RT-TDDFT and molecular dynamics

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Outline

- Introduction
- RT-TDDFT
- MD
- **exciting**
- Tutorials

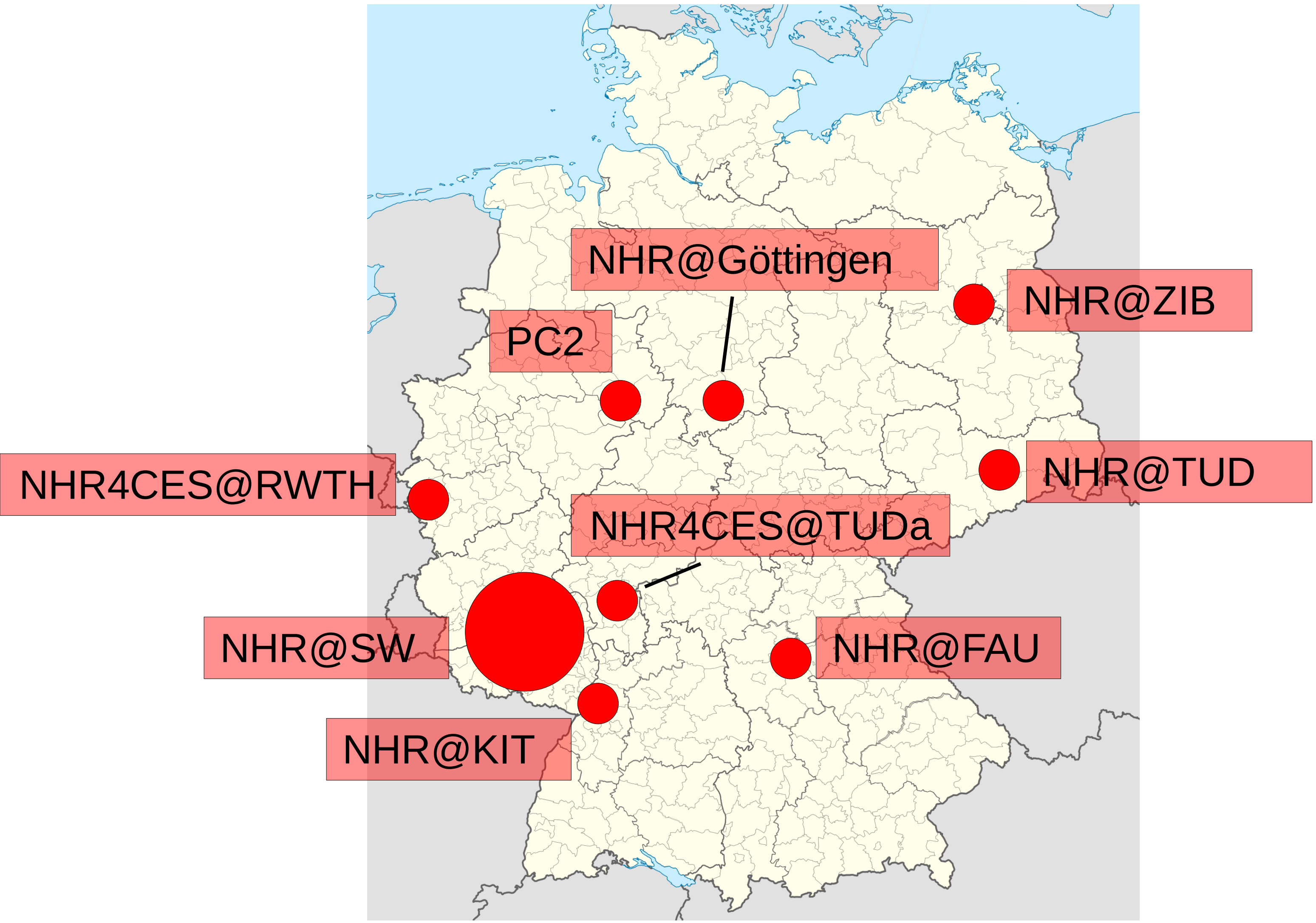
ZIB

- Research institute for **Applied Mathematics** + data-intensive **HPC**
- Research: modeling, simulation and optimization
- Partners

Lufthansa NEC intel SIEMENS SAP Open Grid Europe The Gas Wheel ORACLE

NHR@ZIB

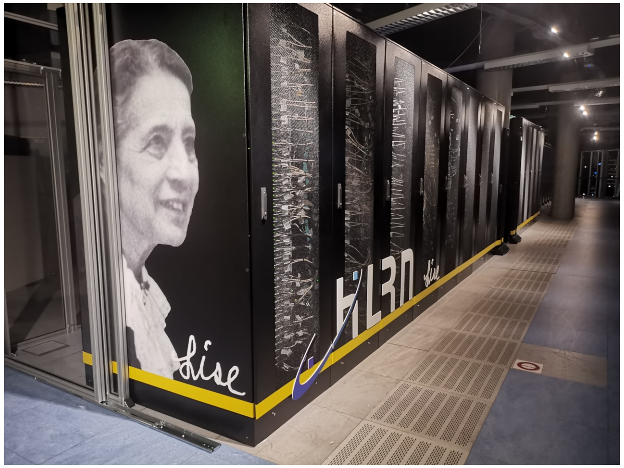
NHR



NHR@Göttingen
NHR@ZIB
PC2
NHR4CES@RWTH
NHR@TUD
NHR4CES@TUDa
NHR@SW
NHR@FAU
NHR@KIT

NHR@ZIB

- Tier-2 level resources, **HPC system “Lise”**
  - ZIB + Berlin University Alliance (FUB, HUB, TUB, Charité)
- Compute projects
  - 1.2 million core-h: 1 year
  - Deadlines: Jan., Apr., Jul., Oct.

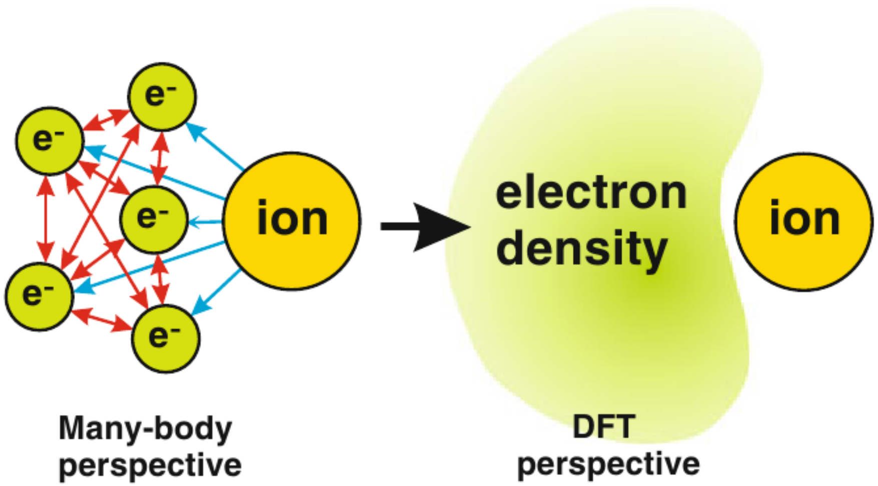


“Lise” #96 (TOP500, Nov. 22)

- 8 Pflop/s: 1270 nodes with 96 cores per node (Intel Xeon), RAM: 384, 768, 1500 GB
- GPUs - 42 nodes with 4x Nvidia A100/80
- Coming soon: nodes with 4x Intel Ponte Vecchio/128

RT-TDDFT

- DFT

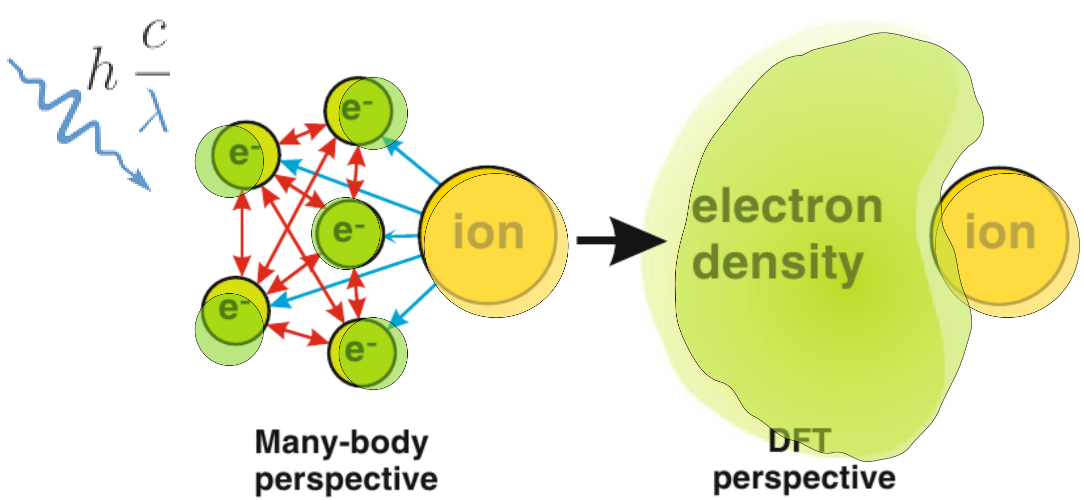


F. Bechstedt. Many-Body Approach to Electronic Excitations: Concepts and Applications

$$\hat{H}\psi_i(\mathbf{r}) = \varepsilon_i \psi_i(\mathbf{r})$$

$$\frac{1}{2}(-\mathrm{i}\nabla)^2 + v_{KS}(\mathbf{r})$$

- Time Dependent DFT



$$\hat{H}(t)\psi_i(\mathbf{r},t) = \mathrm{i}\frac{\partial}{\partial t}\psi_i(\mathbf{r},t)$$

$$\frac{1}{2}\left(-\mathrm{i}\nabla + \frac{1}{c}\mathbf{A}(t)\right)^2 + v_{KS}(\mathbf{r},t)$$

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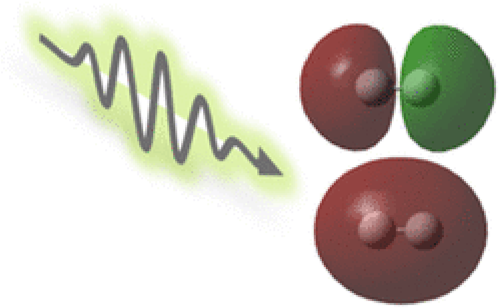
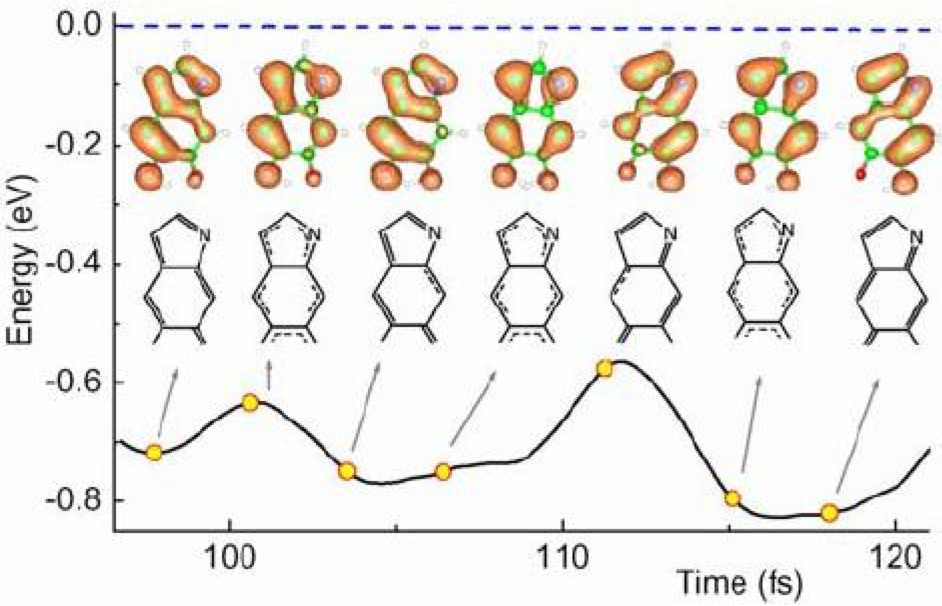
RT-TDDFT

$t = 0$ GS → $|\psi_j^{\mathbf{k}}(0)\rangle, n(\mathbf{r}, 0), v_{KS}(\mathbf{r}, 0)$





Biophysical Journal 95, 4396-4402 (2008)

$$\hat{H}(t) = \frac{1}{2}\left(-\mathrm{i}\nabla + \frac{1}{c}\mathbf{A}(t)\right)^2 + v_{KS}(\mathbf{r}, t)$$

$$\mathbf{A}(t) = -c\int_0^t \mathbf{E}(t')\, dt'$$

$$\mathrm{i}\frac{d}{dt}|\psi_j^{\mathbf{k}}(t)\rangle = \hat{H}(t)|\psi_j^{\mathbf{k}}(t)\rangle$$

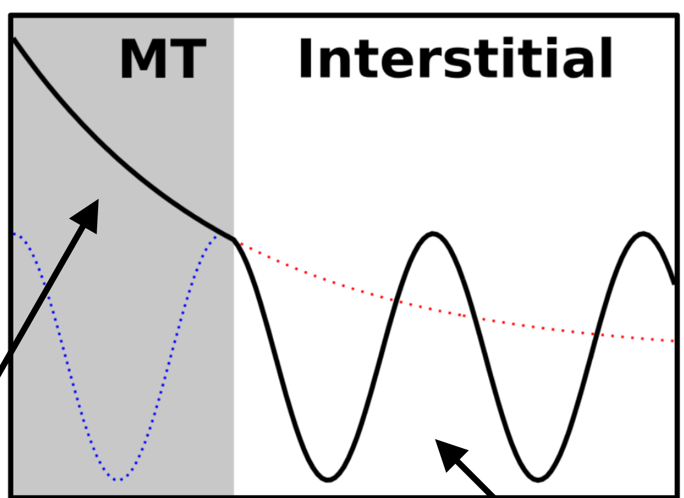
RT-TDDFT

Basis set

$$|\psi_j^{\mathbf{k}}(t)\rangle = \sum_{\mathbf{G}} C_{j\mathbf{G}}^{\mathbf{k}}(t)|\phi_{\mathbf{G}+\mathbf{k}}\rangle + \sum_{\gamma} C_{j\gamma}^{\mathbf{k}}(t)|\phi_{\gamma}\rangle$$

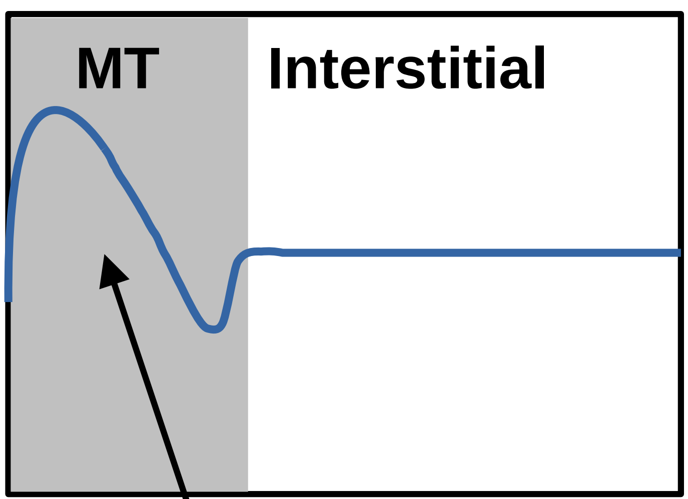
LAPW

lo



$$\sum_{lm} \mathcal{A}_{\nu\mathbf{G}}^{\alpha\mathbf{k}} Y_{lm}(\hat{r}_\alpha) u_{l\alpha}(r_\alpha)$$

$$\frac{1}{\sqrt{\Omega}} e^{i(\mathbf{k}+\mathbf{G})\cdot\mathbf{r}}$$



$$Y_{lm}(\hat{r}_\alpha) v_{l\alpha}(r_\alpha)$$

RT-TDDFT

$$\mathrm{i}\frac{d}{dt}|\psi_j^{\mathbf{k}}(t)\rangle = \hat{H}(t)|\psi_j^{\mathbf{k}}(t)\rangle \rightarrow \mathrm{i}S^{\mathbf{k}}\dot{C}_j^{\mathbf{k}} = H^{\mathbf{k}}C_j^{\mathbf{k}}$$

RK4

Propagator

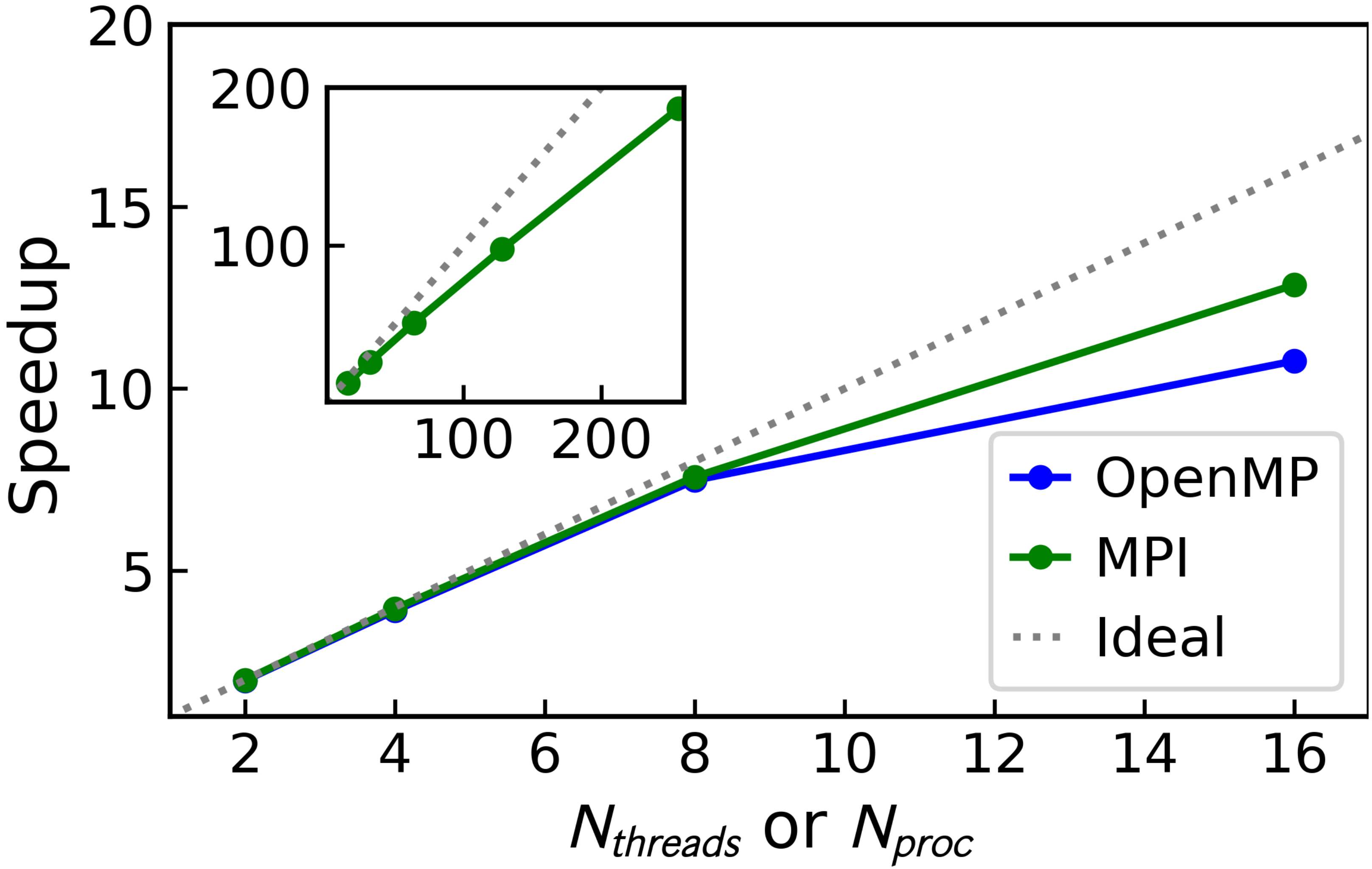
$$C_j^{\mathbf{k}}(t+\Delta t) = \hat{U}(t+\Delta t, t)C_j^{\mathbf{k}}(t)$$

- Simple exponential
- Exponential at midpoint
- Time-reversal symmetry
- Magnus expansion
- Houston states

E.g.: Simple exponential

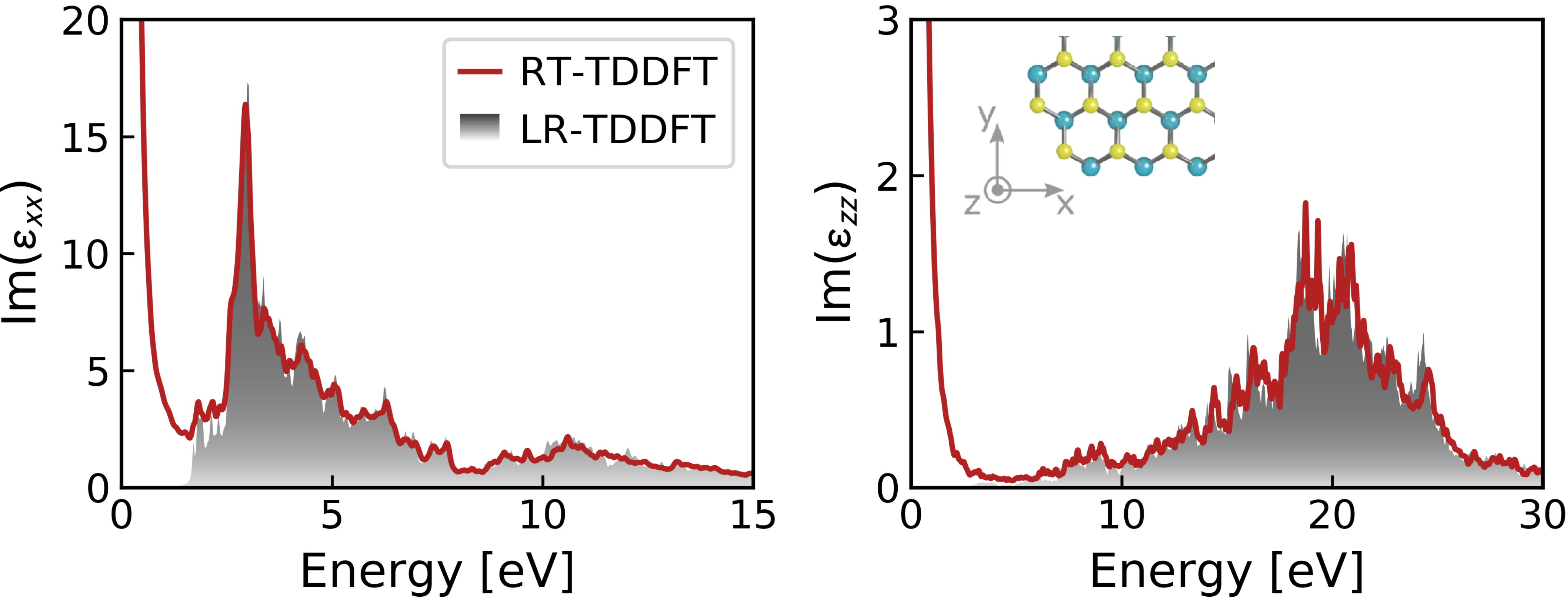
$$\hat{U}(t+\Delta t, t) = \exp[-\mathrm{i}\Delta t(S^{\mathbf{k}})^{-1}H^{\mathbf{k}}(t)]$$

Parallelization



Diamond: 16 x 16 x 16 kpts

TDDFT: time vs. freq.



RT-TDDFT

Current density

$$\mathbf{J}(t) = \frac{\mathrm{i}}{\Omega} \sum_{j\mathbf{k}} w_{\mathbf{k}} f_{j\mathbf{k}} \left\langle \psi_{j\mathbf{k}}(t) \middle| \nabla \middle| \psi_{j\mathbf{k}}(t) \right\rangle - \frac{N\mathbf{A}(t)}{c\,\Omega}$$

Excited electrons

$$m^e_{j\mathbf{k}}(t) = \sum_i f_{i\mathbf{k}} \left| \langle \psi_{j\mathbf{k}}(0) | \psi_{i\mathbf{k}}(t) \rangle \right|^2$$

Holes

$$m^h_{j'\mathbf{k}}(t) = f_{j'\mathbf{k}} - \sum_i f_{i\mathbf{k}} \left| \langle \psi_{j'\mathbf{k}}(0) | \psi_{i\mathbf{k}}(t) \rangle \right|^2$$

$$N_{\mathrm{exc}}(t) = \sum_{j\mathbf{k}}^{j\ \mathrm{unocc}} w_{\mathbf{k}}\, m^e_{j\mathbf{k}}(t) = \sum_{j'\mathbf{k}}^{j'\ \mathrm{occ}} w_{\mathbf{k}}\, m^h_{j'\mathbf{k}}(t)$$

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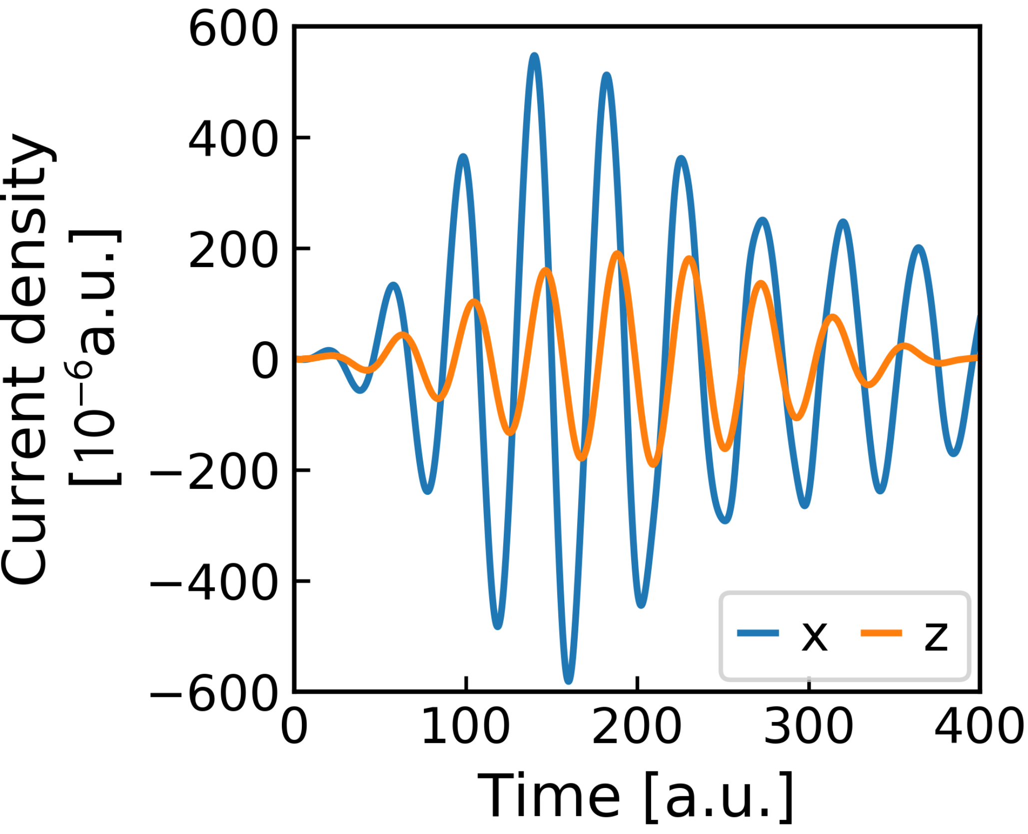
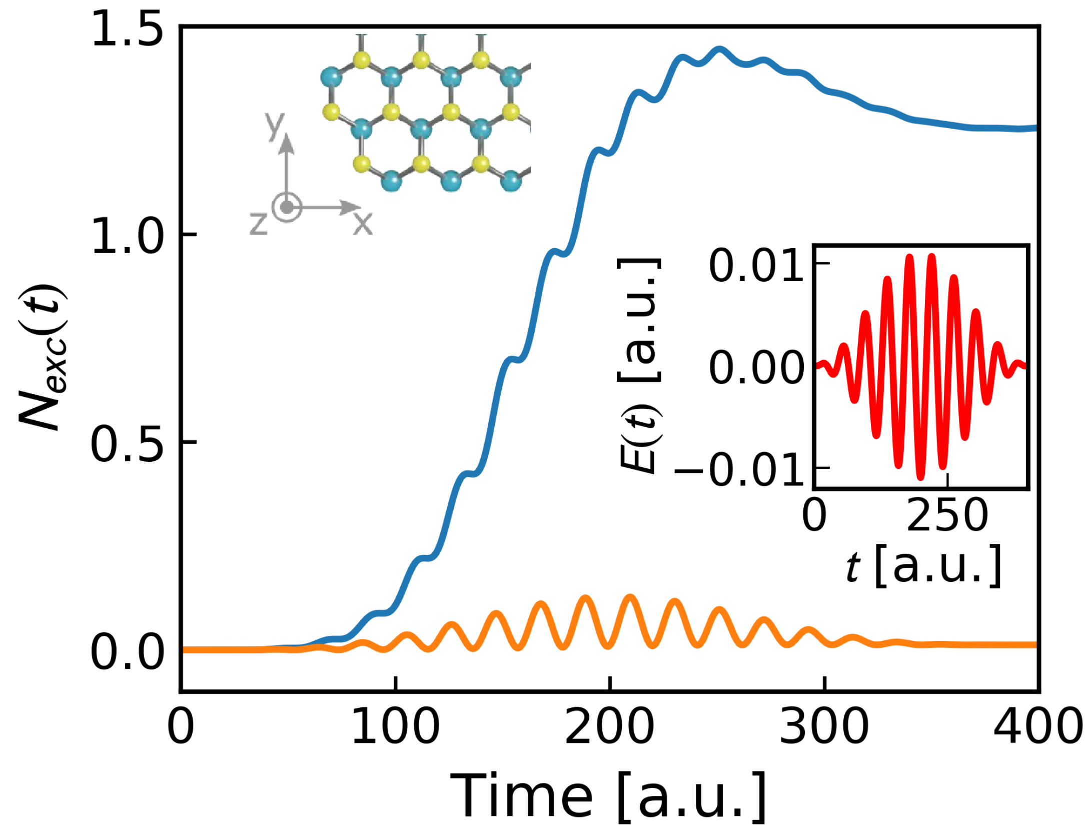
RT-TDDFT

- Excitations

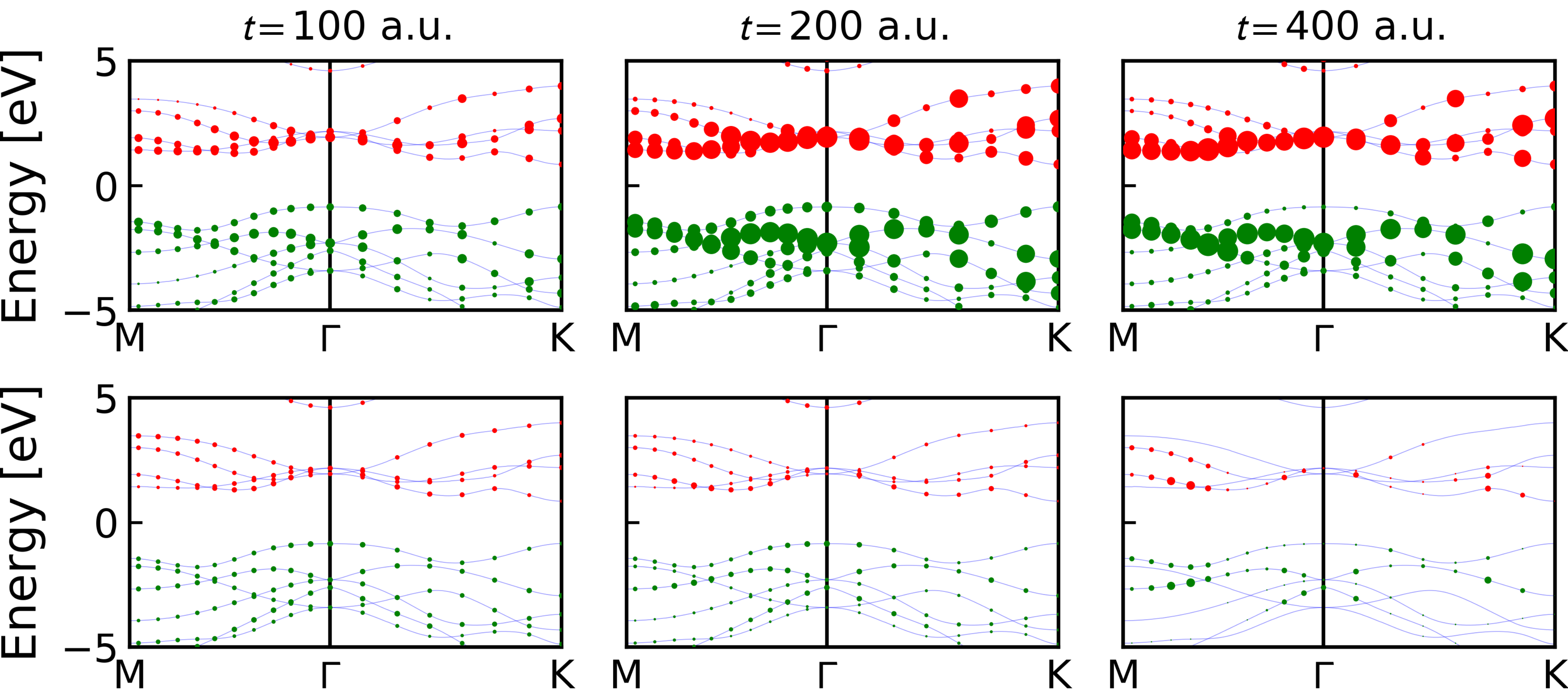




$$\omega_0 = 0.15 \text{ a.u.} = 4.08 \text{ eV}$$

RT-TDDFT

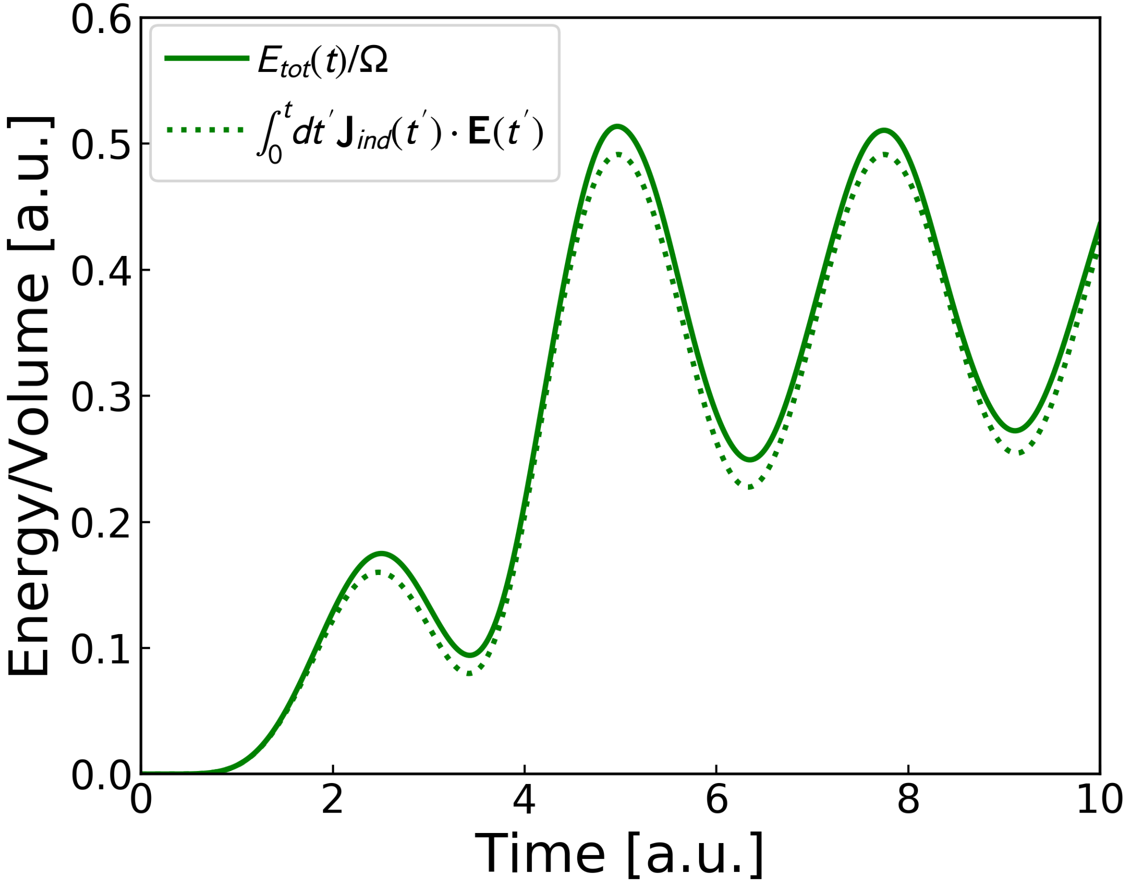
- Excitations



RT-TDDFT

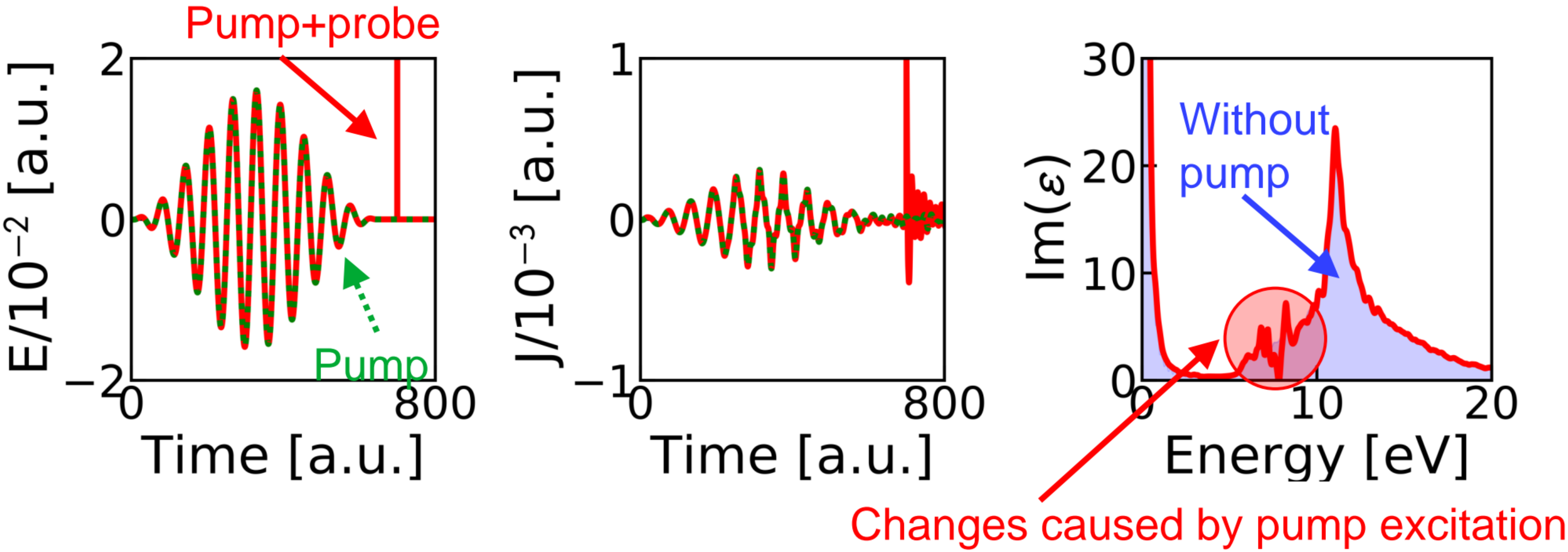
- Energy over time

$$E_{tot}(t) = \frac{1}{\Omega}\sum_{i\mathbf{k}} w_{\mathbf{k}} f_{i\mathbf{k}} \left\langle \psi_i^{\mathbf{k}}(t) \middle| \hat{H}(t) - v_{XC} - \frac{v_H}{2} \middle| \psi_i^{\mathbf{k}}(t) \right\rangle + \frac{E_{XC}(t)}{\Omega}$$



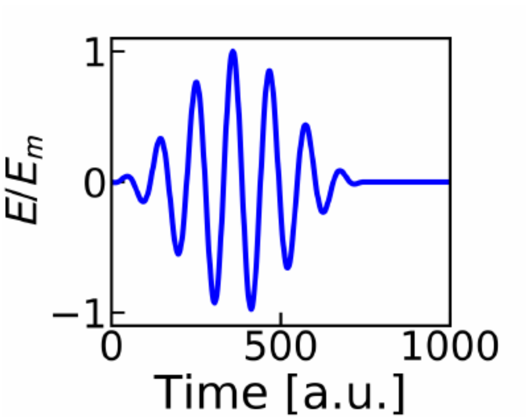
RT-TDDFT

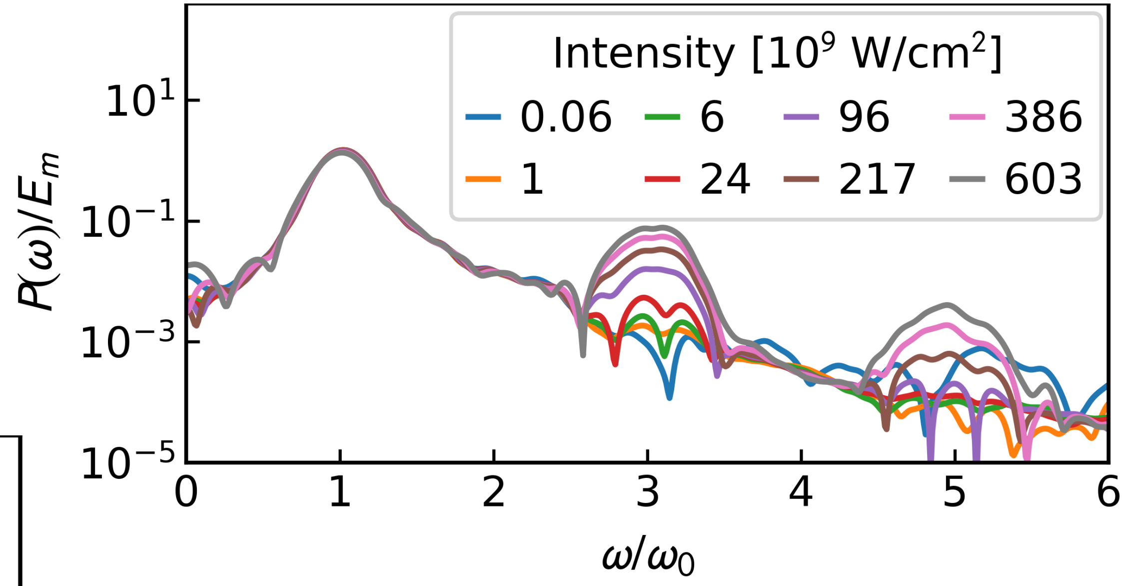
- Pump-probe

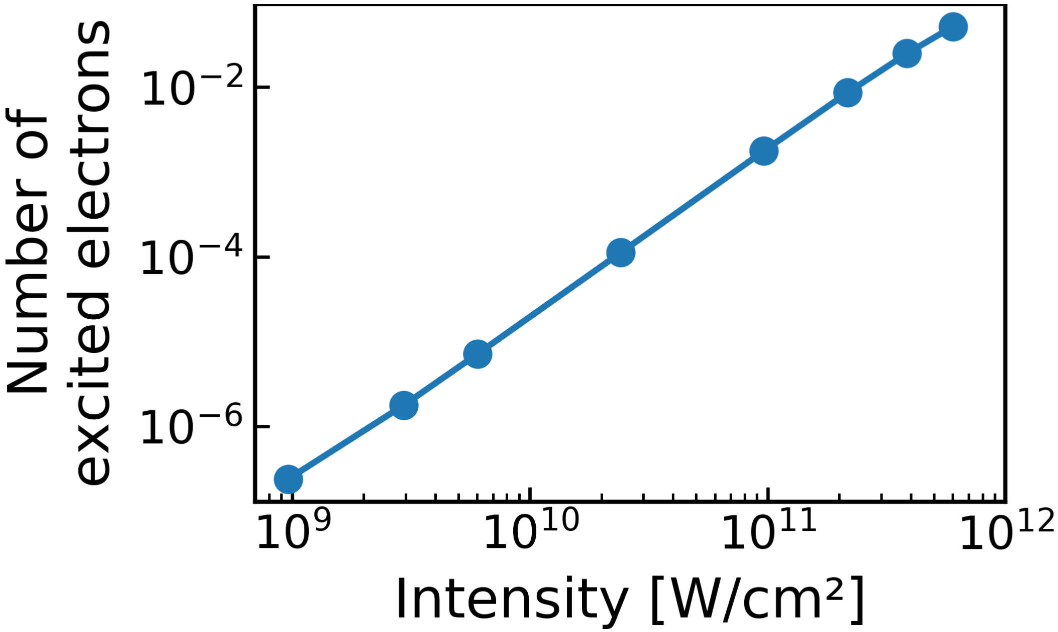


RT-TDDFT

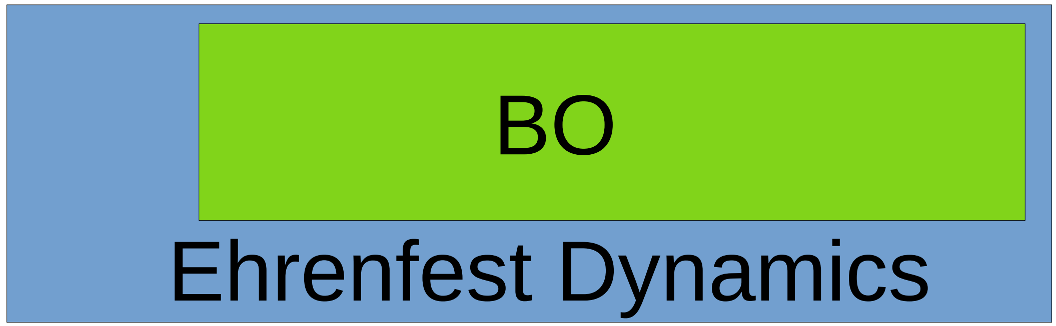
- Higher harmonics







MD



$\mathbf{R}_J(t)$

$$\hat{H}(\mathbf{R}_J(t))|\psi_{el}\rangle = \epsilon|\psi_{el}\rangle$$

NMR@ZIB

MD

BO

Ehrenfest Dynamics

Geometry → Evolve sates (TDDFT) → Forces on ions → Move ions: Newton's law

$\mathbf{R}_J(t)$

$$\hat{H}_{el}(t, \mathbf{R}_J(t))|\psi_{el}(t)\rangle = \mathrm{i}\frac{d}{dt}|\psi_{el}\rangle$$

MD

- Action $\mathcal{A} = \mathcal{A}_c + \mathcal{A}_q$

Classical part: ions

$$\mathcal{A}_c = \int_{t_1}^{t_2} \mathrm{d}t \sum_J \left[\frac{M_J \dot{\mathbf{R}}_J^2}{2} - U(\mathbf{R}_J, t) \right]$$

Quantum part: electrons

$$\mathcal{A}_q = \int_{t_1}^{t_2} \mathrm{d}t \sum_j \left\langle \psi_j \left| \mathrm{i}\frac{\partial}{\partial t} - \frac{\nabla^2}{2} \right| \psi_j \right\rangle + \mathcal{A}_{pot}$$

$\delta\mathcal{A} = 0$ ➡ Equations of motion

MD

Geometry → Evolve sates (TDDFT) → Forces on ions → Move ions: Newton's law

$\mathbf{R}_J(t)$

$$\hat{H}_{el}(t, \mathbf{R}_J(t))|\psi_{el}(t)\rangle = \mathrm{i}\frac{d}{dt}|\psi_{el}\rangle$$

LAPW+lo

Basis: $|\psi_j^{\mathbf{k}}(t)\rangle = \sum_{\nu} C_{j\nu}^{\mathbf{k}}(t)|\phi_\nu(\mathbf{R}_J(t))\rangle$

$$S^{\mathbf{k}}\dot{C}_j^{\mathbf{k}} = -\mathrm{i}H^{\mathbf{k}}C_j^{\mathbf{k}} - B^{\mathbf{k}}C_j^{\mathbf{k}}$$

Time-evolution of coefficients

Dynamics of the Hamiltonian

Change in basis

NoMaR@ZIB

MD

Geometry → Evolve sates (TDDFT) → Forces on ions → Move ions: Newton's law

$$\mathbf{R}_J(t)$$

$$\mathbf{F}_{ext} + \mathbf{F}_{HF} + \mathbf{F}^{(1)}_{corr} = M_J \ddot{\mathbf{R}}_J$$

$$\mathbf{F}_{HF} = -\int \mathrm{d}\mathbf{r}\, n \frac{\partial v_{nucl}}{\partial \mathbf{R}_J}$$

$$-\mathrm{tr}[C^{\dagger}(\underline{\mathcal{H}_J} + HS^{-1}\underline{\mathcal{S}_J})C] - \mathrm{cc}$$

1st order correction to the forces: changes in ***H*** and ***S*** matrices due to the ionic motion

$$\mathbf{F}_{corr} = \mathbf{F}_{core} + \mathbf{F}_{val}$$

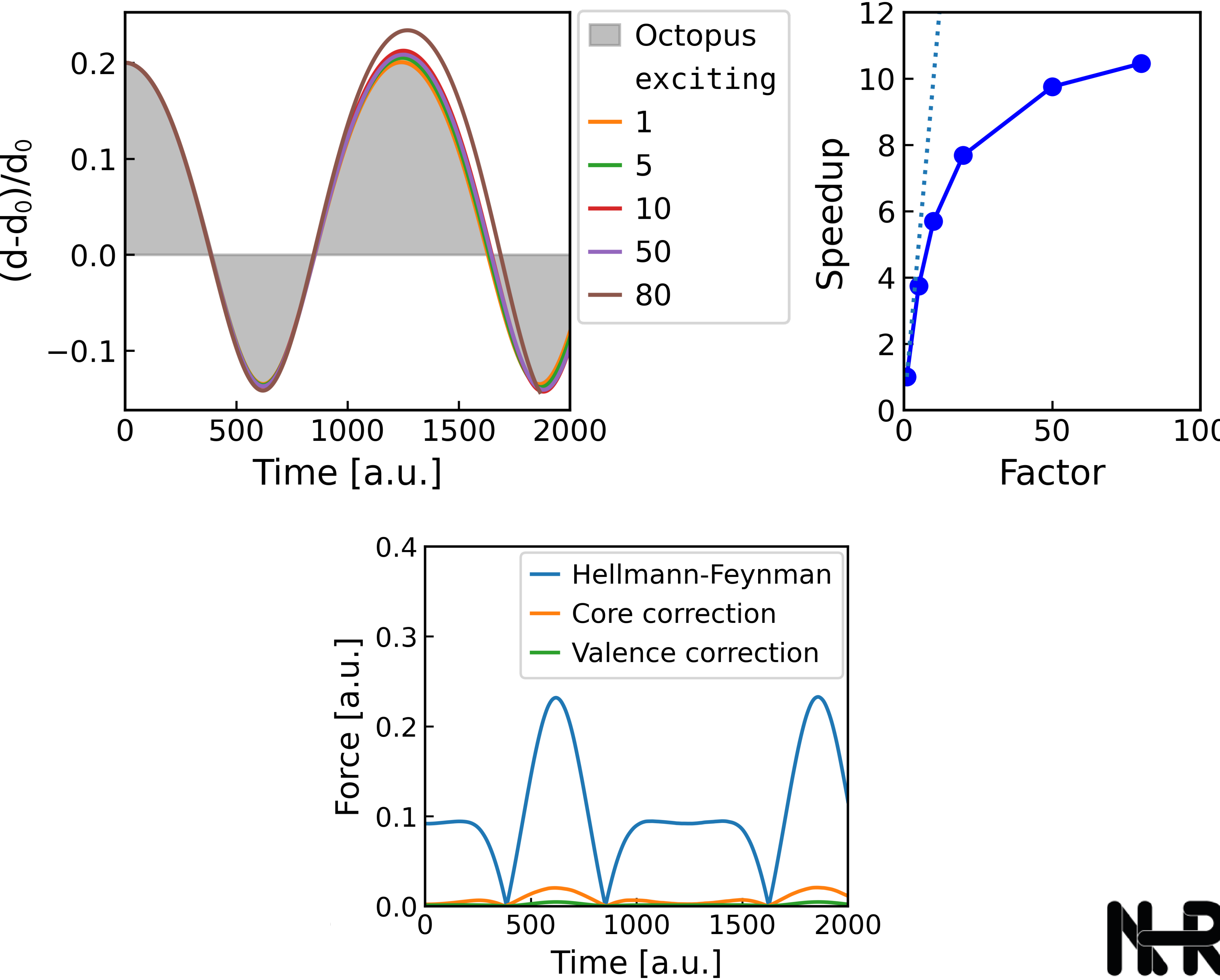
MD

$$\hat{H}_{el}(t, \mathbf{R}_J(t))|\psi_{el}(t)\rangle = \mathrm{i}\frac{d}{dt}|\psi_{el}\rangle$$

$$\mathbf{F}_{ext} + \mathbf{F}_{HF} + \mathbf{F}^{(1)}_{corr} = M_J \ddot{\mathbf{R}}_J$$

$$\Delta t_{el}$$

$$\Delta t_N = n \Delta t_{el}$$



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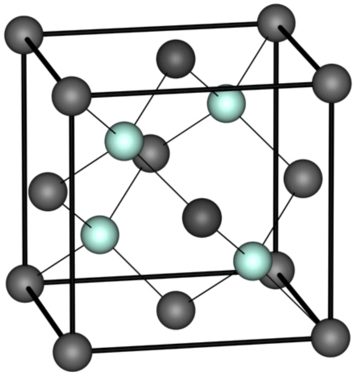
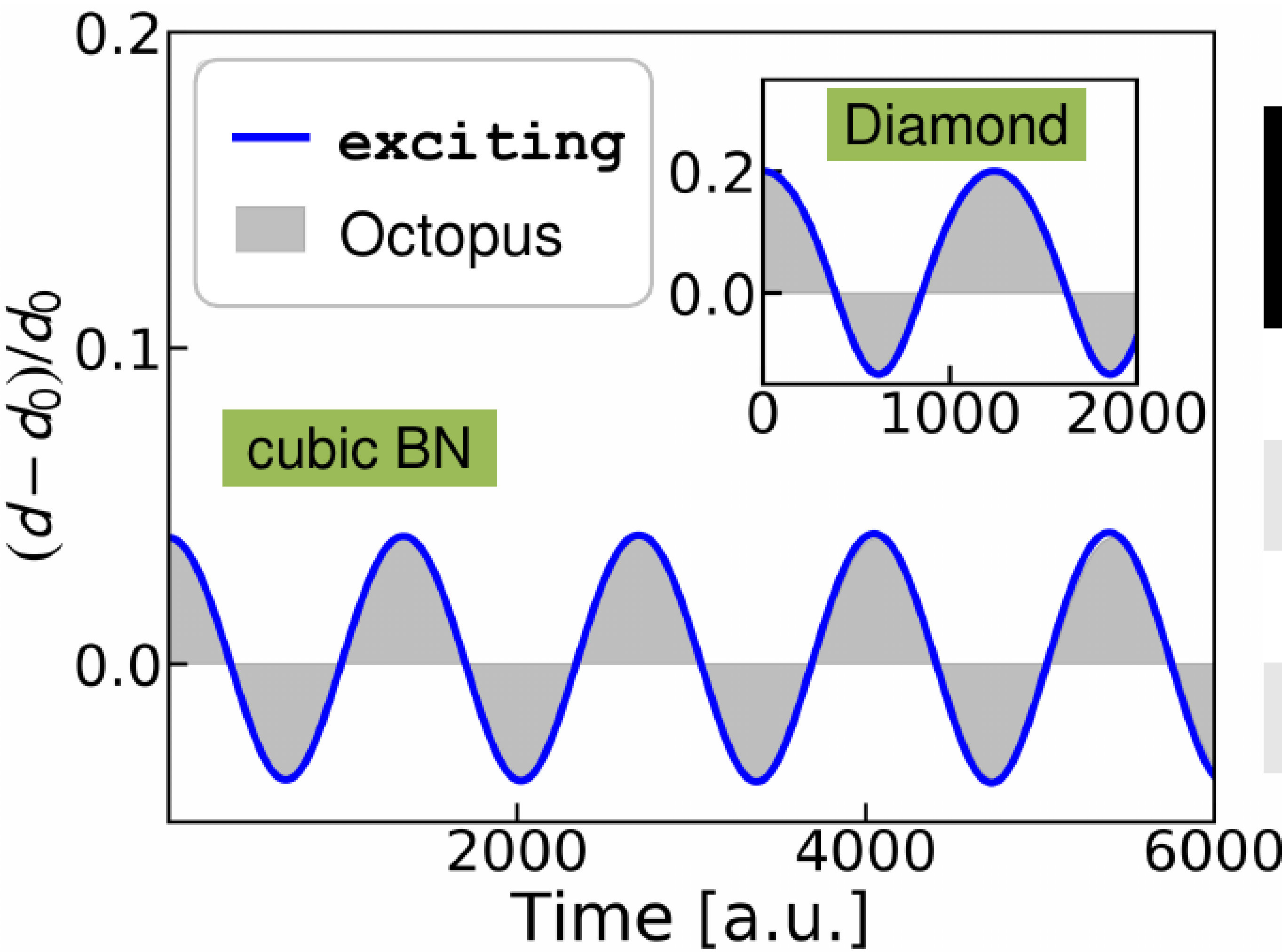


$$\mathbf{b}_1 = (0.00, 0.00, 0.00)$$
$$\mathbf{b}_2 = (0.25, 0.25, 0.25)$$

↓

$$\mathbf{b}_1 = (0.00, 0.00, 0.00)$$
$$\mathbf{b}_2 = (0.25 + \delta, 0.25 + \delta, 0.25 + \delta)$$



	Period [a.u.]	
	C	BN
exciting	1239	1349
Octopus	1242	1354
GS - lin	1091	1294
GS - non	1249	-

exciting

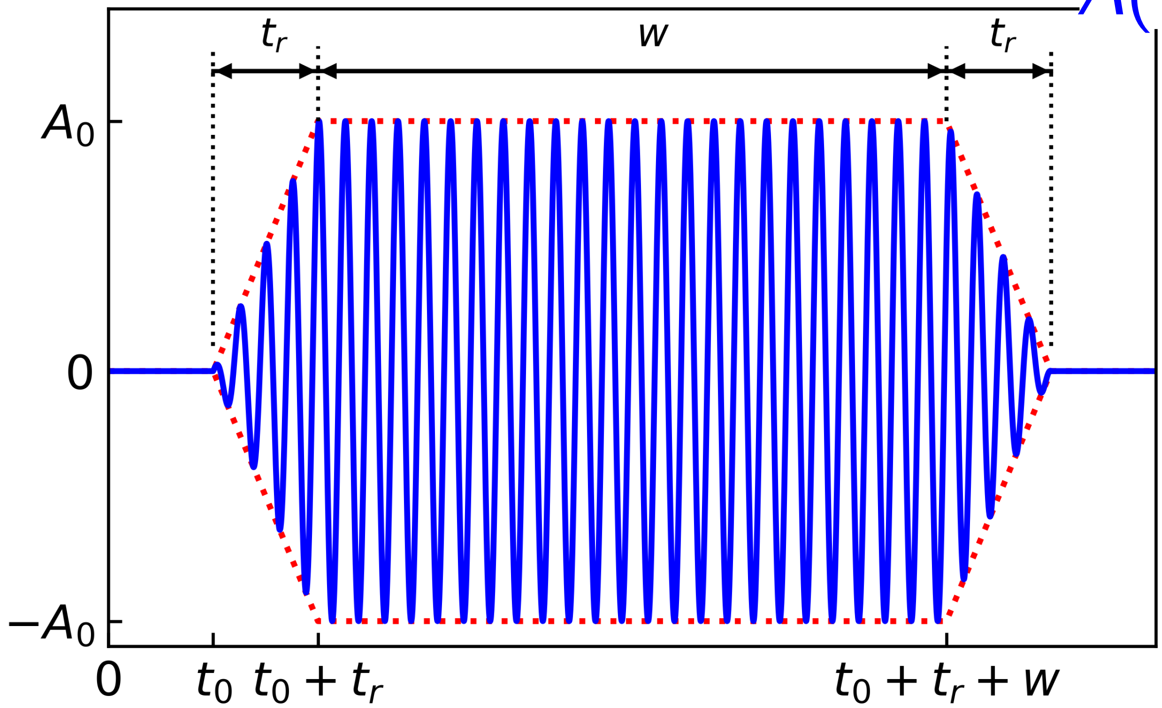
```
<xs
   xstype="RT-TDDFT"
   ngridk="4 4 4"
   rgkmax="5.0d0"
   vkloff="0.01 0.02 0.004"
   nempty="5"
   nosym="true"
   reducek="false">
   <realTimeTDDFT
      propagator="AETRS"
      timeStep="0.25d0"
      endTime="50.d0"
      printTimingGeneral="true"
      calculateNExcitedElectrons="true"
      printAfterIterations="1">
      <laser>
         <trapCos
            amplitude="1.0d0" omega="1.0d0" phase="0.d0"
            t0="0.25d0" riseTime="5.d0" width="30.d0"
            direction="x" />
      </laser>
   </realTimeTDDFT>
</xs>
```

exciting

- Laser pulse

```
<laser>
   <trapCos
      amplitude="1.0d0" omega="1.0d0" phase="0.d0"
      t0="0.25d0" riseTime="5.d0" width="30.d0"
      direction="x" />
</laser>
```

$$A(t) = A_0 f(t) \cos(\omega t + \phi)$$



exciting

- Laser pulse

```
<laser>
   <sinSq
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      amplitude="1.0d0" pulseLength="5.d0" direction="y"/>
</laser>
```
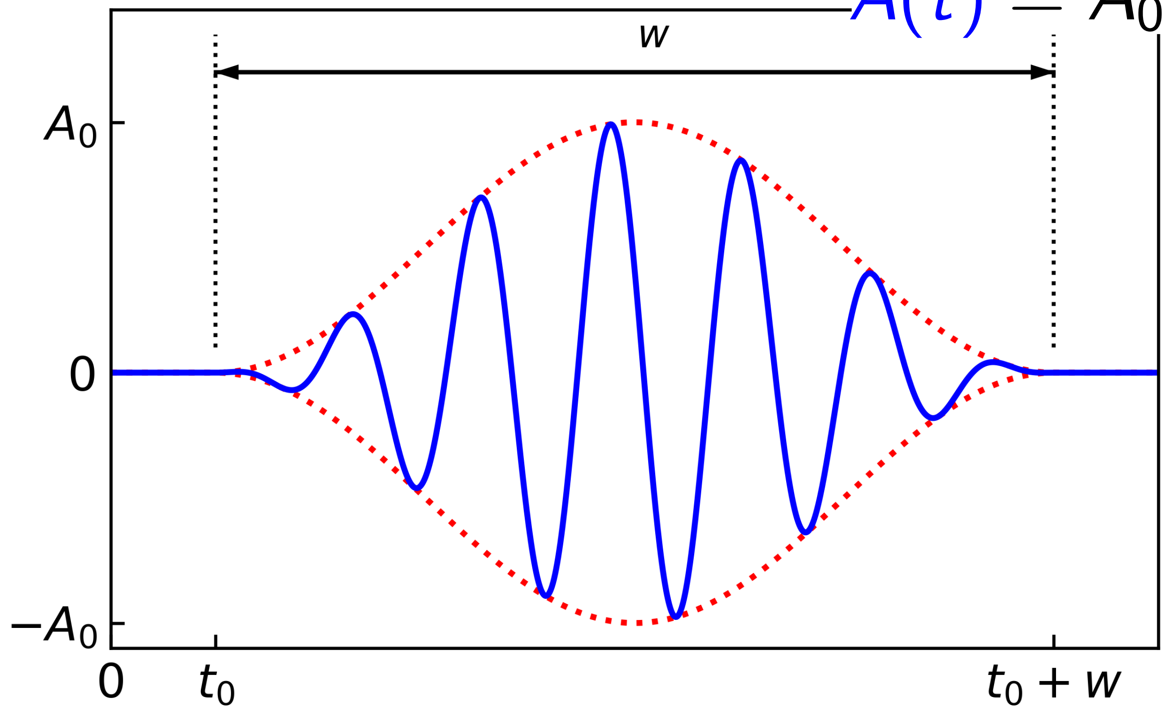

$$A(t) = A_0 f(t) \cos(\omega t + \phi)$$



NOMAD@ZIB

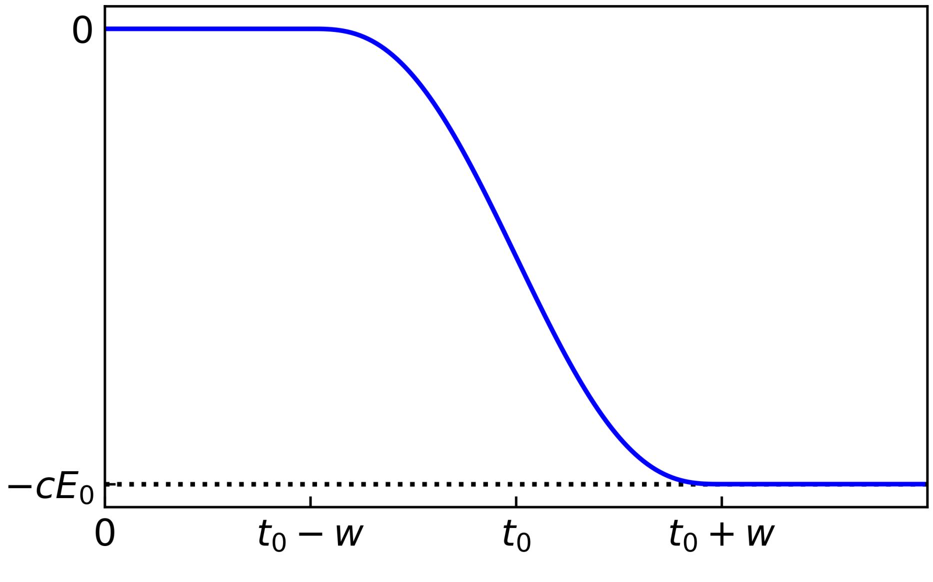
exciting

- Laser pulse

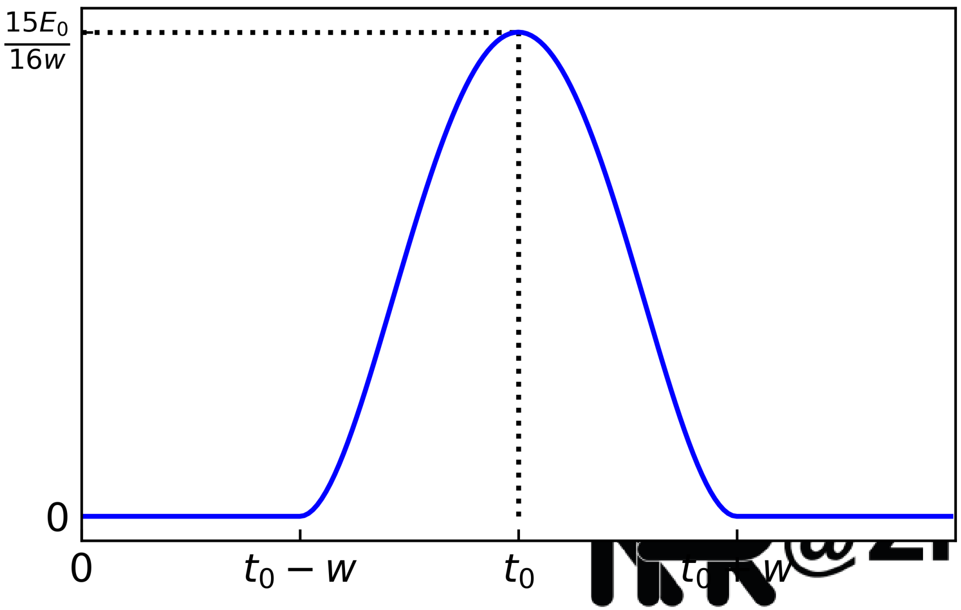
```
<laser>
   <kick t0="1.d0" width="0.1d0" amplitude="0.01d0"
         direction="z"/>
</laser>
```

E_0

$A(t)$



$$E(t) = -\frac{1}{c}\frac{dA}{dt}$$



exciting

- MD

```
<xs … >
    <realTimeTDDFT
       timeStep="0.25d0"
    …
    </realTimeTDDFT>
</xs>

<MD
  type="Ehrenfest"
  printAllForces="true"
  TimeStep="1.0d0"
  integrationAlgorithm="HeunSimplified"/>
</MD>
```

Δt_{el}

$\mathbf{F}_{ext} + \mathbf{F}_{HF} + \mathbf{F}_{core} + \mathbf{F}_{val}$

$\Delta t_N = n \Delta t_{el}$

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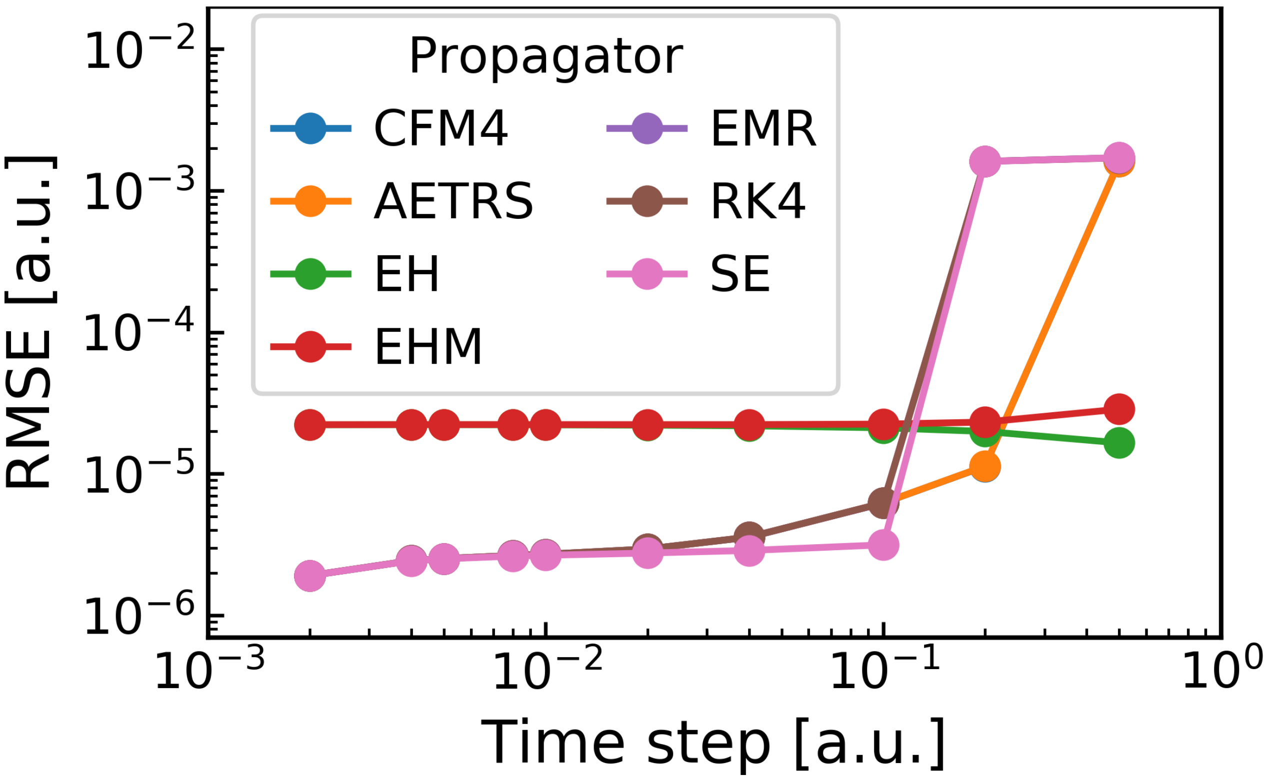
Convergence

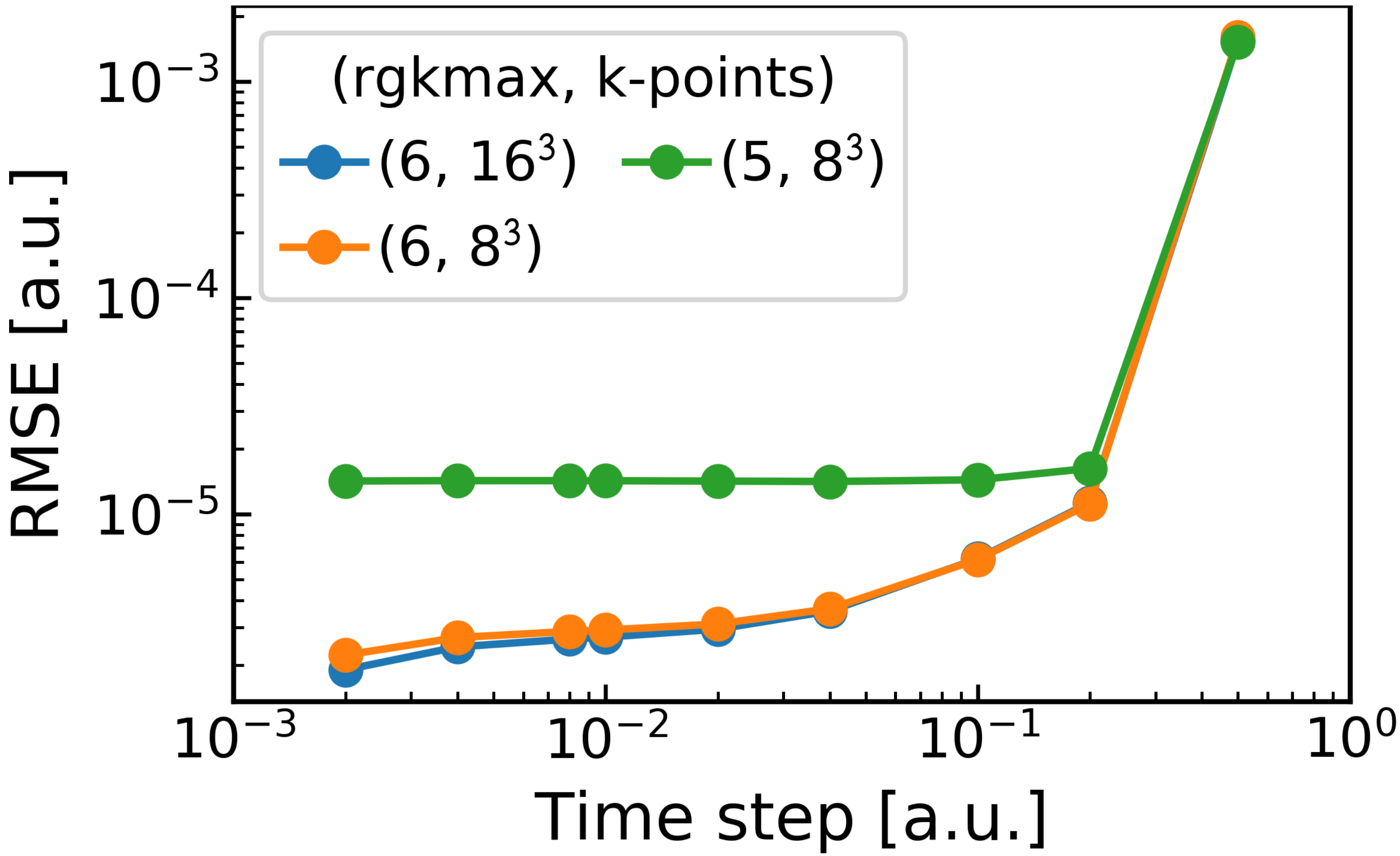
- Critical parameters
  - Time step
  - Basis (rgkmax and lo)
  - k-points

Convergence



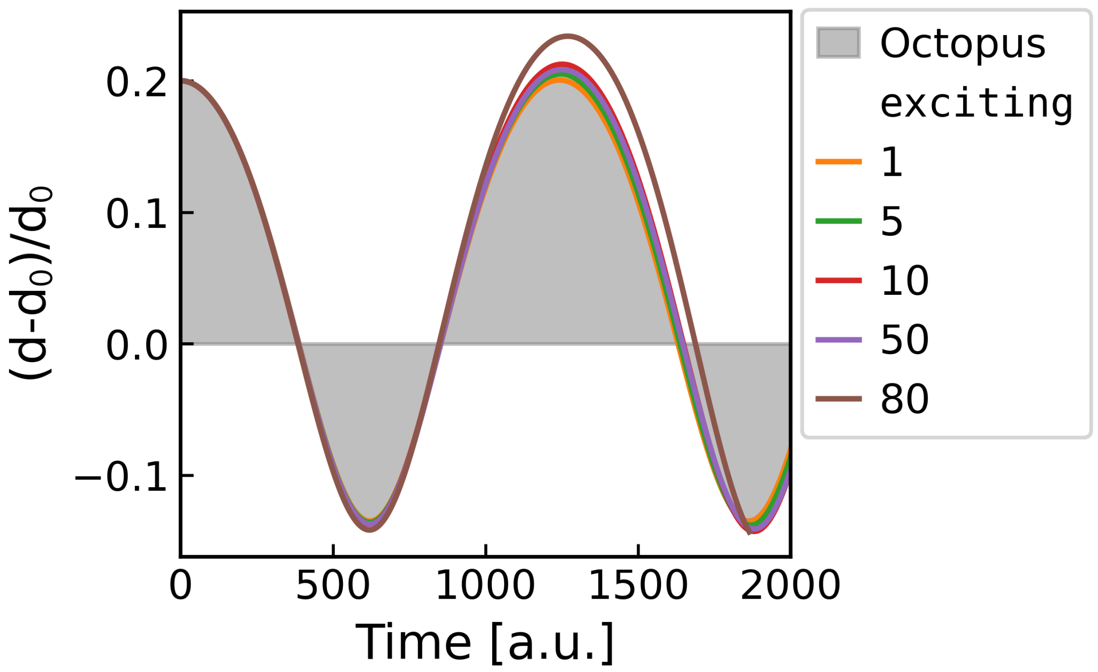
Integrator	Time
SE	1.00
EMR	1.04
RK4	1.08
EHM(5)	1.44
EH(5)	1.46
AETRS	1.92
CFM4	1.97
EH(50)	3.11
EHM(50)	3.16
EHM(100)	8.28
EH(100)	10.68

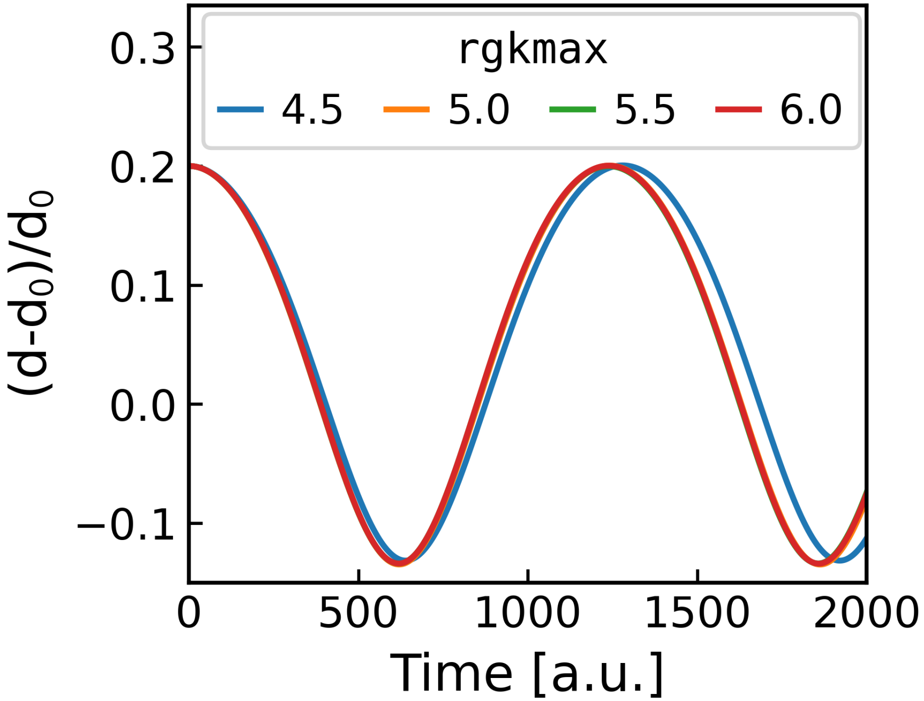
Convergence



Convergence – MD

$$\Delta t_N = n \Delta t_{el}$$





Tutorials

☛ TDDFT:

【b】 Excited states from TDDFT

【b】 Real-time TDDFT

【a】 q-dependent TDDFT

【a】 Many-body kernels for TDDFT calculations

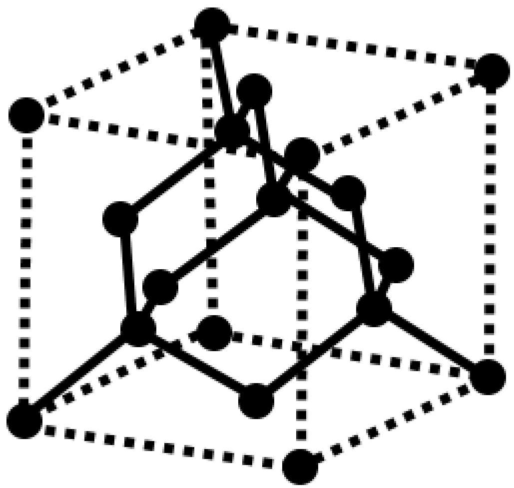
【a】 Simulating pump-probe spectroscopy with RT-TDDFT

【a】 Studying higher-harmonic generation using RT-TDDFT

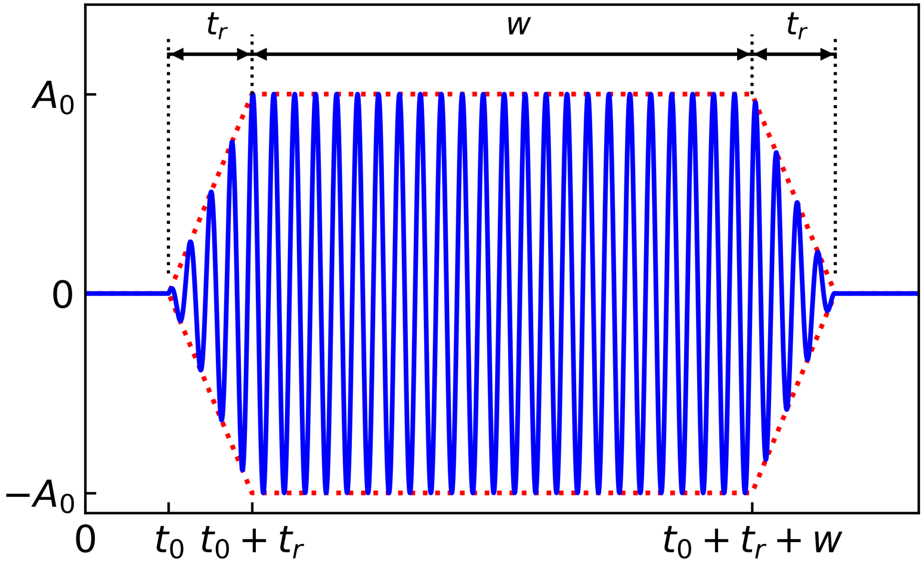
【a】 Real-time TDDFT combined with Molecular Dynamics

Tutorial: RT-TDDFT

- Diamond submitted to a laser with trapezoidal envelope



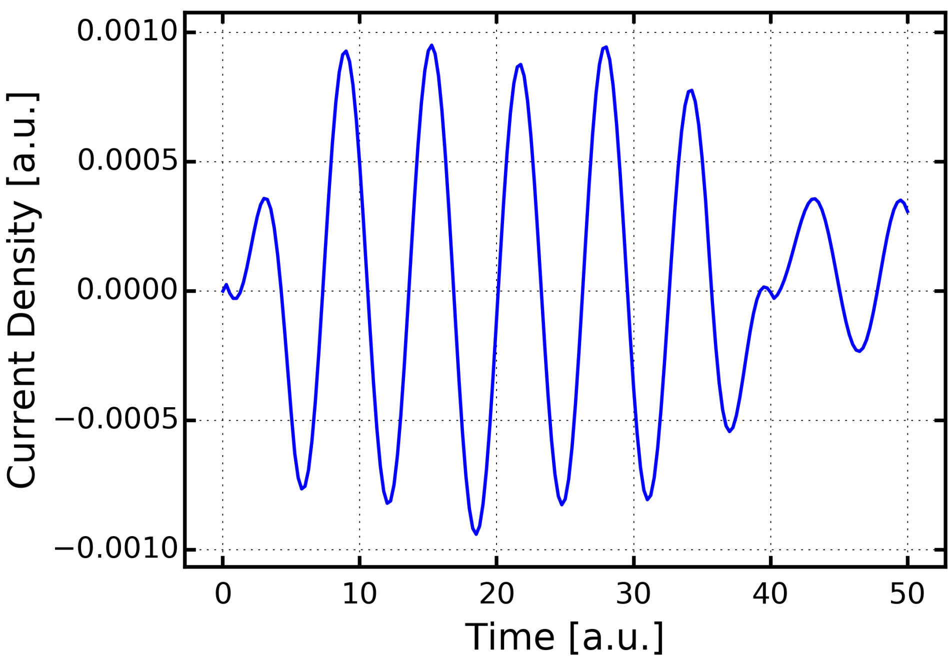
Diamond Structure

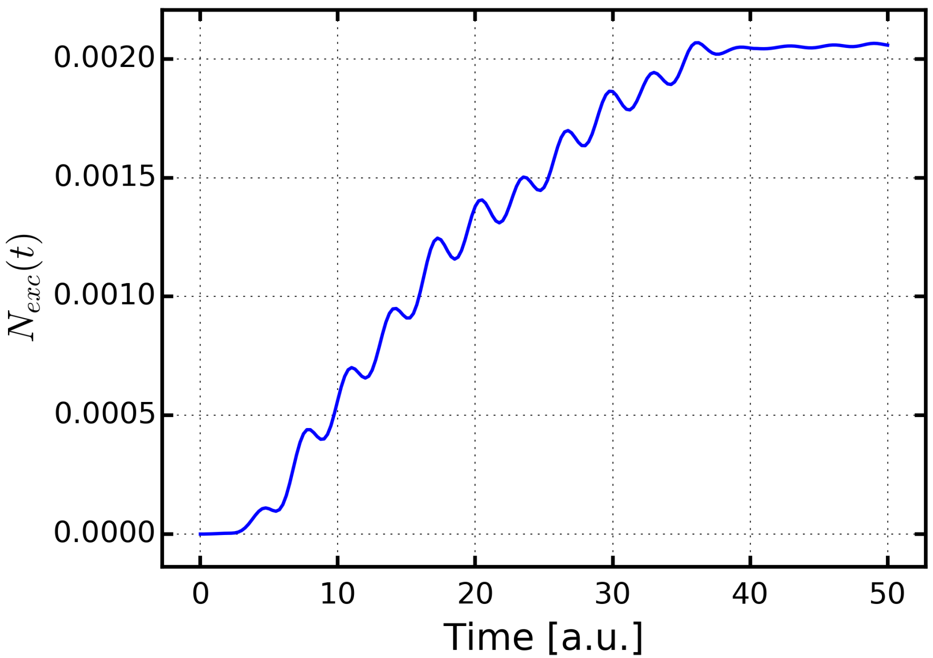


A0 = 1.0 a.u., w = 30 a.u., 27.2 eV
tr = 5.0 a.u.

Tutorial: RT-TDDFT

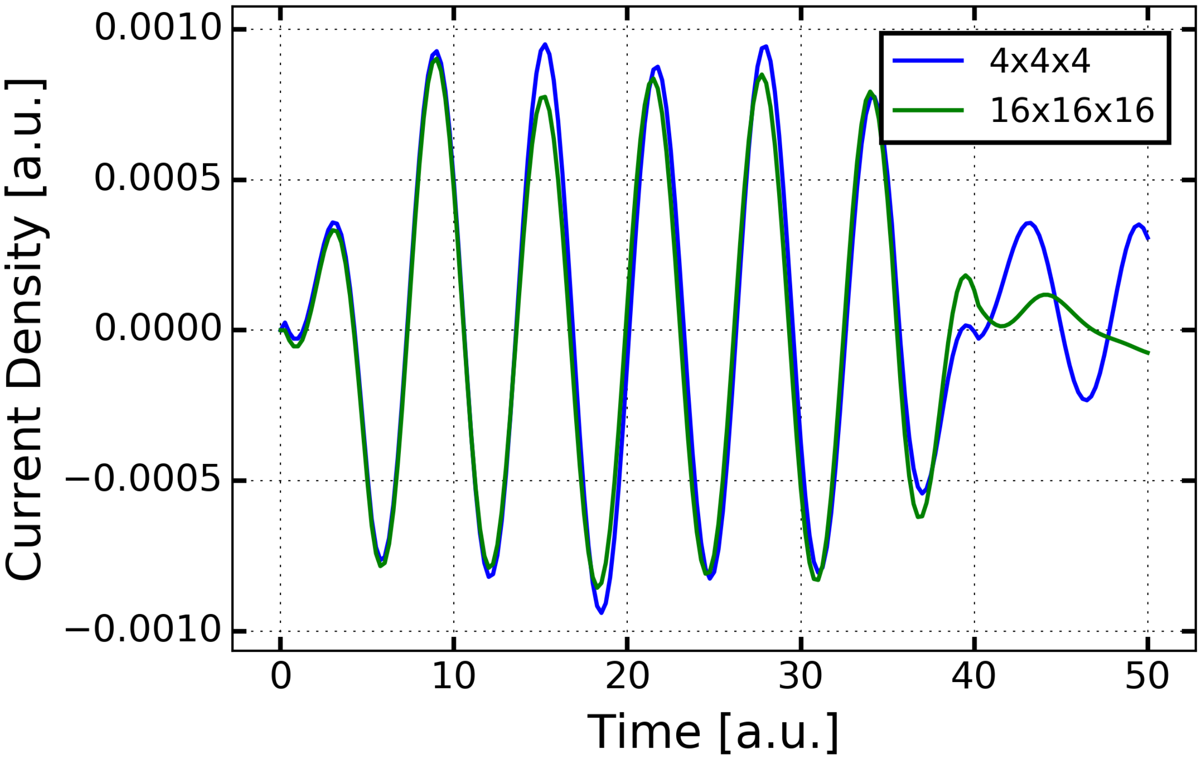
- Currend density and Nexc





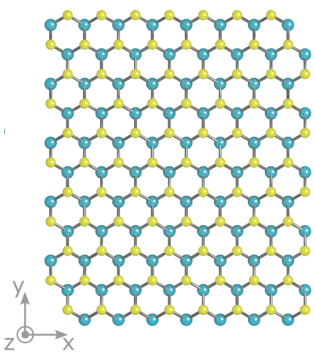
Tutorial: RT-TDDFT

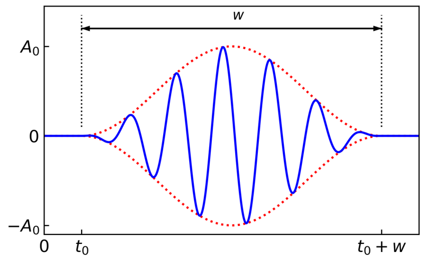
- Convergence: k-points



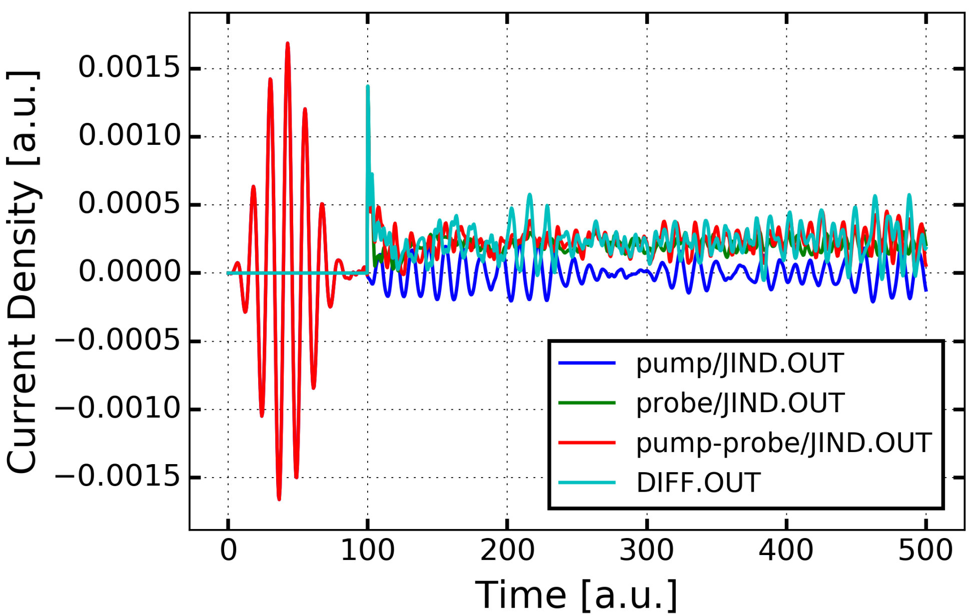
Tutorial: Pump-probe

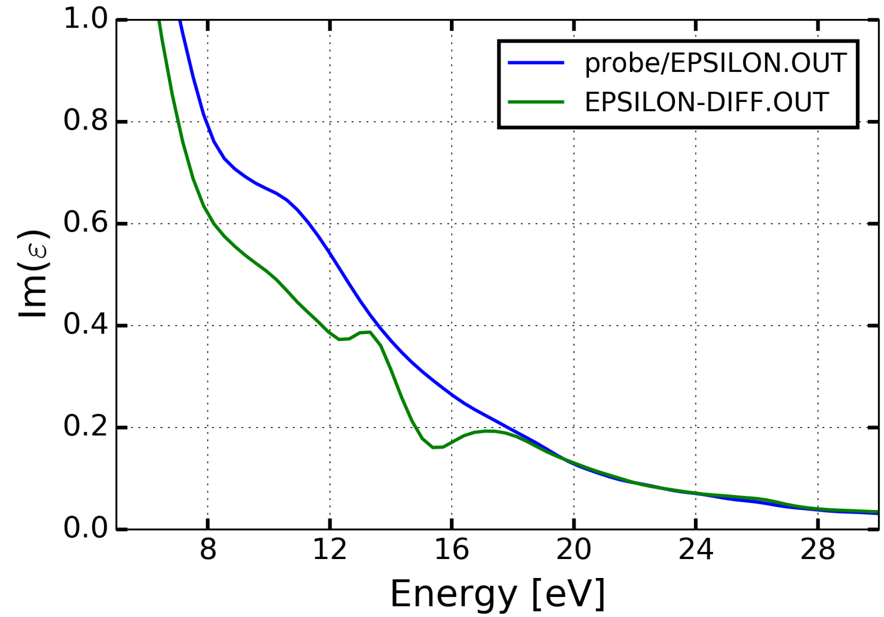
MoS_2





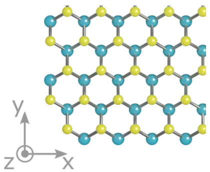
A0 = 20 a.u., w = 80 a.u., 13.6 eV

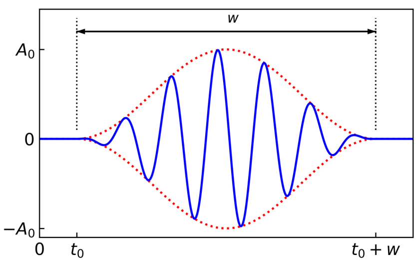


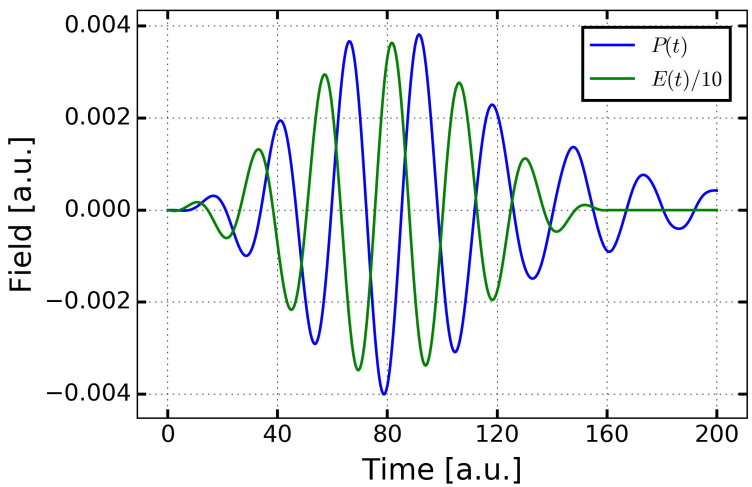


Tutorial: HHG

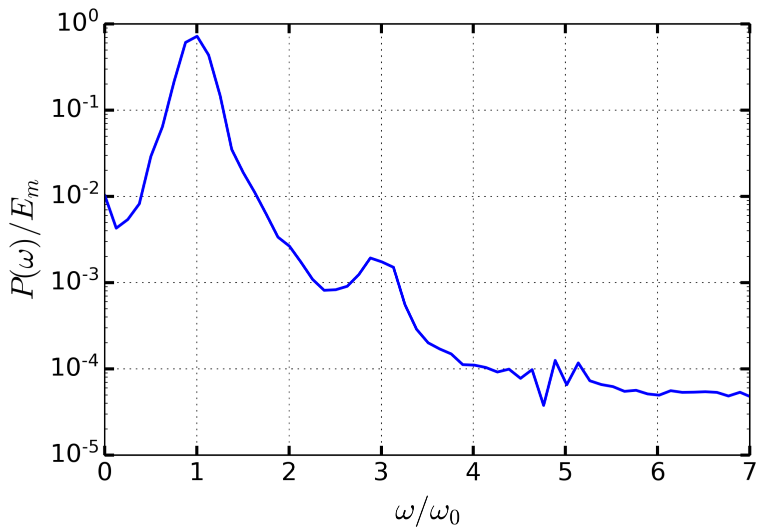
MoS$_2$

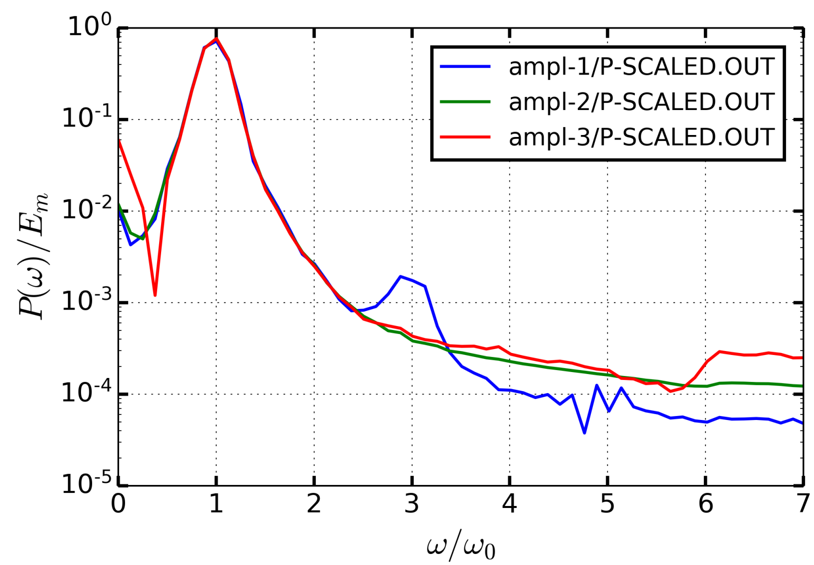






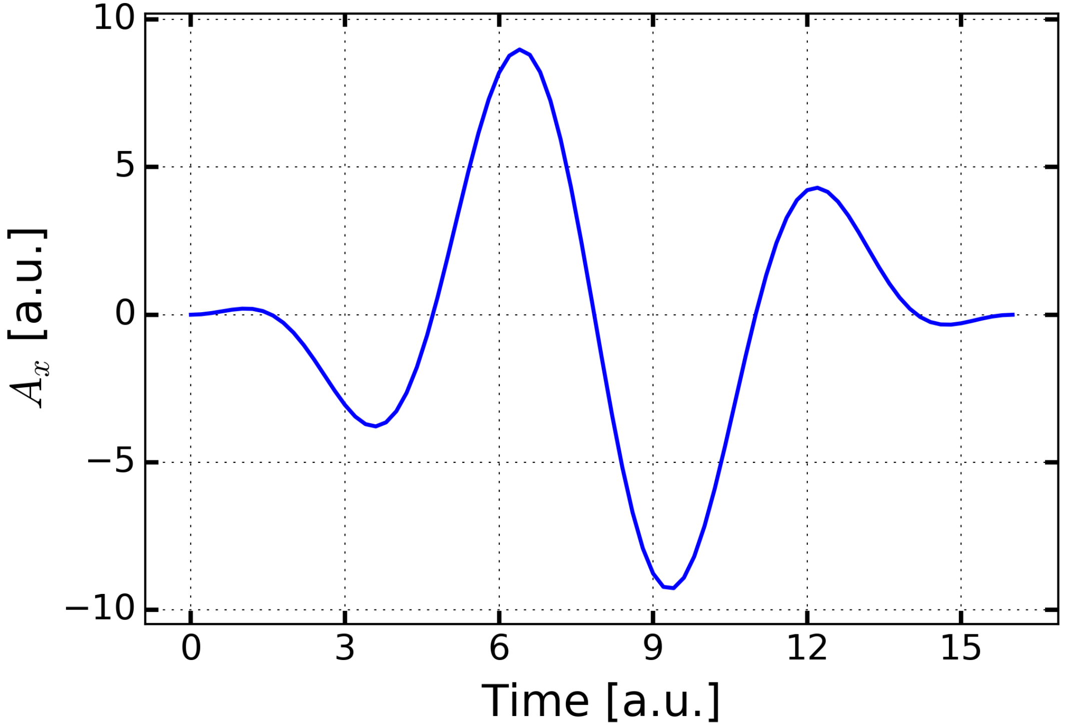
A0 = 20 a.u.,
w = 6.8 eV
I = 4.6×10^{13} W/cm^2





Tutorial: MD

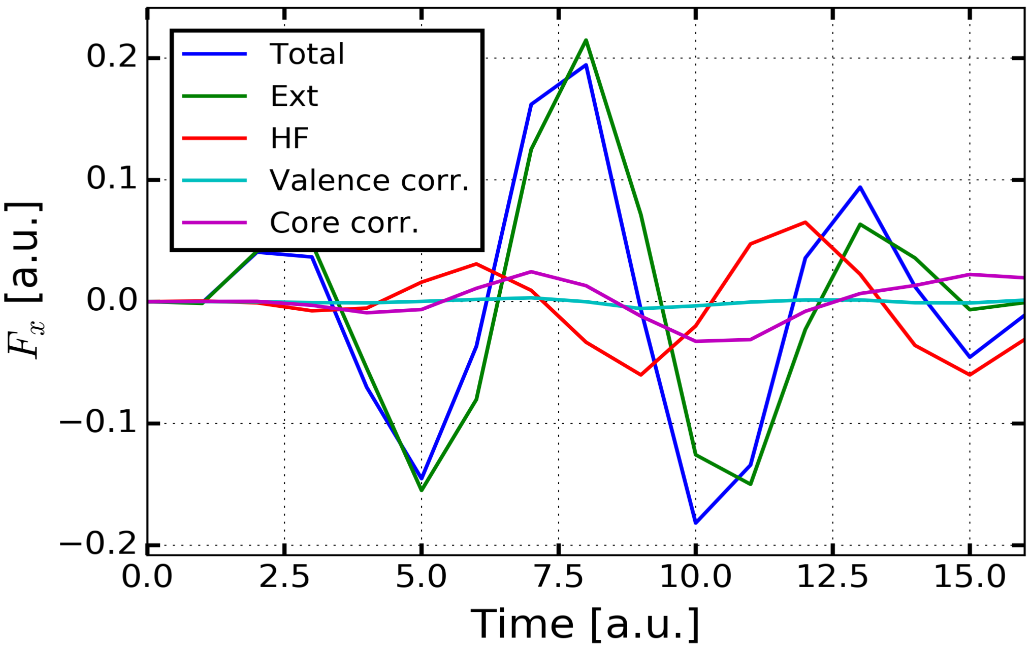
- Ehrenfest Dynamics in BN

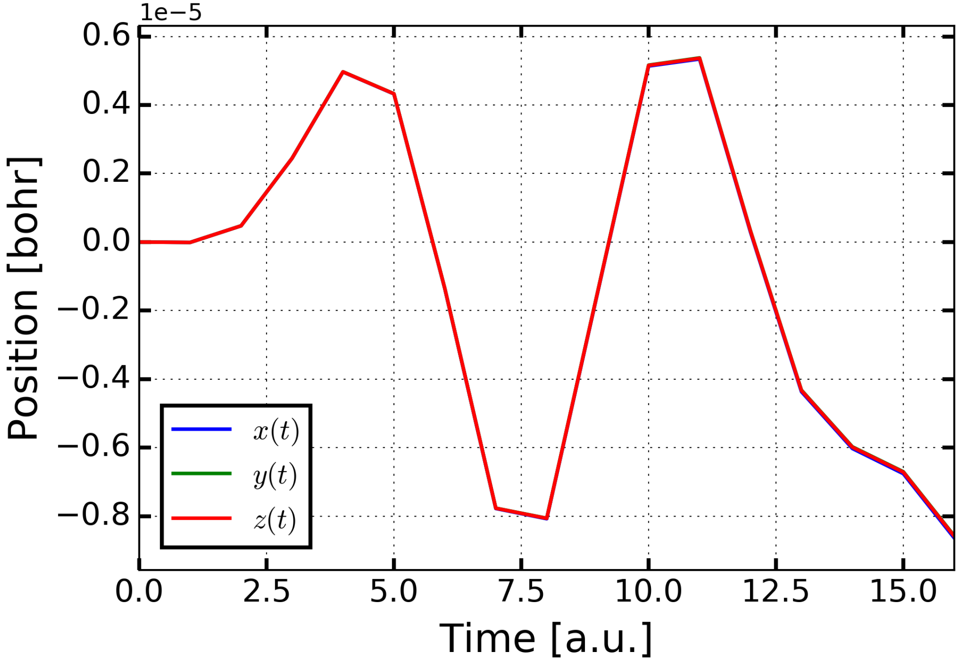


A0 = 10 a.u., w = 16 a.u., 27.1 eV

Tutorial: MD

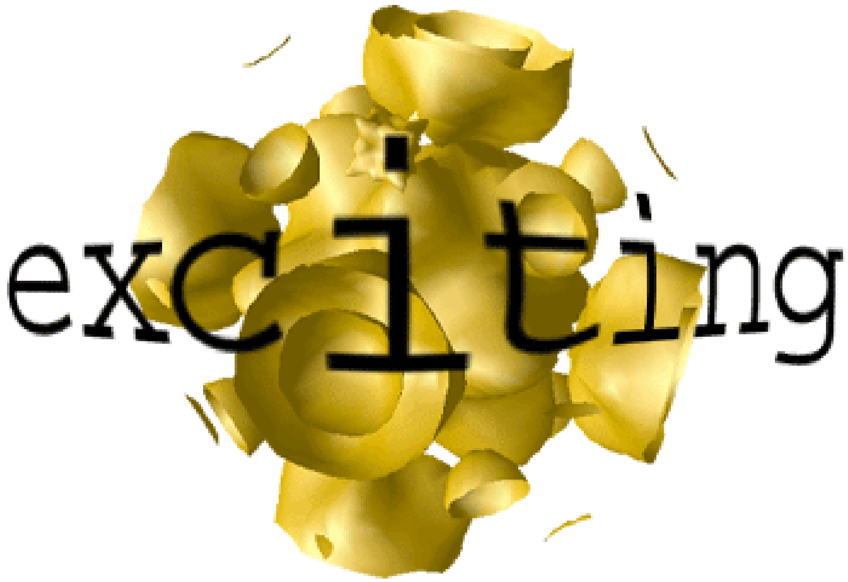
- Forces on B
- Position of B





Summary

- Introduction
- RT-TDDFT
- MD
- **exciting**
- Tutorials



Thank you for your attention