Real-time real-space time-dependent density-functional theory and beyond: a demonstration of the Quantum Dissipative Dynamics package

Jordan HERAUD, Phuong Mai DINH, Tingting GU, Eric SURAUD, Marc VINCENDON
Laboratoire de Physique Théorique, Toulouse, France

Paul-Gerhard REINHARD
Institute for Theoretical Physics, Erlangen, Germany

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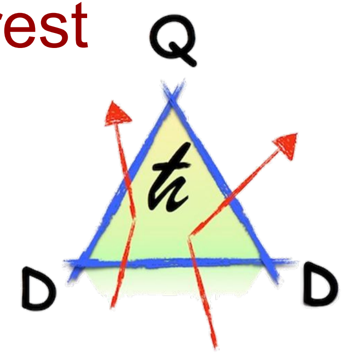
Quantum Dissipative Dynamics: 3 points of interest



1) real-time real-space TDDFT with absorbing boundary condition

Kohn-Sham approach: effective 1-body problem (non-interacting electrons in one effective potential)

$$\hat{U}_{\mathrm{KS}}[\rho(\mathbf{r})] = \hat{U}_{\mathrm{H}}[\rho(\mathbf{r})] + \hat{U}_{\mathrm{xc}}[\rho(\mathbf{r})] \quad \text{with} \quad \hat{U}_{\mathrm{H}}[\rho(\mathbf{r})] = \int d^3\mathbf{r}' \frac{\rho(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}$$

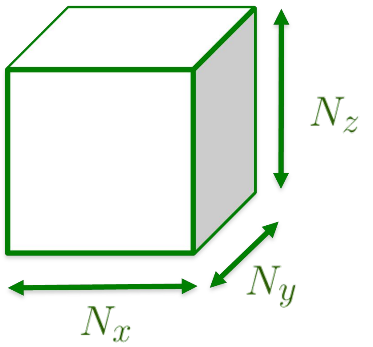
Perdew-Wang functional: $\hat{U}_{\mathrm{xc}}^{\mathrm{LDA}}[\rho(\mathbf{r})] = \hat{U}_{\mathrm{xc}}^{\mathrm{PW}}[\rho(\mathbf{r})]$

TDLDA (adiabatic): $$\left(-\frac{\hat{\mathbf{p}}^2}{2m_e} + \hat{U}_{\mathrm{KS}}[\rho(\mathbf{r},t)] + \hat{V}_{\mathrm{ext}}\right)\varphi_n(\mathbf{r},t) = i\hbar\partial_t\varphi_n(\mathbf{r},t)$$

$$= \hat{V}_{\mathrm{PsP}} + \hat{V}_{\mathrm{las}}$$ coupling with laser field

coupling with ions = nuclei + core electrons depends on position of ions

Real-space on a 3D grid



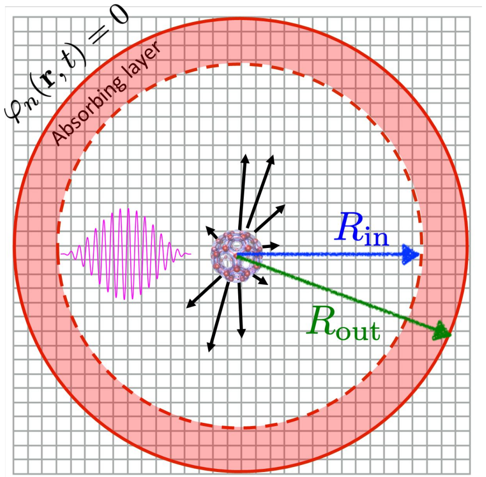
64^3
72^3
96^3
128^3

$$x_i = idx - x_0 \quad , \quad i = 1, \ldots, N_x$$
$$y_j = jdy - y_0 \quad , \quad j = 1, \ldots, N_y$$
$$z_k = kdz - z_0 \quad , \quad k = 1, \ldots, N_z$$

$$\varphi_n(\mathbf{r}, t) := \varphi_n(x_i, y_j, z_k, t)$$

Critical parameter:
size of the numerical grid
(N_x N_y N_z)

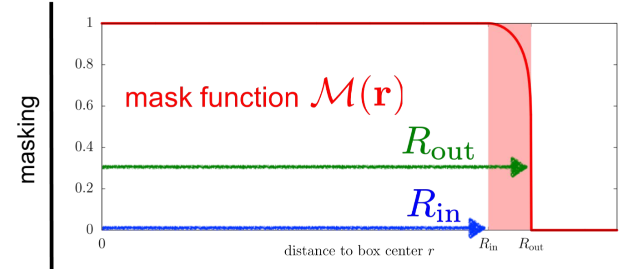
Treatment of electronic emission



Absorbing boundary conditions (masking)
⇒ Avoid reflections on box edges

Consequence: $|\varphi_n(\mathbf{r}, t)|^2 < 1$

$$\varphi_n(\mathbf{r}, t) \xrightarrow{\text{time propag.}} \phi_n(\mathbf{r}) = \mathcal{T} e^{-i\hbar \int_t^{t+dt} dt' \hat{U}_{\mathrm{KS}}(t')} \varphi_n(\mathbf{r}, t)$$



$$\varphi_n(\mathbf{r}, t + dt) = \mathcal{M}(\mathbf{r})\, \phi_n(\mathbf{r})$$

Real-time propagation …

Explicit real-time propagation (not in frequency domain)

Solve $i\hbar\partial_t\varphi_n(\mathbf{r},t) = \hat{U}_{\mathrm{KS}}\ \varphi_n(\mathbf{r},t)$ by time discretisation

$$\varphi_n(\mathbf{r},t+dt) = \mathcal{T}\exp\left(-i\hbar\int_t^{t+dt} dt'\hat{U}_{\mathrm{KS}}(t')\right)\varphi_n(\mathbf{r},t)$$

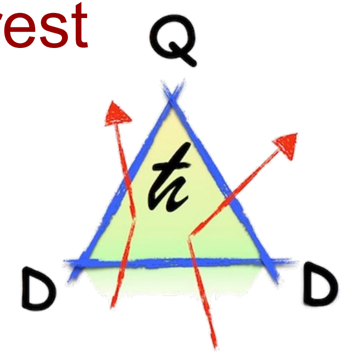
time propagator

$$= \exp\left[-i\hbar\frac{dt}{2}\hat{V}(t+dt)\right]\ \exp\left[-i\hbar\,dt\,\hat{T}\right]\ \exp\left[-i\hbar\frac{dt}{2}\hat{V}(t)\right]\ \varphi_n(\mathbf{r},t)$$

TV splitting

Wopperer, Dinh, Reinhard, Suraud, Phys. Rep. 562 (2015) 1
Dinh, Vincendon, Coppens, Suraud, Reinhard, Computer Phys. Comm. 270 (2022) 108155

Quantum Dissipative Dynamics: 3 points of interest



2) Ehrenfest dynamics of the ions

$$M_I \frac{d^2}{dt^2}\mathbf{R}_I = -\nabla_{\mathbf{R}_I} E_I$$

$$E_I = \frac{1}{2}\sum_{I\neq J} \frac{Z_I Z_J}{|\mathbf{R}_I - \mathbf{R}_J|} + E_{\mathrm{PsP}}\left(\rho, \{\mathbf{R}_I\}\right) + E_{\mathrm{ext}}(\{\mathbf{R}_I\}, t)$$

Non-adiabatic coupling of ions and valence electrons

Quantum Dissipative Dynamics: 3 points of interest

3) Extension of the dynamic: aims to develop/study dissipative methods

→ https://www.lpt.ups-tlse.fr/qdd/index.php?article6/papers

Relaxation Time Approximation (RTA): exponential relaxation to instantaneous equilibrium state

P.-G. Reinhard, E. Suraud, Annals of Physics, Volume 354, (2015), pages 183-202

Stochastic (STDHF): Monte-Carlo-like exploration of the dynamical correlations by a perturbative residual 2-body coupling

E. Suraud, P-G. Reinhard, New J. Phys. 16, 063066 (2014)

Average Stochastic (ASTDHF): Consideration of the monte-Carlo trajectories as a mixed state (common mean-field fluctuations)

L. Lacombe, P. M. Dinh, P.-G. Reinhard, E. Suraud, J. Phys. B 49, 245101 (2016)

Hands-on activity 0: compilation, execution

Hands-on activity 1: ground-state calculation of Na_9^+

Hands-on activity 2: optical response of Na_9^+

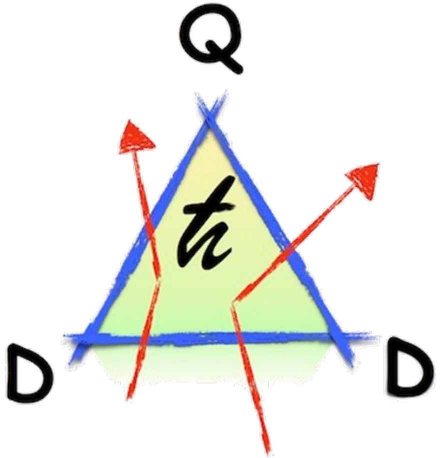
Hands-on activity 3: input files for a laser dynamics

Hands-on activity 4: PhotoElectron Spectrum (PES) of Na_9^+

Hands-on activity 5: Ion dynamics

Hands-on activity 6: Pump - prob dynamics of Na_9^+

Hands-on activity 0: compilation, execution



Hands-on activity 0: compilation, execution

→ download archive for the TIMES school demonstration:
https://git.irsamc.ups-tlse.fr/jheraud/TIMES_QDD_DEMO/archive/TIMES_school_Hamburg.zip

src/qdd/ → source subfolder

- *.F90
- cuda/cu*.F90
- Makefiles/
- Makefile

src/auxiliary/ → tools source subfolder (PES, measure points)

doc/ → User manual

TIMES/ → Demonstration inputs files and scripts

bin/

Fortran

CLI program, Makefile for the compilation (gfortran, ifort, nvfortran)

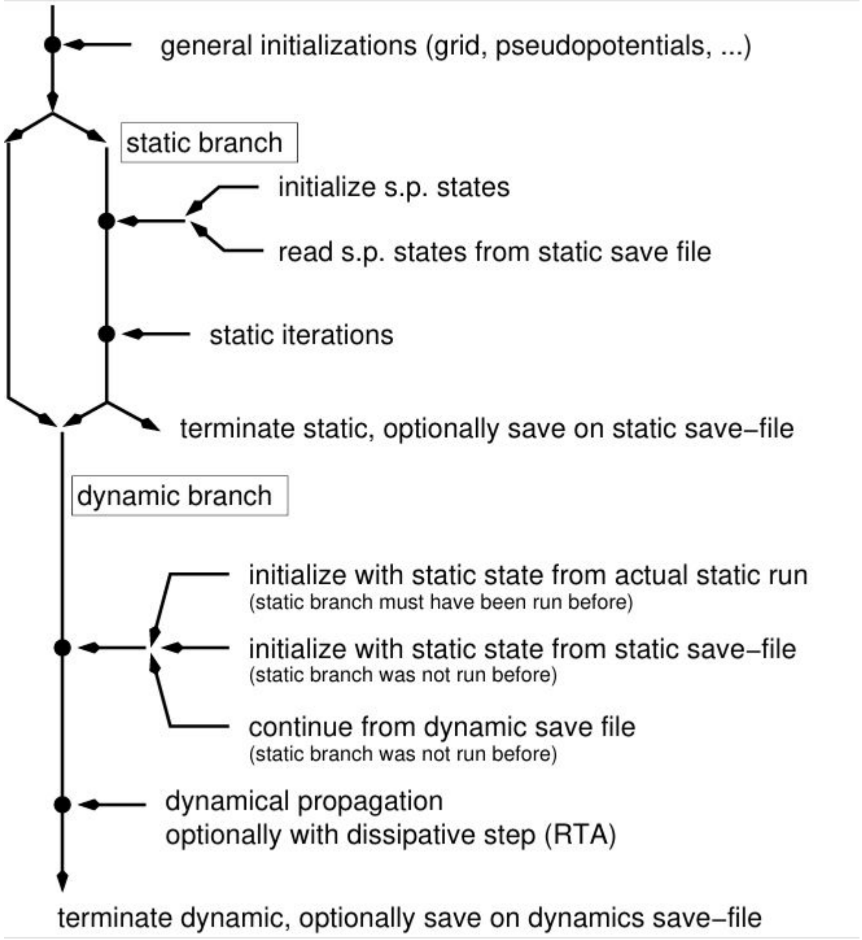
Hands-on activity 0: Makefile: options for the executable target

- look at src/qdd/Makefile
- choose your target
  -
  -
  -
- execute “make” command
- find the qdd executable in bin/

```
### Makefile
#    * gfortran     (the GNU Fortran compiler)
#    * ifort        (the Intel Fortran compiler)
#    * nvfortran    (the Nvidia Fortran compiler)
COMPILER = nvfortran

# FFT_TYPE: FFT solvers
# Available options:
#    * FFTW
#    * MKL
FFT_TYPE = MKL

# OS: select operating system. Ignored if:
FFT_TYPE = FFTW,
# otherwise ignored.
# Available options:
#    * LINUX
#    * MAC
OS = LINUX
...
```

```
MKL_PATH = $(MKLROOT)
#FFTW_PATH =
$(HOME)/Developer/fftw-3.3.8

OMP = NO
DYNOMP = NO

LINK_STATIC = NO

### DEBUG: enable debugging
DEBUG = NO

OMP = NO

NO_QDD_INFO = YES
FINDIFF = NO
NUMEROV = NO
RAREGAS = NO
FSIC = NO
EXTENDED = NO
STOCHASTIC = NO
...
```

Hands-on activity 0: flow



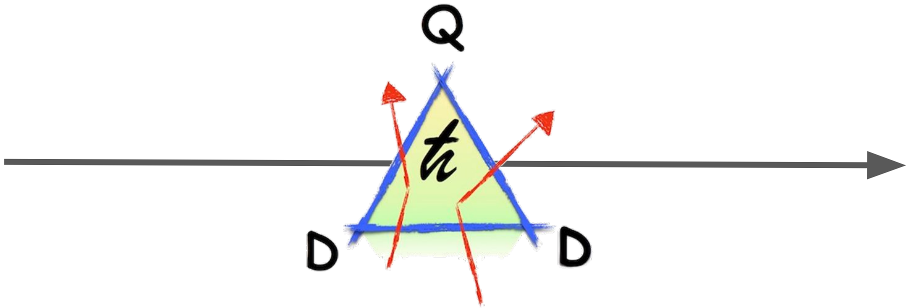
Hands-on activity 1: ground-state calculation of Na_9^+

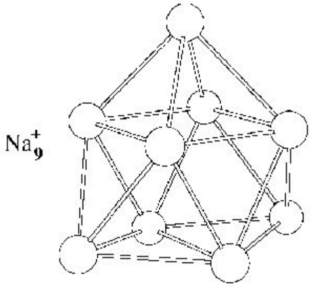
input files:

for005

for005.na9p

for005ion.na9p





imaginary time scheme

Hands-on activity 1: Input files Na_9^+

for005

```
'na9p'
```

for005ion.na9p

```
  4.5212        -1.5412         3.6610     11
  1.5412         4.5211         3.6610     11
 -1.5412        -4.5211         3.6610     11
 -4.5211         1.5412         3.6610     11
  4.3592         2.1428        -1.9822     11
  2.1427        -4.3592        -1.9821     11
 -4.3593        -2.1427        -1.9822     11
 -2.1428         4.3593        -1.9822     11
 6.92613E-05 -5.51499E-05  -6.7127     11
```

x_I y_I z_I Z_I

coordinates (a_0) atomic number

for005.na9p

```
&GLOBAL
nelect=8,nion=9,numspin=2,
nspdw=4,
dx=0.8,kxbox=72,kstate=8,
b2occ=0.0,deocc=0.0,
ifsicp=2,ipsptyp=0,
&END

&STATIC
occmix=1D0,
e0dmp=1.1,
epswf=1.8,
epsoro=1.0e-8,
ismax=1000,
ifhamdiag=0,
isaves=10, tstat=.false.,
&END

&DYNAMIC
dt1=0.1,
itmax=0,
&END
```

Hands-on activity 1: execution, ground state of Na_9^+

terminal:

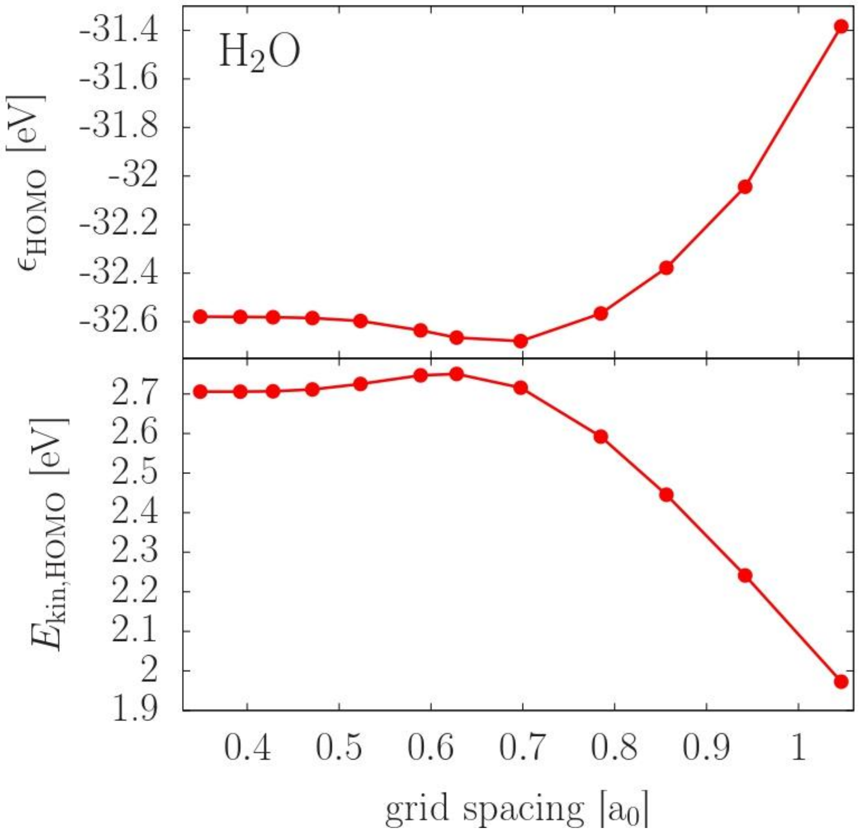
```
::> ls
for005
for005ion.na9p
for005.na9p
qdd_gfortran
::> ./qdd_gfortran
```

Is the RSAVE file created?

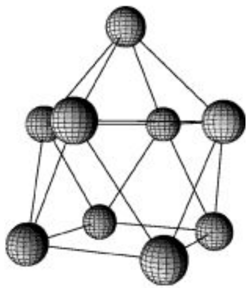
Is ismax sufficiently large?

what happen if dx change?

Hands-on activity 1: importance of grid spacing



Hands-on activity 2: optical response of Na_9^+



→ see: Kümmel, S., Reinhard, PG. & Brack, M. Structure and optic response of the $Na_9{}^+$ and $Na_{55}{}^+$ clusters. *Eur. Phys. J. D* 9, 149–152 (1999). https://doi.org/10.1007/s100530050416

Hands-on activity 2: optical response of Na_9^+

for005.na9p

```
&STATIC
occmix=1D0,
e0dmp=1.1,
epswf=1.8,
epsoro=1.0e-8,
ismax=0,
ifhamdiag=0,
isaves=10, tstat=.false.,
&END

...
```

disable static (ismax=0)

```
&DYNAMIC
irest=0,isaved=1000,

itmax=20000,
dt1=0.1, (multiple of Ry-1)

nabsorb=4,
jesc=10,

jdip=10,
jdiporb=10,jquad=10,
jinfo=10,jdip=10,
jenergy=10,jstinf=10,
jnorms=10,jquad=10,

centfx=0.005,
centfy=0.005,
centfz=0.005,
&END
```

continuing dynamics (SAVE file)

time propagation parameters

absorbing boundary conditions parameters

output observables printing parameters

initial boost

$$\varphi_i(\vec{r},0) \rightarrow e^{i\vec{P}_{boost}\cdot\vec{r}}\varphi_i(\vec{r},0)$$

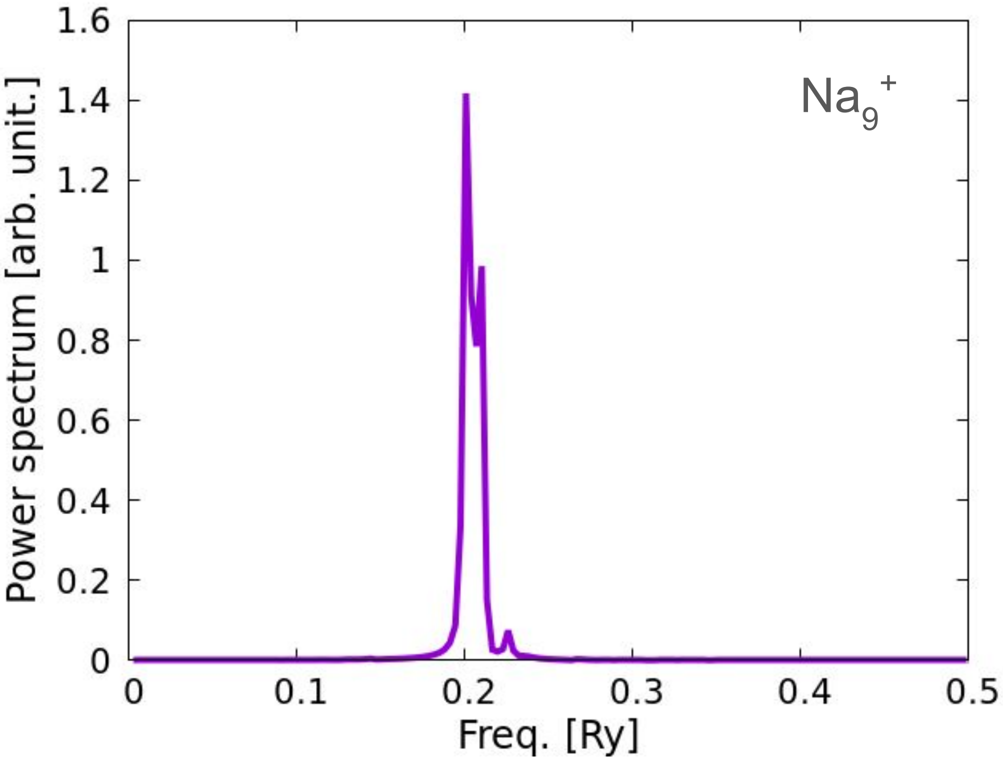
Hands-on activity 2: optical response of Na_9^+

Boost excitation → dipole moment in time → Fourier transform → optical response

$$\mathbf{D}(t) = \sum_{n=1}^{N} \langle \varphi_n(\mathbf{r},t) | \hat{\mathbf{r}} | \varphi_n(\mathbf{r},t) \rangle$$

→ use spectr2.f in src/auxiliairy

```
::> cd src/auxiliary/
::> gfortran spectr2.f -o spectr2
::> cp spectr2 <your_folder>
::> cp run_spectr.sh <your_folder>
::> cd <your_folder>
::> ./run_spectr.sh
::> gnuplot plot_spectr2.plt
```



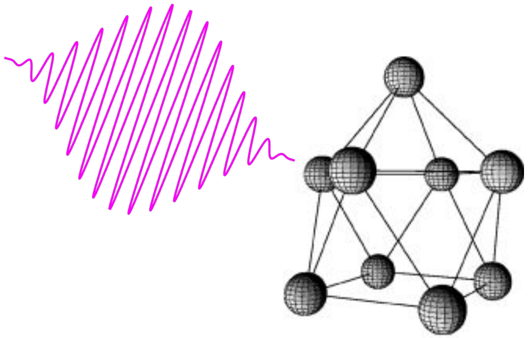
Hands-on activity 2: propagator and time step

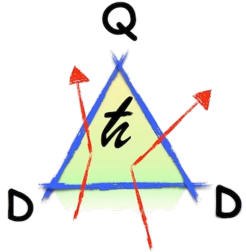
What is the influence of time step? (keep T_{max})

‘dt1’ = 0.1 Ry^{-1} → dt = 0.00484 fs = 4.84 as !!

Is the exponential propagator more robust?

Hands-on activity 3: laser dynamics





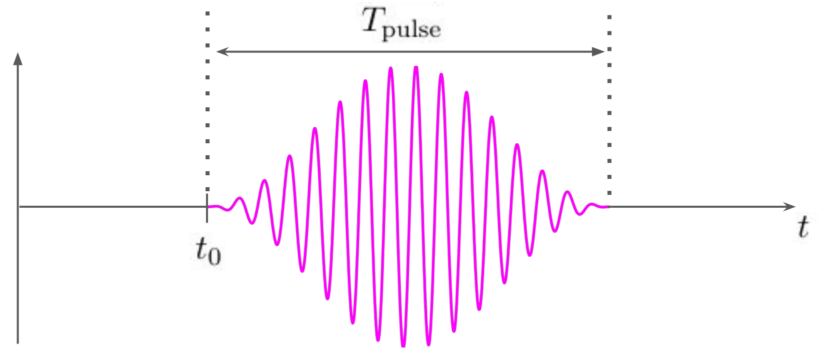
Hands-on activity 3: input files for a laser dynamics

for005.na9p

$$V_{ext}(\mathbf{r}, t; \omega_{las}, \mathbf{E}_0, T_{pulse}, \phi_{las}, t_0) =$$

$$e\,\mathbf{E}_0\, f(t)\cdot\mathbf{r}\;\cos\left(\omega_{las}(t - t_0 - \tfrac{1}{2}T_{pulse}) - \phi_{las}\right)$$

$$f(t) = \begin{cases} \sin^2\left(\pi \dfrac{t-t_0}{T_{pulse}}\right) & \text{for} \quad t - t_0 \in [0, 2T_{pulse}] \\ 0 & \text{else} \end{cases}$$




```
&DYNAMIC
irest=0,isaved=1000,

itmax=20000,
dt1=0.1,  (multiple of Ry-1)

nabsorb=4,
jesc=10,

jdip=10,
jdiporb=10,jquad=10,
jinfo=10,jdip=10,
jenergy=10,jstinf=10,
jnorms=10,jquad=10,

itft=3, deltat=24.0,tnode=0,
e1x=0.0, e1y=0.0, e1z=1.0,
omega=0.189, e0=0.005,
&END
```

continuing dynamics (SAVE file)

time propagation parameters

absorbing boundary conditions parameters

output observables printing parameters

laser parameters

Hands-on activity 3: laser frequency - on/off-resonance

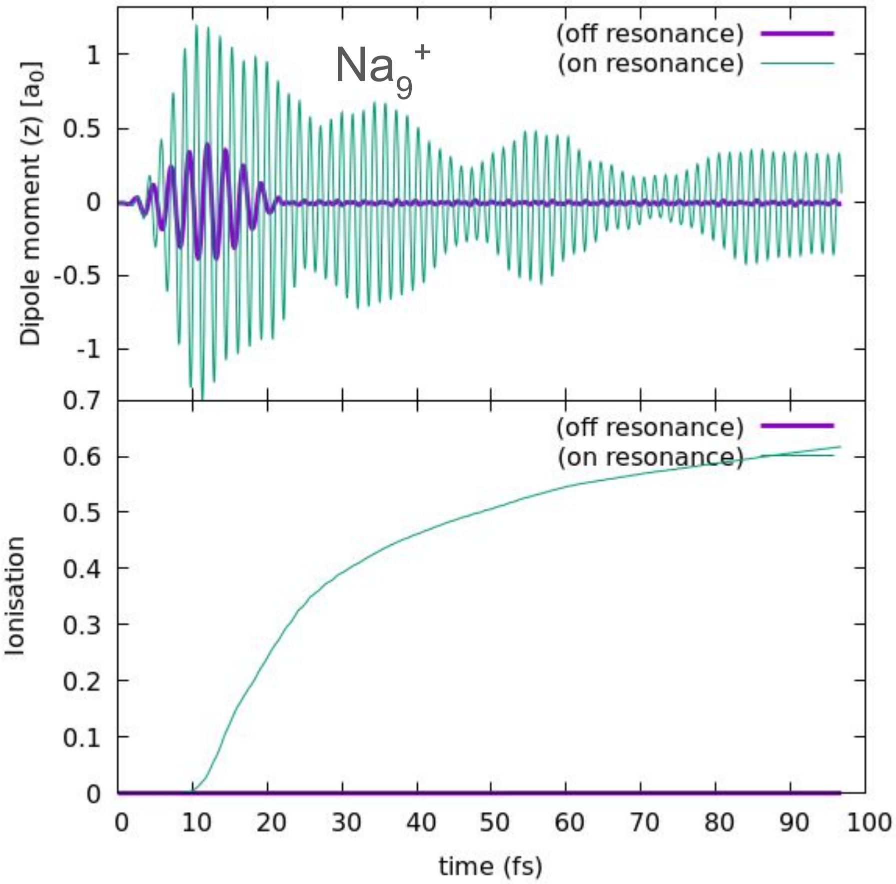
By sweeping the laser frequency, observe the resonance frequencies.

— $\hbar\omega_{laser}$ = 2.57 eV

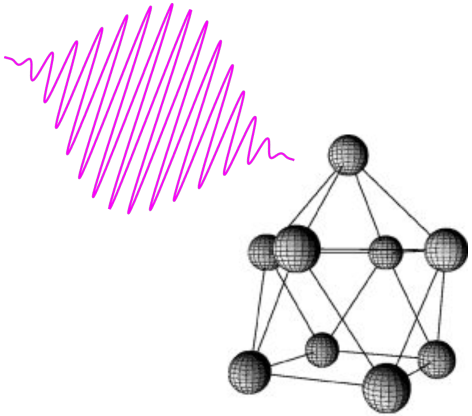
— $\hbar\omega_{laser}$ = 1.69 eV

Total electronic emission (ionisation):

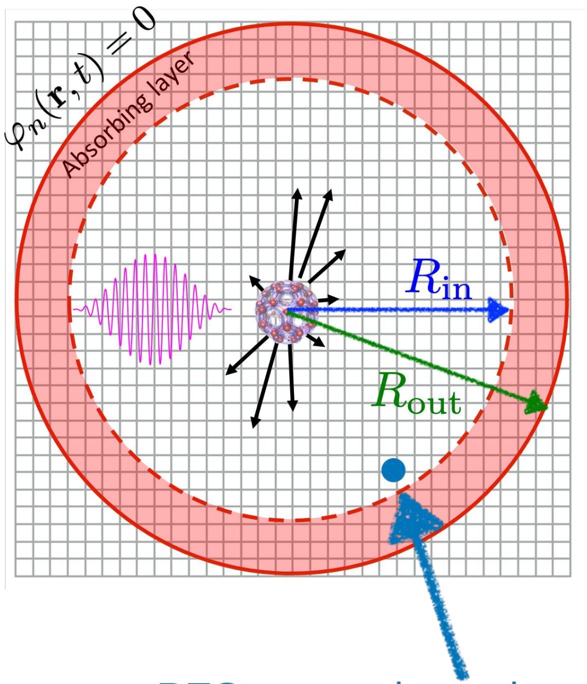
$$N - \sum_{n=1}^{N} \left|\varphi_n(\mathbf{r}, t)\right|^2$$



Hands-on activity 4: PhotoElectron Spectra (PES) of Na_9^+



Hands-on activity 4: PES of Na_9^+



PES measuring point r_m

- Photoelectron spectra (PES):
  store kin. energy of w.f. at measuring points just before mask

$$\phi_i(r_m, E_{kin}) = \frac{1}{\sqrt{2\pi}} \int \mathrm{dt} e^{i\omega t} \varphi_i(r_m, t)$$

$$Y_{r_m}(E_{kin}) = \sum_{i=1}^{N_e} \sqrt{E_{kin}} \mid \phi_i(r_m, E_{kin}) \mid^2$$

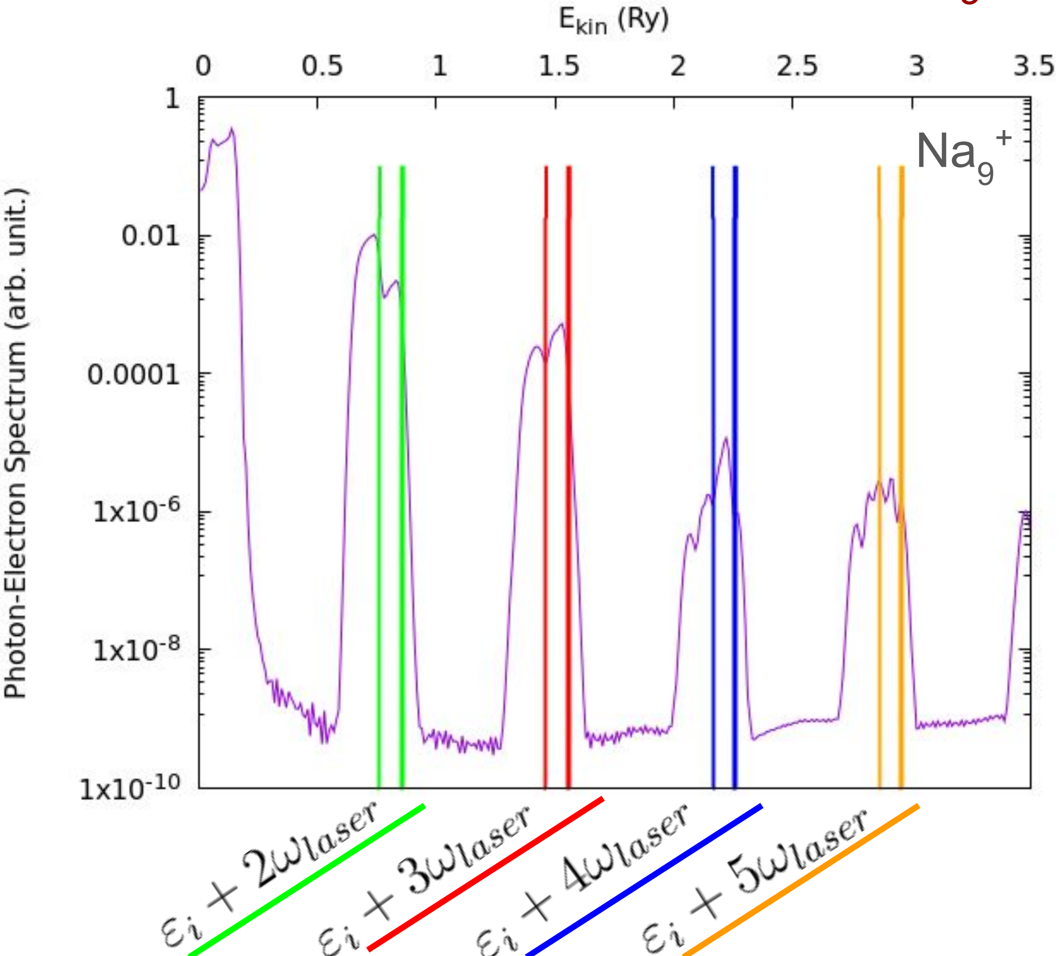
Hands-on activity 4: PES of Na_9^+

```
&DYNAMIC
irest=0,isaved=1000,

itmax=20000,
dt1=0.1,  (multiple of Ry-1)

nabsorb=4,
jesc=10,

jdip=10,
jdiporb=10,jquad=10,
jinfo=10,jdip=10,
jenergy=10,jstinf=10,
jnorms=10,jquad=10,
jMP=20,

itft=3, deltat=36.0,tnode=0.025,
e1x=0.0, e1y=0.0, e1z=1.0,
omega=0.7, e0=0.107,
&END
```

→ use analyze-MP.f and analyze-PES.f in src/auxiliairy

```
::> cd src/auxiliary/
::> gfortran analyze-MP.f -o analyze-MP
::> gfortran analyze-PES.f -o analyze-PES
::> cp analyze-MP <your_folder>
::> cp analyze-PES <your_folder>
::> cd <your_folder>
::> ./analyze-MP
< na9p
::> ./analyze-PES
< na9p
::> gnuplot plot_PES.plt
```

Hands-on activity 4: PES of Na_9^+

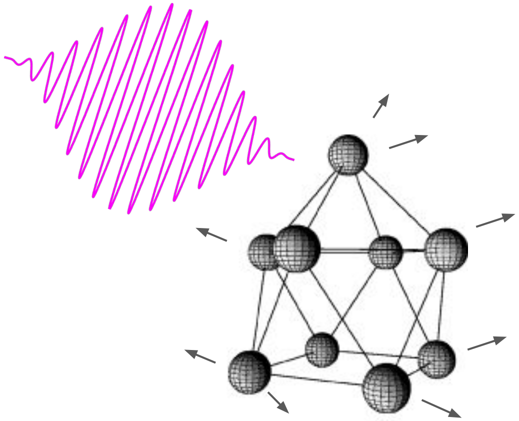


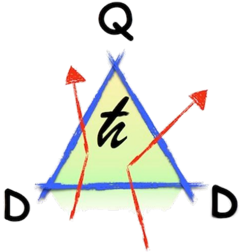
→ use analyze-MP.f and analyze-PES.f in src/auxiliairy

```
::> cd src/auxiliary/
::> gfortran analyze-MP.f -o analyze-MP
::> gfortran analyze-PES.f -o analyze-PES
::> cp analyze-MP <your_folder>
::> cp analyze-PES <your_folder>
::> cd <your_folder>
::> ./analyze-MP
< na9p
::> ./analyze-PES
< na9p
::> gnuplot plot_PES.plt
```

→ Multi-Photon Absorption

Hands-on activity 5: Ion dynamics of Na_9^+





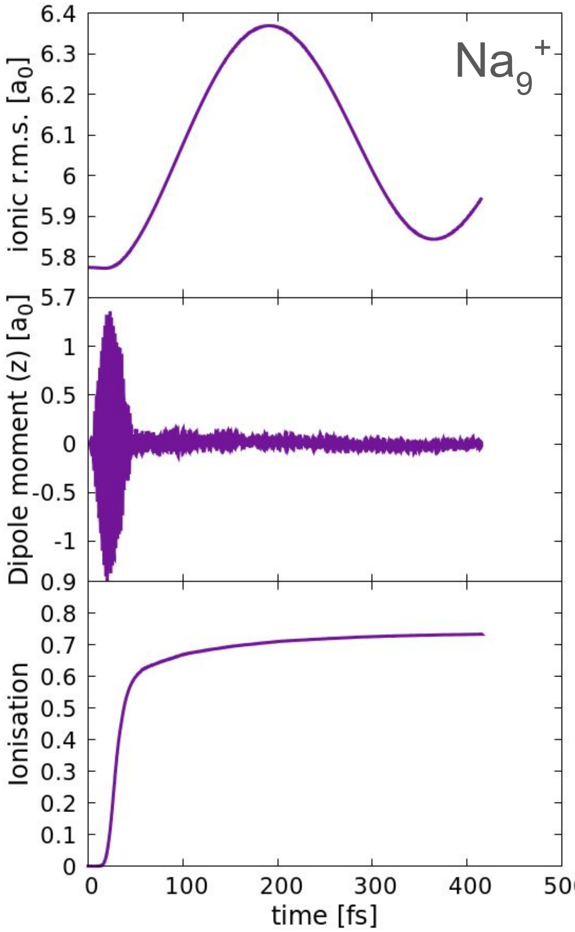
Hands-on activity 5: Ion dynamics of Na_9^+

```
&DYNAMIC
irest=0,isaved=1000,
itmax=20000,
dt1=0.1,
nabsorb=4,
jesc=10,

ionmdtyp=2,
modionstep=20,
jpos=20,
jvel=20,
jposcm=20,
jgoemion=20,

jdip=10,jdiporb=10,jquad=10,
jinfo=10,jdip=10,jenergy=10,
jstinf=10,jnorms=10,jquad=10,
itft=3, deltat=24.0,tnode=0,
e1x=0.0, e1y=0.0, e1z=1.0,
omega=0.17, e0=0.012,
&END
```

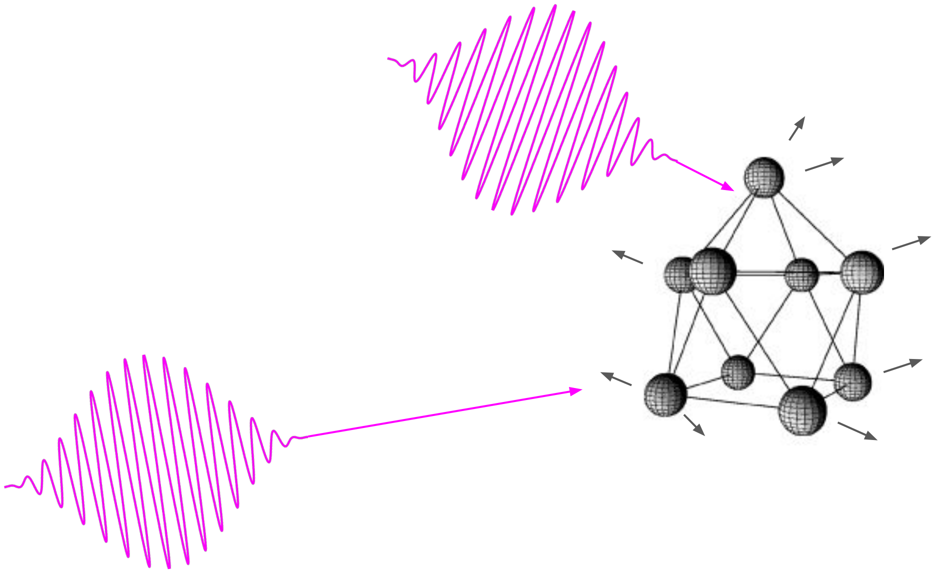
for005.na9p

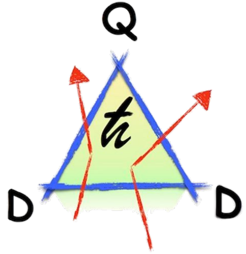
parameters of ion dynamics
& printing parameters
of output observables

— $\hbar\omega_{laser}$ = 2.3 eV



Hands-on activity 6:Pump - prob dynamics of Na_9^+





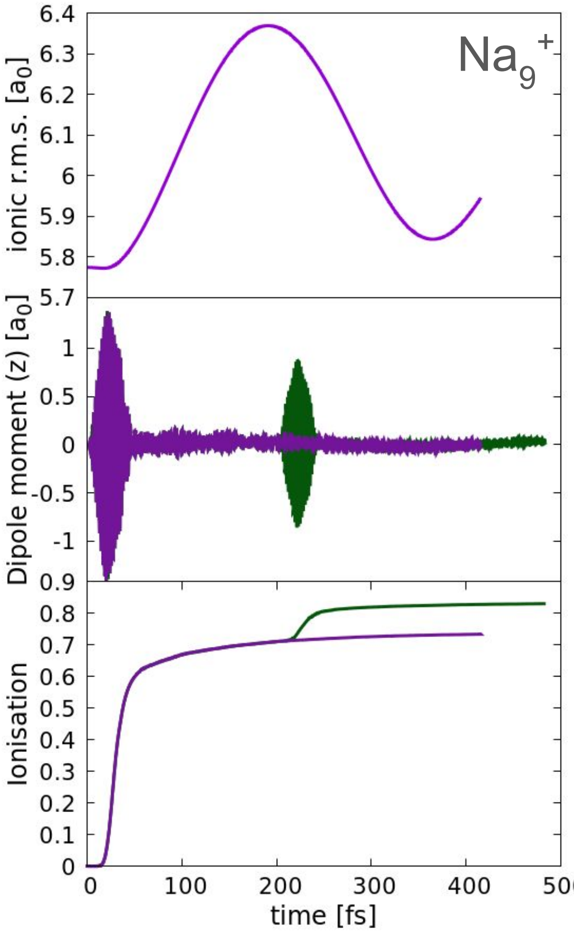
Hands-on activity 6: Pump - prob dynamics of Na_9^+

- Pump: $\hbar\omega_{pump}$ = 2.3 eV

```
itft=3, deltat=48.0, tnode=0.025,
e1x=0.0, e1y=0.0, e1z=1.0,
omega=0.17, e0=0.014,
```

- Prob: $\hbar\omega_{prob}$ = 2.3 eV

```
e0_2=0.0034, omega2=0.169,
deltat2=48.0,
e2x=0.0, e2y=0.0, e2z=1.0,
tstart2=200.0,
tstart2=390.0,
```

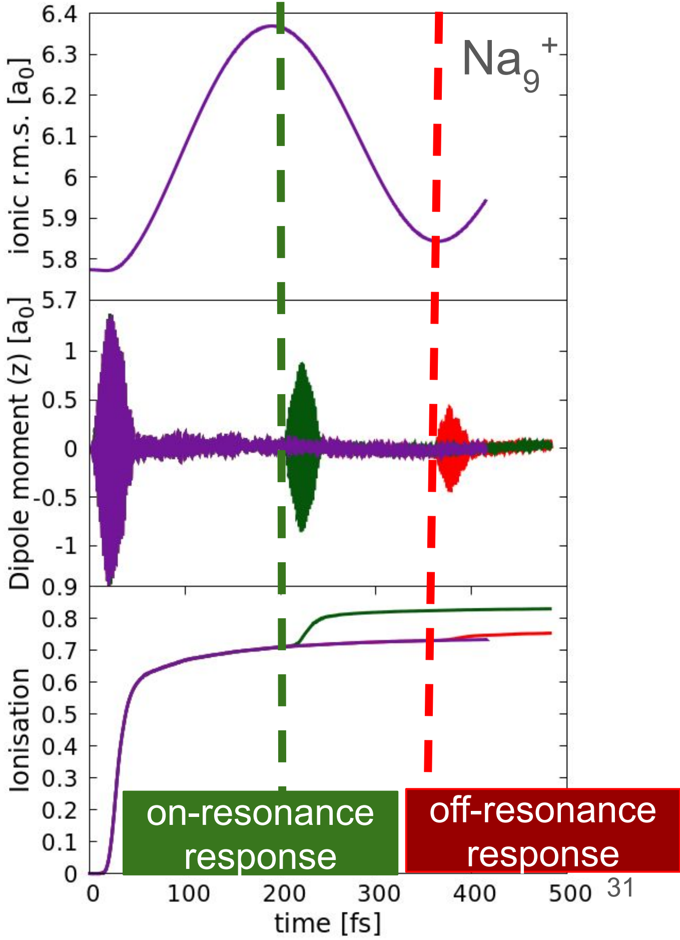


Hands-on activity 6: Pump - prob dynamics of Na_9^+

Mie plasmon frequency $\omega_{\mathrm{pl}} \propto \frac{Q}{R^{3/2}}$

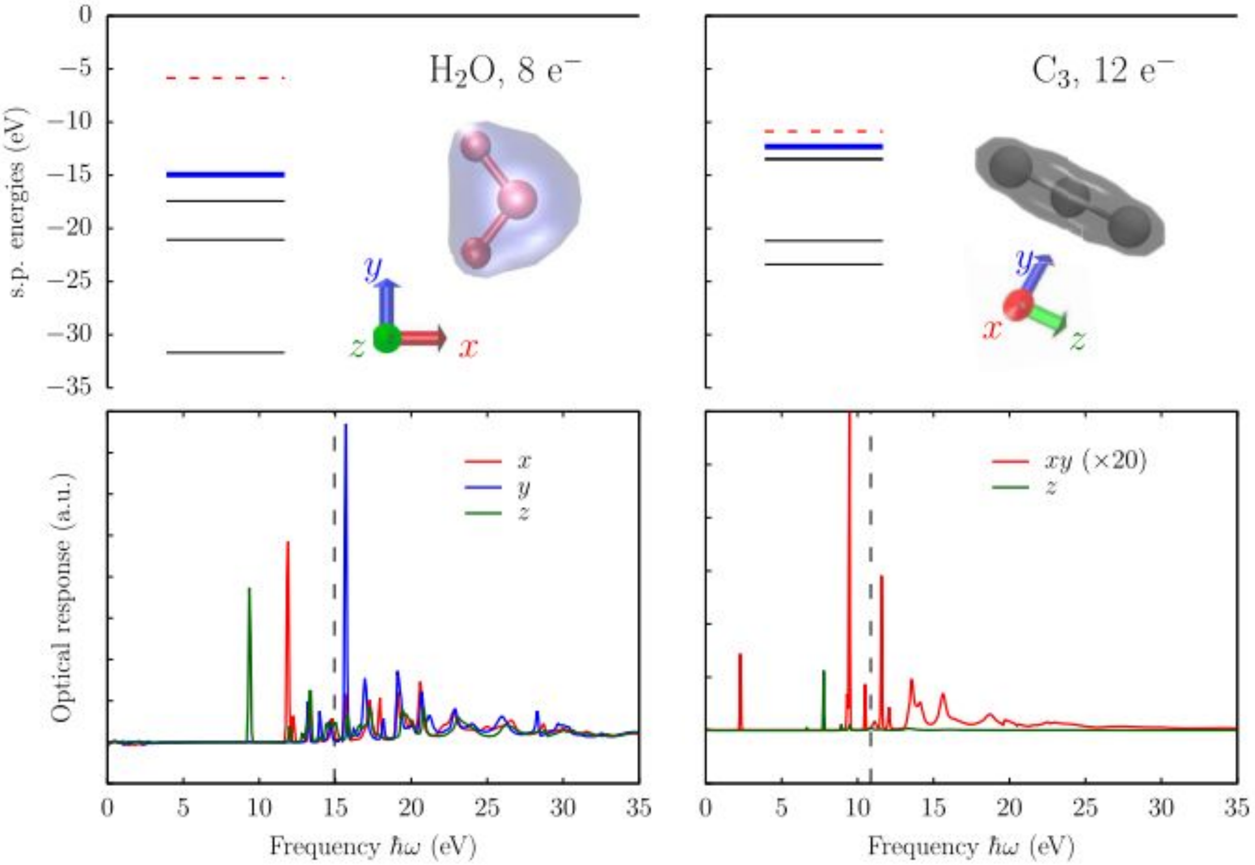
$\hbar\omega_{pump} = \hbar\omega_{prob} =$ 2.3 eV

- Pump:
  - extracts 0.7 electron $\Longrightarrow$
  - triggers an ionic breathing mode
  - Large r.m.s. give more resonant with 2.3 eV than small ones
- Probe:
  - play with delay between pump and probe
  - more ionisation means resonant response
  - delay $\leftrightarrow$ ionic dynamics



Enjoy the QDD code

Other systems



Other systems