×
MD	√	√	√	×	●	×	●	●
PIMD	√	√	×	×	×	×	×	×
TypeBasis	NAO[2]	PW[3]	RSG[3]	PW[4]	RSG/NAO	RSG	Gaussian	RSG[3]
NumBasis/N_a	10	10^3	10^4	10^5	10^4/10	10^4	10^2	10^4
TimeStep/as	50	50	1	1	10	1	2.5	1

[√: Realized] [●: Realized but problematic] [×: Not realized]

You P, et al. Wiley Interdisciplinary Reviews: Computational Molecular Science, 2020: e1492.

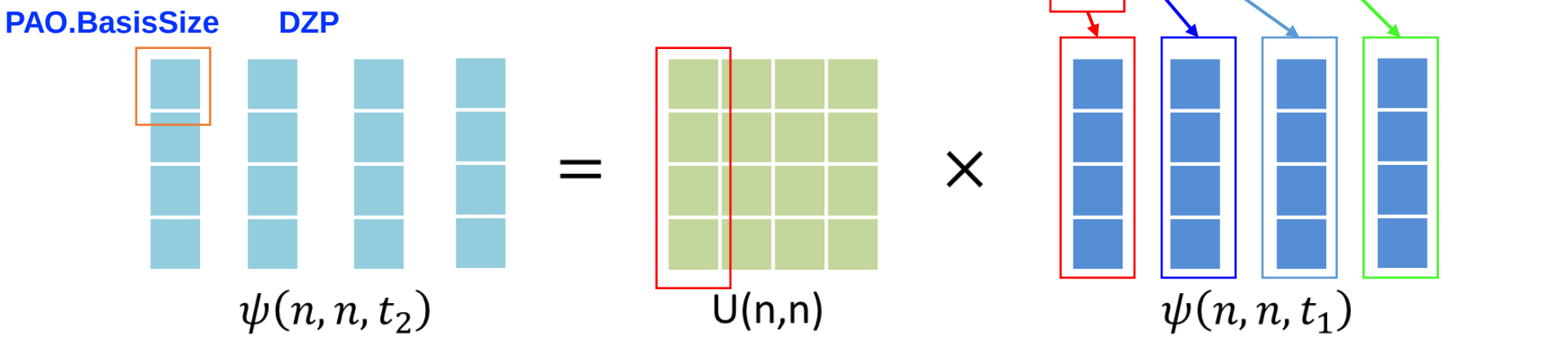
Numerical time propagation

Local atomic basis sets ϕ_μ and real-time propagation

$$\psi_i(t_2) = \hat{U}(t_2, t_1)\psi_i(t_1)$$

$$\hat{U}(t_2, t_1) \approx \mathrm{e}^{-i\hat{H}(\mathrm{t}_1+\frac{\Delta t}{2})} \approx \frac{1-iS^{-1}H\Delta t/2}{1+iS^{-1}H\Delta t/2}\psi_i(t_1)$$

$$\psi_i = \sum_\mu c_\mu^i \phi_\mu \;;\; H_{\mu v} = \langle \phi_\mu | \hat{H} | \phi_v \rangle \;;\; S_{\mu v} = \langle \phi_\mu | \phi_v \rangle$$



Lian C et al., Advanced Theory and Simulations, 2018, 1(8): 1800055.

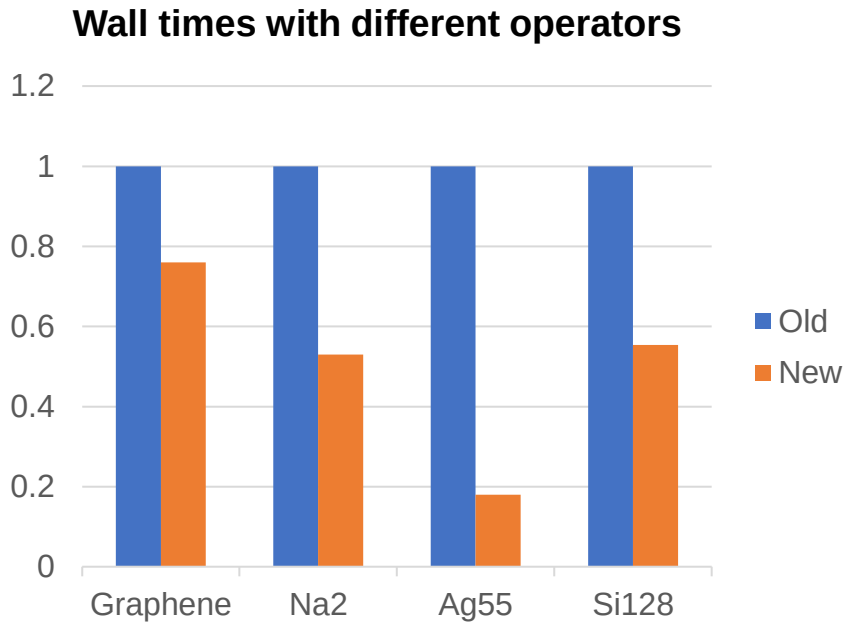
Update: New Evolution Operator

By reducing the number of communications, the program is accelerated by 2-5 times.

$$\widehat{U}(t_2, t_1) = \frac{1-iS^{-1}H\Delta t/2}{1+iS^{-1}H\Delta t/2}\psi_i(t_1)$$

	Operator	No. comm.
Old	$C(t+dt) = \frac{1-iS^{-1}Hdt/2}{1+iS^{-1}Hdt/2}C(t)$	5
New	$C(t+dt) = \frac{S-iHdt/2}{S+iHdt/2}C(t)$	3

TD.NewInv T



Self-consistency in static DFT and TDDFT

Static DFT:

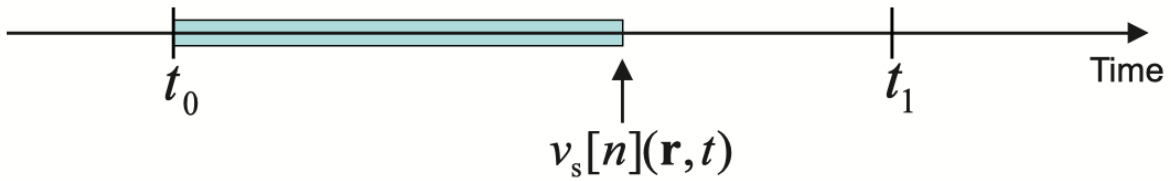
$$\left[-\frac{\nabla^2}{2}+v_s^0[n_0](\mathbf{r})\right]\varphi_j(\mathbf{r})=\varepsilon_j\varphi_j(\mathbf{r}) \longrightarrow \sum_j\left|\varphi_j(\mathbf{r})\right|^2=n_0(\mathbf{r})$$

Density $n_0(\mathbf{r}')$ over all space

TDDFT:

$$\left[-\frac{\nabla^2}{2}+v_s[n](\mathbf{r},t)\right]\varphi_j(\mathbf{r},t)=i\frac{\partial}{\partial t}\varphi_j(\mathbf{r},t) \longrightarrow \sum_j\left|\varphi_j(\mathbf{r},t)\right|^2=n(\mathbf{r},t)$$

Density $n(\mathbf{r}',t')$ over all space and times $t'\le t$



Ullrich C A. Time-dependent density-functional theory: concepts and applications[M]. OUP Oxford, 2011.

RT-TDDFT in electromagnetic

Velocity gauge & Length gauge

$$\boldsymbol{H} = \frac{1}{2m}\left(\boldsymbol{P} + \frac{e\boldsymbol{A}}{c}\right)^2 + V + \frac{e\hbar}{2mc}\boldsymbol{\sigma}\cdot(\boldsymbol{\nabla}\times\boldsymbol{A}) - e\Phi$$

Dipole approximation

$$\frac{e\hbar}{2mc}\boldsymbol{\sigma}\cdot(\boldsymbol{\nabla}\times\boldsymbol{A}) = \boldsymbol{0},\ \boldsymbol{E}(\boldsymbol{r},t) = \boldsymbol{E}(\boldsymbol{r},t)$$

Maxwell's equations

$$\boldsymbol{B} = \boldsymbol{\nabla}\times\boldsymbol{A}$$

$$\boldsymbol{E} = -\boldsymbol{\nabla}\Phi - \frac{1}{c}\frac{\partial\boldsymbol{A}}{\partial t}$$

Velocity gauge

$$\boldsymbol{E} = -\frac{1}{c}\frac{\partial\boldsymbol{A}}{\partial t}, \Phi = 0$$

$$\boldsymbol{A} = -c\int\boldsymbol{E}\,dt$$

$$\boldsymbol{H} = \frac{1}{2m}\left(\boldsymbol{P} + \frac{e\boldsymbol{A}}{c}\right)^2 + V$$

TD.GaugeField

Length gauge

$$\boldsymbol{E} = -\boldsymbol{\nabla}\Phi, \boldsymbol{A} = 0$$

$$\Phi = -\boldsymbol{E}\boldsymbol{r}$$

$$\boldsymbol{H} = \frac{\boldsymbol{P}^2}{2m} + V + e\boldsymbol{E}\boldsymbol{r}$$

ExternalElectricField

Ernotte G, et al. Physical Review B, 2018, 98(23): 235202.
Lian C, et al. Advanced Theory and Simulations, 2018, 1(8): 1800055

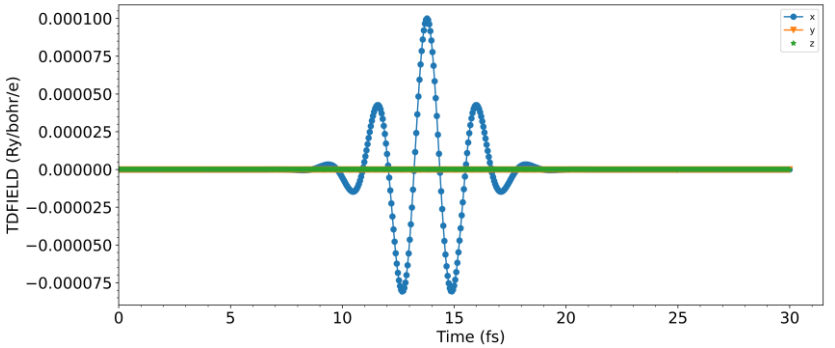
The shape of electric field

Gaussian form wavepackage

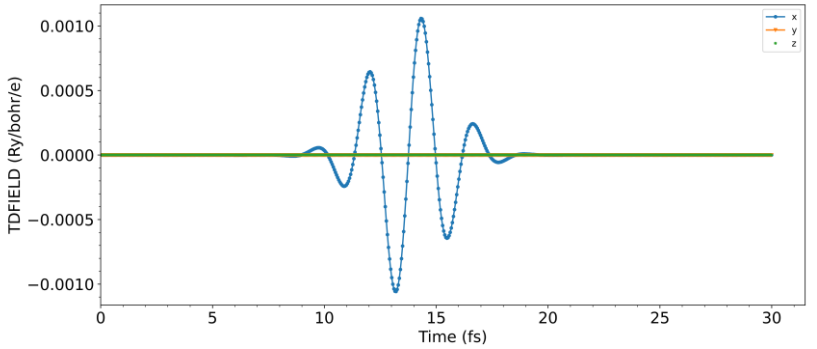
$$\boldsymbol{E}(t) = \boldsymbol{E_0}\cos(2\pi f t)\exp[-\frac{(t-t_0)^2}{2\sigma^2}]$$

- $\boldsymbol{E_0}$ **TD.GaugeField/ExternalElectricField**
- f **TD.LightFrequency 0.44 fs^{-1}**
- t_0 **TD.LightInitialTime 13.78 fs**
- σ **TD.LightTimeScale 2.44 fs**

ExternalElectricField 0.0001 0 0



TD.GaugeField 0.0001 0 0

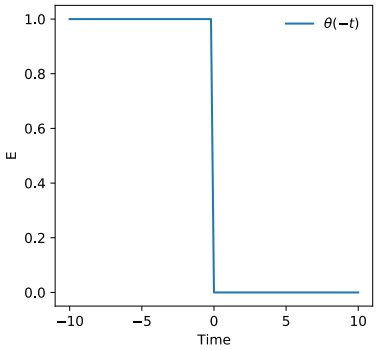


The shape of electric field

$\theta(-t)$

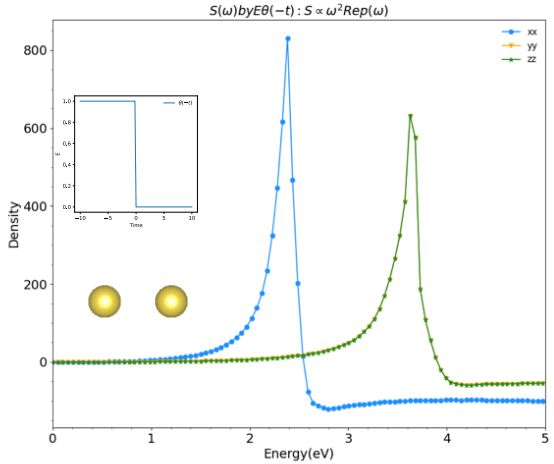
$$\boldsymbol{E}(t) = \boldsymbol{E_0}\theta(-t),$$

- $\theta(-t)$ **TD.DeltaElectricField T**
- $\boldsymbol{E_0}$ **TD.GaugeField/ExternalElectricField**



$$(\boldsymbol{H}_0 + e\boldsymbol{E}\boldsymbol{r})\phi_i(t_0) = \epsilon_i^{\boldsymbol{E}}\phi_i^{\boldsymbol{E}}(t_0)$$
$$\psi_i(t) = U(\boldsymbol{H}_0, t, t_0)\phi_i^{\boldsymbol{E}}(t_0)$$

RT-TDDFT($\theta(-t)$,tdap)



Optical absorption strength

$$\alpha_{\mu v}(\omega) = \frac{i\omega p_\mu(\omega)}{E_v^0}, S_{\mu\mu}(\omega) = \frac{2m\omega^2}{\hbar^2 e^2}\frac{\mathrm{Re}\{p_\mu(\omega)\}}{\pi E_\mu^0}$$

The shape of electric field

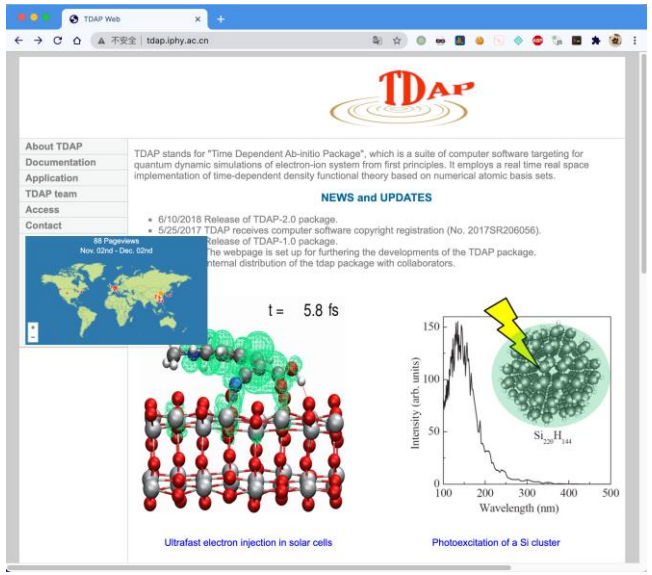
Circularly polarized light or any shape

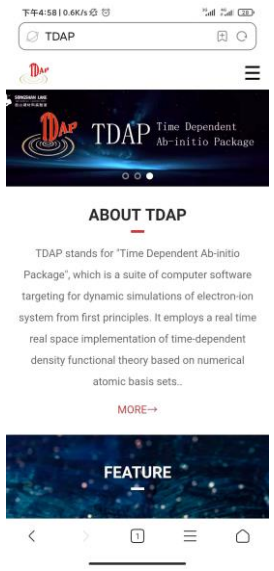
$$\boldsymbol{E}(t) = \boldsymbol{E}_{0i}\boldsymbol{F}_i(t), i = x, y, z$$

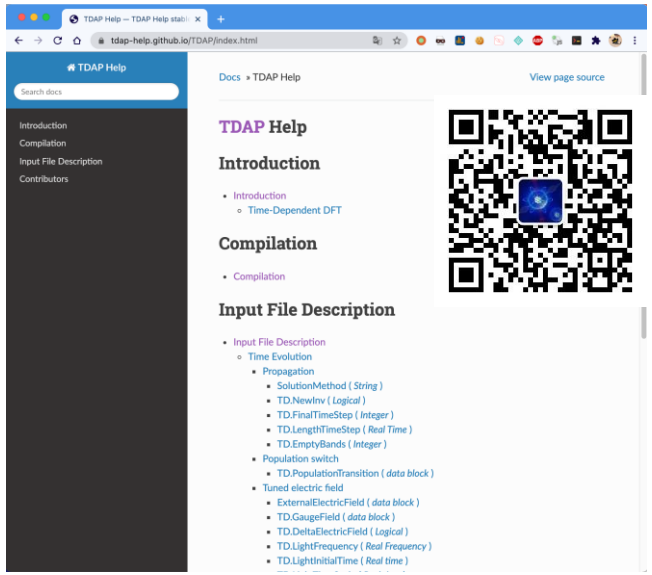
- $\boldsymbol{E_0}$ **TD.GaugeField/ExternalElectricField**
- $\boldsymbol{F}$ **TD.EnvFromFile**

Websites

- Home http://tdap.iphy.ac.cn/
- Home(building) http://tdap.sslab.org.cn/
- Document(building) https://tdap-help.github.io/TDAP/index.html
- Discussion https://github.com/TDAP-help/Discussion_TDAP

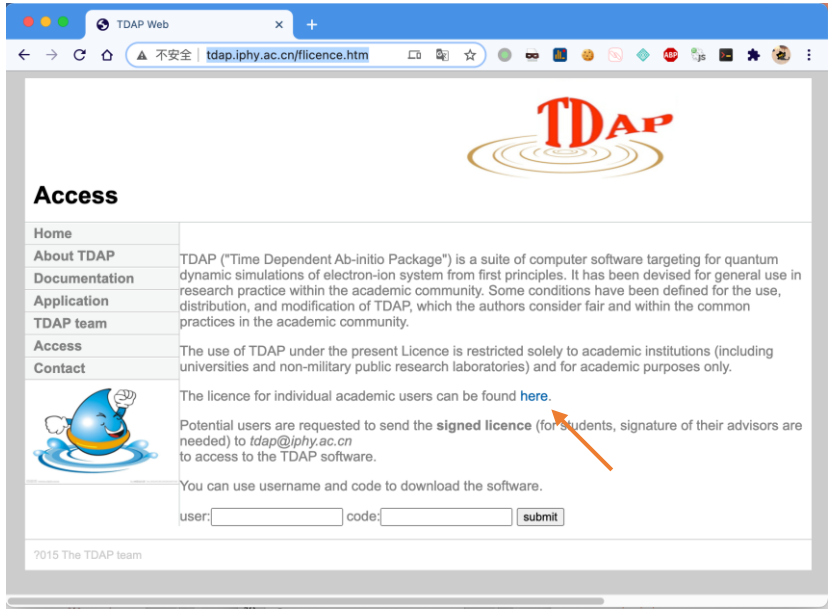


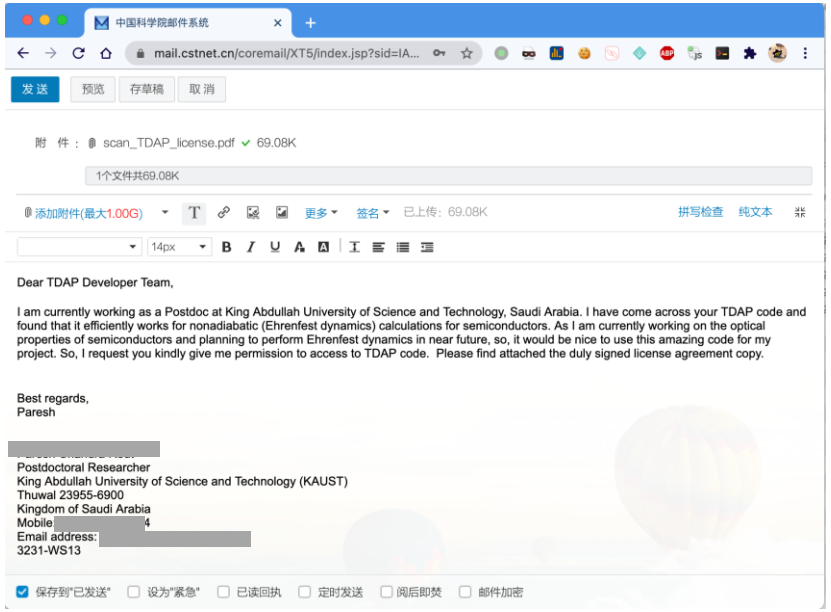




Access

1. Download license file from tdap.iphy.ac.cn
2. **Print** the license and sign it
3. **Scan** the license and send it to tdap@iphy.ac.cn with the following information：
   name, country, address, organization, contact, purpose





Compilation steps

Steps 1

Serial and parallel compilers

- Serial: gcc and gfortran
- Parallel:
  - mvapich2-2.3.1
  - openmpi-1.10.3

Steps 2

Linear Algebra Library

- √ Netlib:
  - BLAS
  - LAPACK
  - ScaLAPACK
- × ~~MKL~~

Steps 3

TDAP

```
cd Obj
../Src/obj_setup.sh
../Src/configure --enable-mpi
vi arch.make
make
```

https://tdap-help.github.io/TDAP/
https://cndaqiang.github.io//2018/09/12/gun-openmpi-siesta/
https://cndaqiang.github.io/2019/06/08/mac-code/

How to run Ehrenfest MD (Hands_on_1)

Input file (parameter, structure, K-mesh): input.fdf

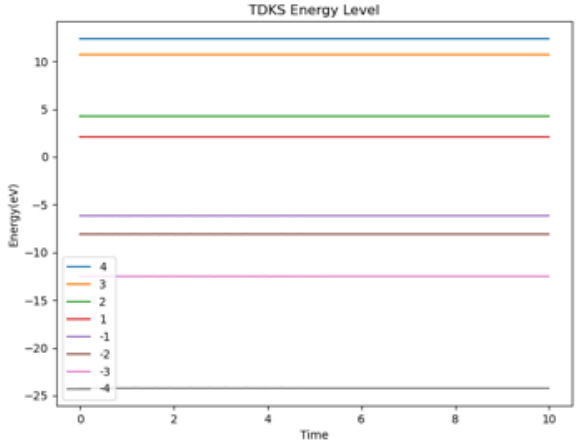
```
#DFT
XC.functional GGA
XC.authors  PBE
SCFMustConverge T

#MD
SolutionMethod      evolve
MD.TypeOfRun        verlet
MD.FinalTimeStep      500
TD.FinalTimeStep    500
MD.LengthTimeStep     0.00 fs
TD.LengthTimeStep   0.01 fs
MD.InitialTemperature  300 k

%block kgrid_Monkhorst_Pack
1 0 0 0.0
0 1 0 0.0
0 0 1 0.0
%endblock kgrid_Monkhorst_Pack
```

```
AtomicCoordinatesFormat  Fractional
LatticeConstant  1.0  Ang

NumberOfAtoms    3
NumberOfSpecies  2

%block LatticeVectors
      10.0       0.0000000000       0.0000000000
      0.0        10.0               0.0000000000
      0.00       0.00               10.0
%endblock LatticeVectors

%block ChemicalSpeciesLabel
  1    1    H
  2    8    O
%endblock ChemicalSpeciesLabel

%block AtomicCoordinatesAndAtomicSpecies
   0.44820475    0.41355314    0.41547532  1      1  H
   0.57091037    0.41168595    0.50808773  1      2  H
   0.47461484    0.41168595    0.50808773  2      3  O
%endblock AtomicCoordinatesAndAtomicSpecies
```

Pseudopotentials: Element.psf

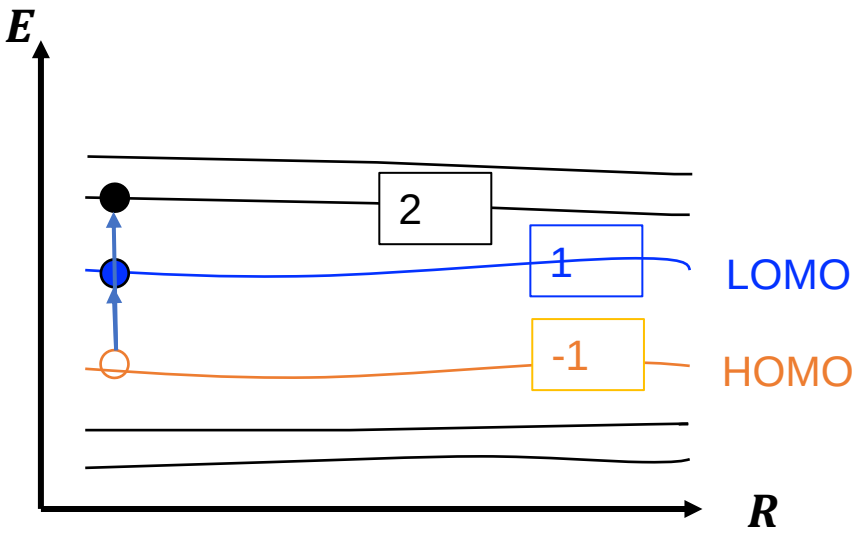
https://siesta.icmab.es/SIESTA_MATERIAL/Databases/Pseudopotentials/periodictable-intro.html

```
[cndaqiang@mommint Hands_on_1]$ls
H.psf  input.fdf  O.psf  result
[cndaqiang@mommint Hands_on_1]$mpirun -np 10 tdap < input.fdf | tee result
Running on 10 processors
There are 1 iamges
Siesta Version:                                  tdap-2.2.3, based on siesta-3.2-pl-5
Architecture  : x86_64-unknown-linux-gnu--unknown
Compiler flags: mpif90 -g -O2 -ffree-line-length-none
PARALLEL version

* Running on   10 nodes in parallel
>> Start of run:   2-DEC-2020  20:17:36

>> End of run:   2-DEC-2020  20:18:44
[cndaqiang@mommint Hands_on_1]$../getenergy.sh
[cndaqiang@mommint Hands_on_1]$../plot.py
read from ./energy.dat
[cndaq
```



The way to excite electrons

- **Ultrafast laser radiation**
  - **Velocity gauge & Length gauge**
- **Electron-phonon coupling**
  - **Change the initial structure and speed of atoms**
- **Population switch**

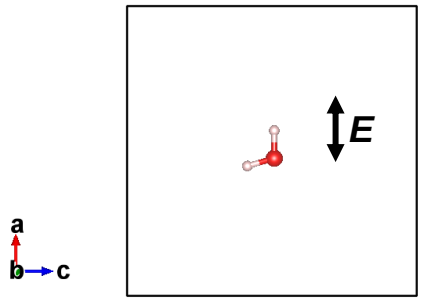


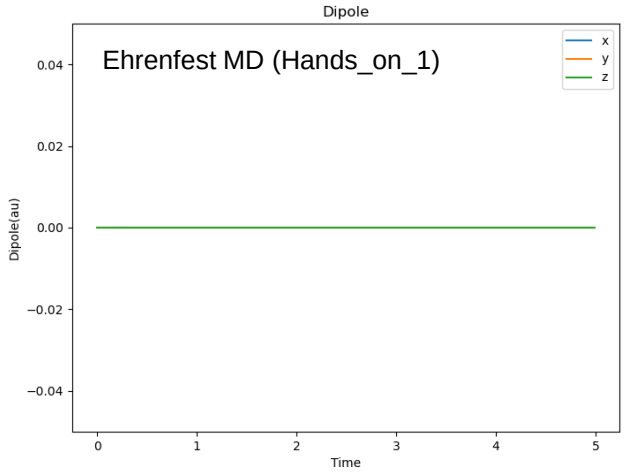

```
%block TD.PopulationTransition
-1 2 0.5
-1 1 0.5
%endblock TD.PopulationTransition
```

Ultrafast laser radiation $\theta(-t)$ (Hands_on_2)

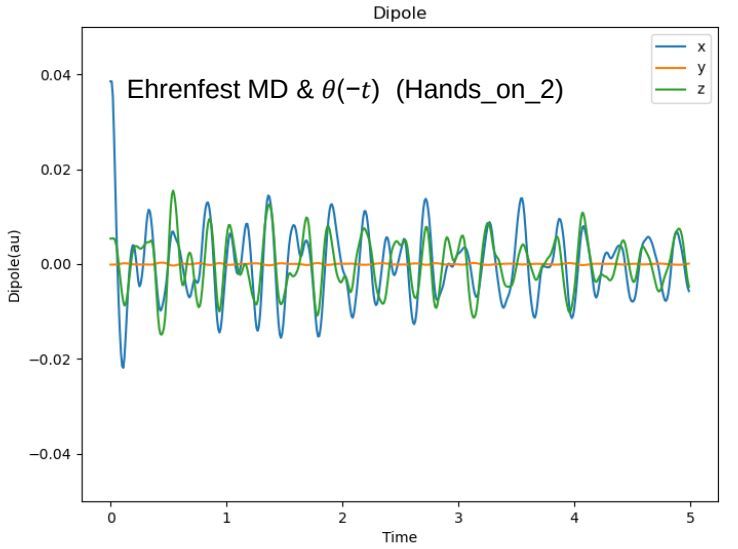
input.fdf

```
TD.DeltaElectricField T
%block ExternalElectricField
0.001 0.0 0.0 Ry/Bohr/e
%endblock ExternalElectricField
```





$\theta(-t)$ Field



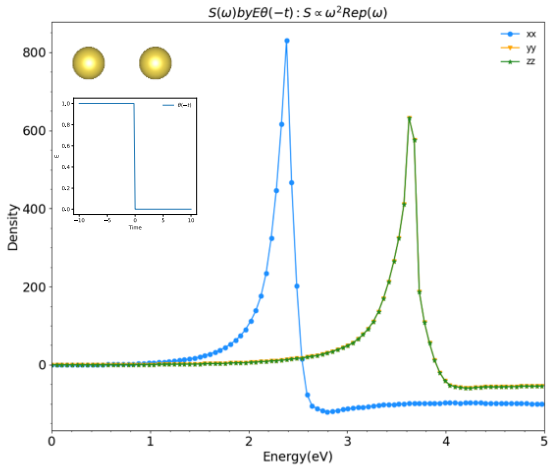
Optical absorption strength

$$\alpha_{\mu\nu}(\omega) = \frac{i\omega p_\mu(\omega)}{E_v^0}, S_{\mu\mu}(\omega) = \frac{2m\omega^2}{\hbar^2 e^2}\frac{\mathrm{Re}\{p_\mu(\omega)\}}{\pi E_\mu^0}$$

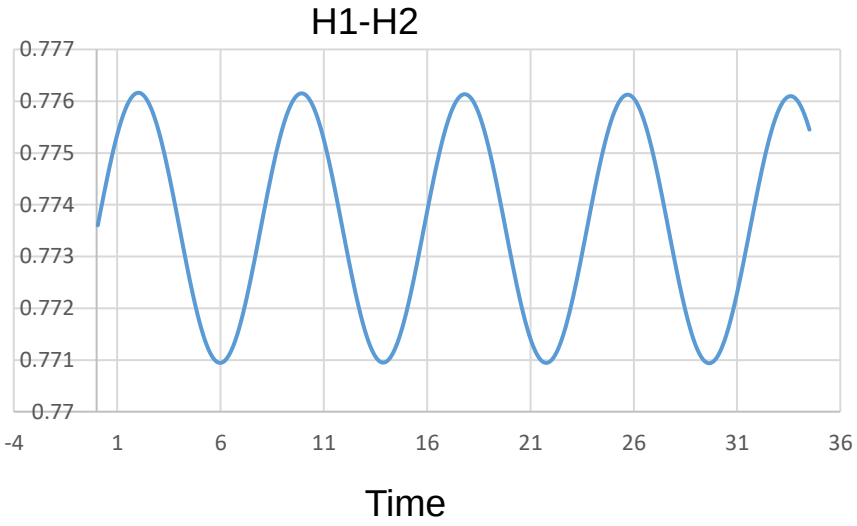
Spectrum

Absorption spectrum of Na2 by FFT[Dipole]

RT-TDDFT($\theta(-t)$,tdap)



Vibration spectrum of H2 @UCAS Yunfei Bai by FFT[bond distance]



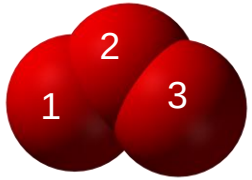
experiment 4155cm^{-1}

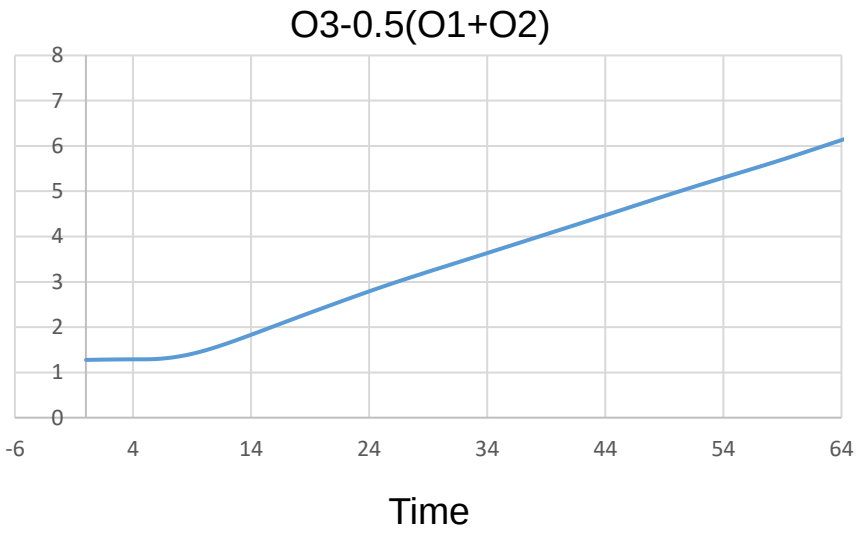
simulation 4219cm^{-1}

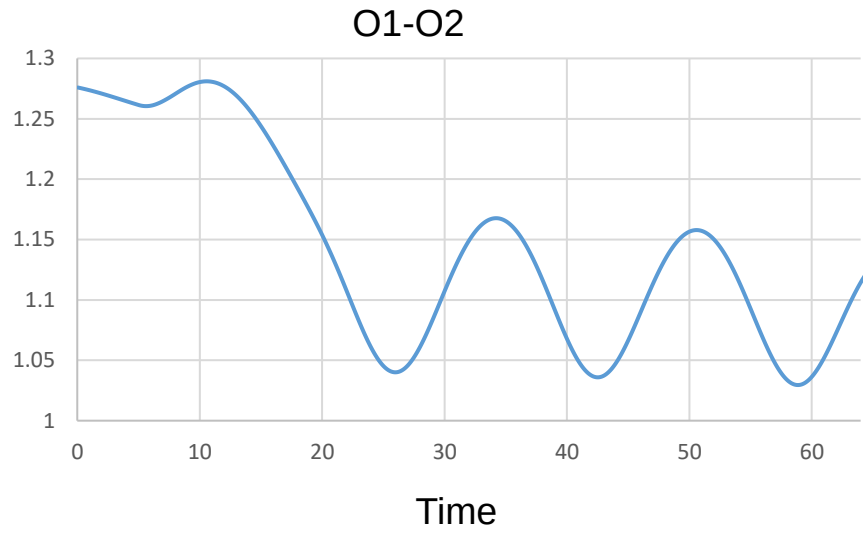
Population switch @UCAS Yunfei Bai

Ozone decomposition

```
%block TD.PopulationTransition
-1 2 1
%endblock TD.PopulationTransition
```







Hands on

Band projection

TD.WriteDMOfSelectiveOrbitals T

TD.PartialDMBand

TD.PartialDMSumOrbitals

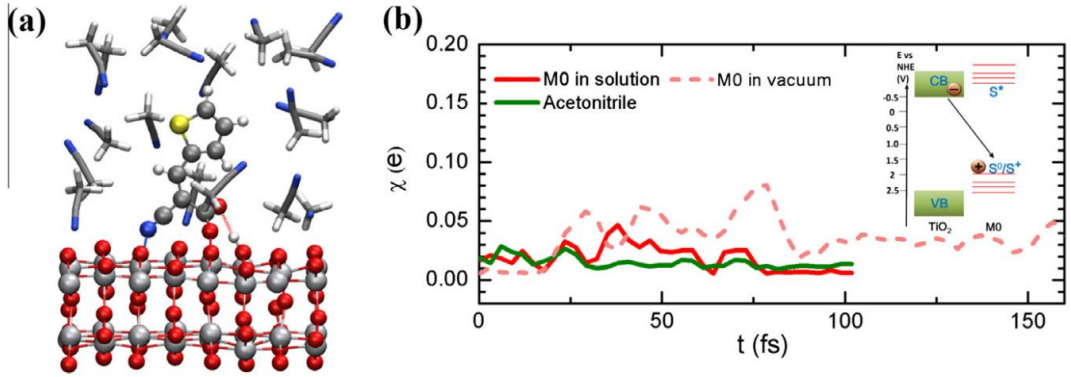


Fig. 9. (a) Schematic diagram of cyanoacrylic ligand M0 dye adsorbed onto a 1 × 4 anatase slab, surrounded by acetonitrile solvent molecules. Molecules presented as sticks are acetonitrile. Color scheme: Ti – light gray, O – red, C – dark gray, N – blue, S – gold, H – white. (b) Photo-excited electron distribution on the M0 molecule (red) and solvent molecules (green) after injected into the TiO_2 CB at the organic dye/TiO_2/electrolyte heterointerface. Solid lines indicate results in solvent, while dashed lines correspond to results in vacuum. The inset shows the schematic diagram for recombination between the photo-excited electrons in TiO_2 conduction band and the holes in M0 dye. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

Time

Ma W, Zhang J, Yan L, et al. Recent progresses in real-time local-basis implementation of time dependent density functional theory for electron–nucleus dynamics[J]. Computational Materials Science, 2016, 112: 478-486.

Others

Many TDAP

mpirun -np $NP tdap -ni $IMAGE -i input.fdf

```
[cndaqiang@mommint ECD.in.27]$ls
input_0  input_1  input_2
[cndaqiang@mommint ECD.in.27]$for i in $(ls); do echo $i: $(ls $i); done
input_0: H.psf input.fdf O.psf
input_1: H.psf input.fdf O.psf
input_2: H.psf input.fdf O.psf
[cndaqiang@mommint ECD.in.27]$mpirun -np 30 tdap -ni 3 -i input.fdf
Running on 30 processors
There are 3 iamges
Change dir to input_N
```

Restart

4.2 Restart a TDDFT-MD calculation

To restart a calculation, the wavefunction and the atomic positions are needed. The atomic positions can be obtained in the file systemLabel.XV, and the wavefunction should be output using the following tag:

TD.WriteWaveFunctionStep (*integer*): If TD.WriteWaveFunctionStep = x, it means to output the wavefunction every x step to the file systemLabel*step*.TDWFSX. *step* is the certain step at which the wavefunction is output.

Default value: `1000`

TD.ReadWaveFunction (*logical*): Whether to read wavefunction from the file systemLabel.TDWFSX. Note: the systemLabel is not followed by *step*.

Default value: `false`

For instance: :

After a calculation,

```
mkdir restartdir
cp H.psf  O.psf  siesta.EIG  siesta.PAR  input.fdf  structure.fdf  siesta.XV \
siesta.VERLET_RESTART siesta.TDWFSX  restartdir/
```

Add this in restartdir/input.fdf

```
TD.ReadWaveFunction              T
MD.UsesaveXV T
```

Ma W, Zhang J, Yan L, et al. Recent progresses in real-time local-basis implementation of time dependent density functional theory for electron–nucleus dynamics[J]. Computational Materials Science, 2016, 112: 478-486.

Conclusions

- TDAP is an effective nonadiabatic excited state molecular dynamic computational package.
  - Photoexcitation
  - Ultrafast electron injection
  - Ultrafast laser-induced phase transition
  - Absorption spectrum
  - Laser-induced decomposition
  - …

- Home http://tdap.iphy.ac.cn/
- Home(building) http://tdap.sslab.org.cn/
- Document(building) https://tdap-help.github.io/TDAP/index.html
- Discussion https://github.com/TDAP-help/Discussion_TDAP

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Peiwei You

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Zhengwei Nie

…