Science and Technology Facilities Council

Scientific Computing

Real-Time Time-Dependent Density Functional Theory in ONETEP

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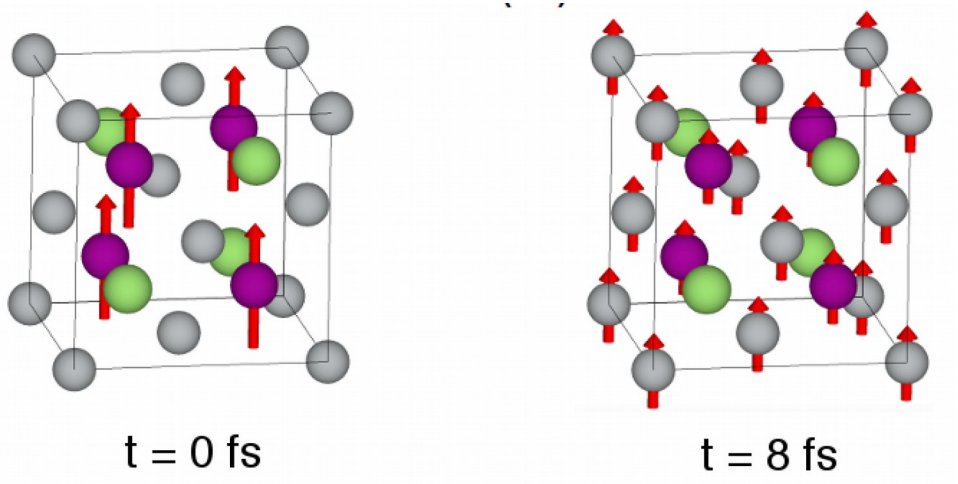
What is RT-TDDFT?

$$i\frac{\partial}{\partial t}\psi_j(\mathbf{r},t) = \left[\frac{1}{2}\left(-i\boldsymbol{\nabla} - \frac{1}{c}\mathbf{A}_{\text{ext}}(t)\right)^2 + v_{\text{ext}}(\mathbf{r},t) + v_{\text{HXC}}[n](\mathbf{r},t)\right]\psi_j(\mathbf{r},t)$$

$$n(\mathbf{r},t) = \sum_j |\psi_j(\mathbf{r},t)|^2$$

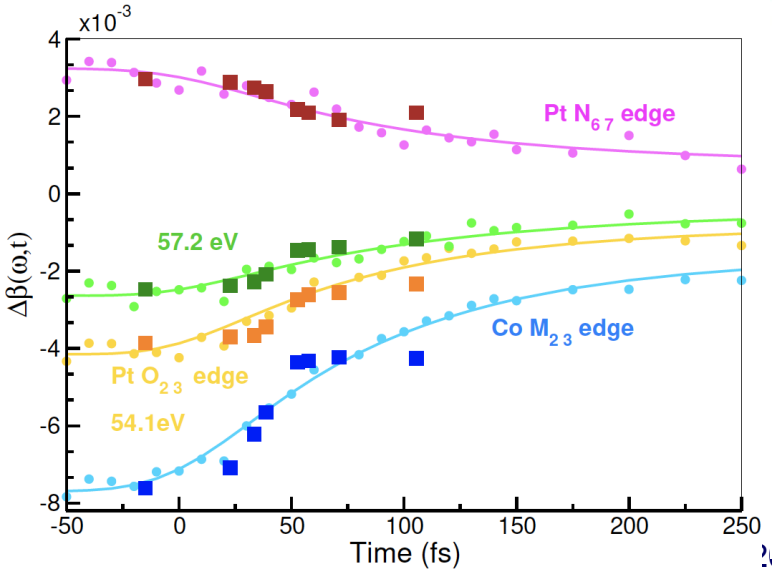
- Extension of DFT to calculate electron dynamics due to time-dependent phenomena (e.g. laser pulses)
- **Non-linear** effects automatically captured. Pump-probe.
  - Normally TDDFT used for absorption spectra in linear-response regime.
- Adiabatic approximation used for XC potential
- Good for first ~100fs (can add electron-ion coupling to go longer).

RT-TDDFT uses

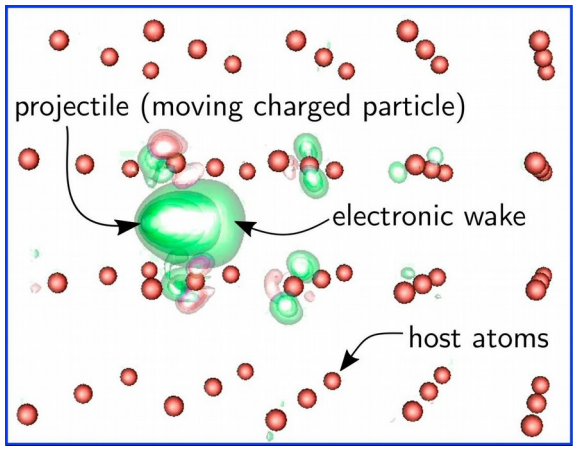


- Optically induced inter-site spin transfer

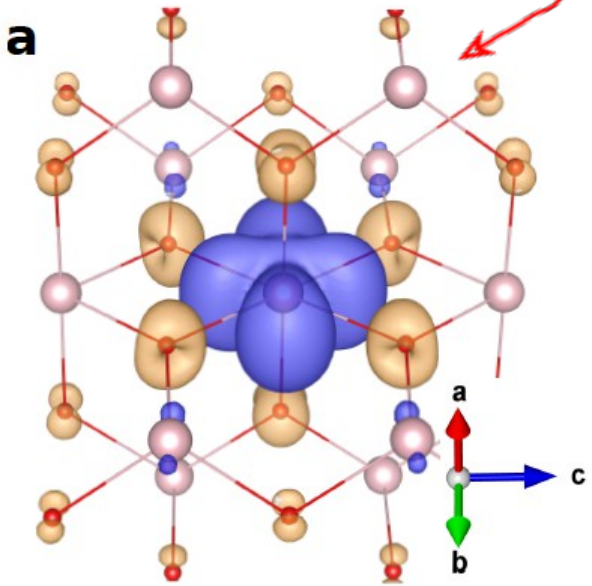
doi:10.1038/srep38911

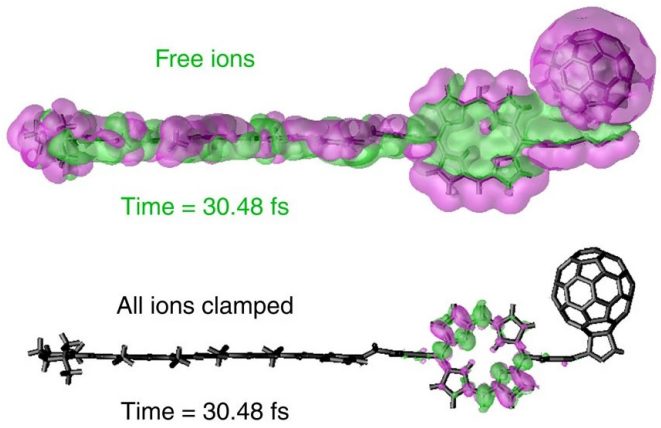


Doi: 10.1103/PhysRevLett.124.077203



doi: 10.1016/j.commatsci.2018.03.064





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ONETEP+TDDFT I:LvN equation

TDKS Hamiltonian

$$\hat{H}_{\mathrm{S}}(t) = \hat{T} + \hat{V}_{\mathrm{XC}}[n(t)] + \hat{V}_{\mathrm{ext}} + \mathbf{E}(t) \cdot \mathbf{r}$$

where $\mathbf{E}(t)$ is time-dependent electric field, i.e. the laser.
Then the TDKS equation is

$$i\partial_t |\psi(t)\rangle = \hat{H}_{\mathrm{S}}(t)|\psi(t)\rangle$$

which leads to the quantum Liouville equation (or Liouville-von-Neumann equation)

$$i\partial_t \rho = -i[\hat{H}_{\mathrm{S}}(t), \rho]$$

$$i\dot{\mathbf{K}} = \mathbf{S}^{-1}\mathbf{H}\mathbf{K} - \mathbf{K}\mathbf{H}\mathbf{S}^{-1}$$

ONETEP+TDDFT II:Propagators

$$i\dot{\mathbf{K}} = \mathbf{S}^{-1}\mathbf{H}\mathbf{K} - \mathbf{K}\mathbf{H}\mathbf{S}^{-1}$$

$$\mathbf{K}(t) = \mathbf{U}(t,t_0)\mathbf{K}(t_0)\mathbf{U}^{\dagger}(t,t_0) \qquad \mathbf{U}(t,t_0) = \mathcal{T}e^{-i\int_{t_0}^{t} dt' \mathbf{S}^{-1}\mathbf{H}(t')}$$

$$\mathbf{U}^{\mathrm{CN}}(t+\Delta t,t) = (\mathbb{1} + i\frac{1}{2}\Delta t\mathbf{S}^{-1}\mathbf{H})^{-1}(\mathbb{1} - i\frac{1}{2}\Delta t\mathbf{S}^{-1}\mathbf{H})$$

- Other propagators: 4th order taylor, RK4, AETRS, Cf4 magnus
- Often need H at times at or between t+Δt
  - Extrapolate H
  - In practice, self-consistency at each timestep ignored

ONETEP+TDDFT III:Solids

- Gauge transform electric field in dipole approximation to a purely time-dependent vector potential

$$\hat{H}_{\mathrm{S}}(t) = \frac{1}{2}\left(\hat{\mathbf{p}} - \frac{1}{c}\mathbf{A}(t)\right)^2 + \hat{V}_{\mathrm{XC}}[n(t)] + \hat{V}_{\mathrm{ext}}$$

$$= \hat{T} + \hat{V}_{\mathrm{XC}}[n(t)] + \hat{V}_{\mathrm{ext}} - \frac{1}{c}\hat{\mathbf{p}} \cdot \mathbf{A}(t)$$

$$\mathbf{A}(t) = -\frac{1}{c}\frac{\partial \mathbf{E}(t)}{\partial t}$$

ONETEP+TDDFT IV:RTLR

$$\boldsymbol{\alpha}(\omega) = \frac{\boldsymbol{\mu}(\omega)}{\mathbf{E}(\omega)} \qquad \boldsymbol{\mu}(t) = \int d^3 r \; \boldsymbol{r}\, n(\boldsymbol{r}, t) \qquad \boldsymbol{\mu}(\omega) = \mathcal{F}(\boldsymbol{\mu}(t) - \boldsymbol{\mu}(0))$$

Absorption Spectrum

$$\sigma_A(\omega) = \frac{4\pi\omega}{c}\Im\bar{\alpha}(\omega)$$

$$\boldsymbol{\sigma}_{\mu\nu}(\omega) = \frac{\mathbf{J}_\mu(\omega)}{\mathbf{E}_\nu(\omega)} \qquad \epsilon(\omega) = 1 + i\frac{4\pi}{\omega}\sigma(\omega)$$

Delta 'kick'

$$E(t) = \kappa\,\delta(t)$$

$$E(\omega) = \kappa$$

$$A(t) = -c\,\kappa\,\Theta(t)$$

$$\rho(\mathbf{r}, \mathbf{r}', t = 0^+) = e^{-i\boldsymbol{\kappa}\cdot(\mathbf{r}'-\mathbf{r})}\rho(\mathbf{r}, \mathbf{r}', t = 0)$$

$$\mathbf{K} \approx \mathbf{K}_0 + i\vec{\kappa}\cdot(\mathbf{K}_0\vec{\mathbf{D}}\mathbf{S}^{-1} - \mathbf{S}^{-1}\vec{\mathbf{D}}\mathbf{K}_0)$$

Running RT-TDDFT in ONETEP I

- Setup the same as LR-TDDFT
  - GS (SINGLEPOINT)
  - COND

- Basic input
  - TASK: TDDFT
  - tddft_duration e.g. 413.4 au = 10fs
  - tddft_timestep e.g. 0.01 au

Running RT-TDDFT in ONETEP II: Lasers

- Lasers Block (up to 10)

$$\boldsymbol{E}(t) = \boldsymbol{A}\, f(t, t_{0,} \sigma) \sin(\omega(t - t_0) + \phi) \qquad f(t, t_{0,} \sigma) = \left(e^{-\frac{(t-t_0)^2}{2\sigma^2}} \right)$$

```
%block lasers
E -0.0017 0.0 0.0 0.18374246655 0.0 444.5 247.256104728
%endblock lasers
```

- Type: E,A,D
- Amplitude+polarization
- Envelope: Gaussian centered at t_0 with FWHM $d = 2\sqrt{2\ln 2}\,\sigma$
- Carrier frequency ω and phase φ

Running RT-TDDFT in ONETEP III: Other input parameters

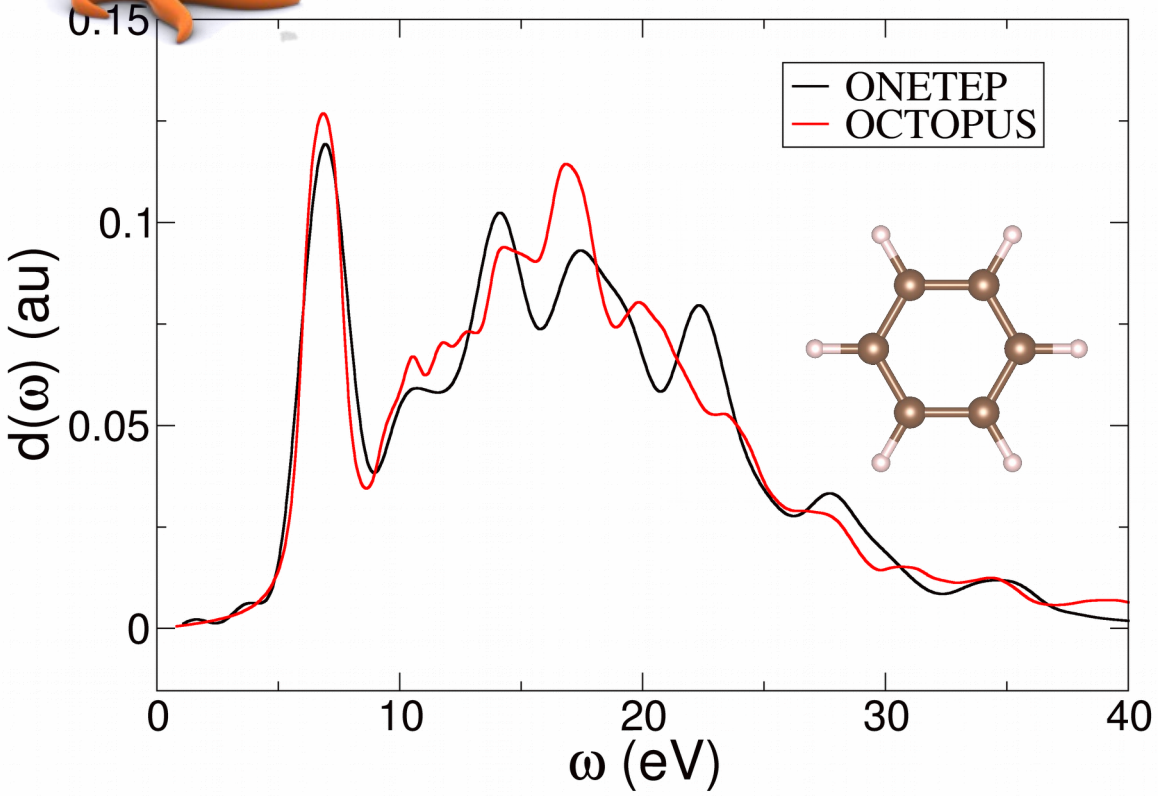
- Kick: tddft_dipole_kick_strength 0.001 0.00 0.00
- Restart: writes kernel periodically (and at end)
  - tddft_write_restart: 100
  - tddft_restart: T
  - tddft_restart_from: 100
- Outputinterval: write buffer to reduce I/O
  - tddft_output_interval 100
- tddft_inv_overlap_exact, tddft_eig_analysis, tddft_resolve_gs, tddft_bare_ks, tddft_fourier, tddft_hub_proj_only

Running RT-TDDFT in ONETEP IV: Outputs

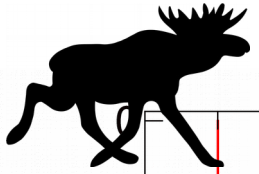
- **Electric fields** (and vector potential)
- **Dipole moment**
- **Current**
  - (for finite systems, derivative of dipole)
  - Prints total and paramagnetic currents
- **Energy**: Norm, idempotency error, E[n], E_{KS}[n]
- **Forces** (if requested)

Comparison to other TDDFT codes

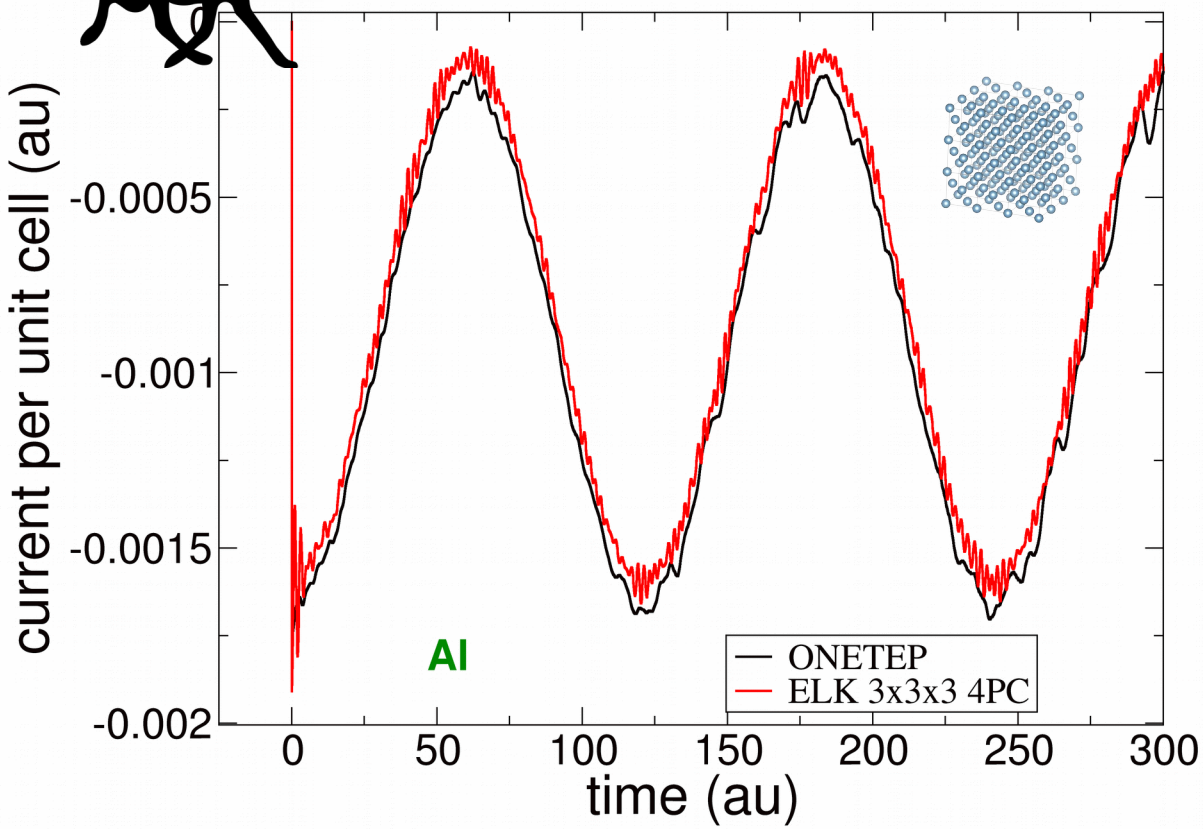
Benzene



OCTOPUS: www.octopus-code.org
Big-Prefactor O(N^2)

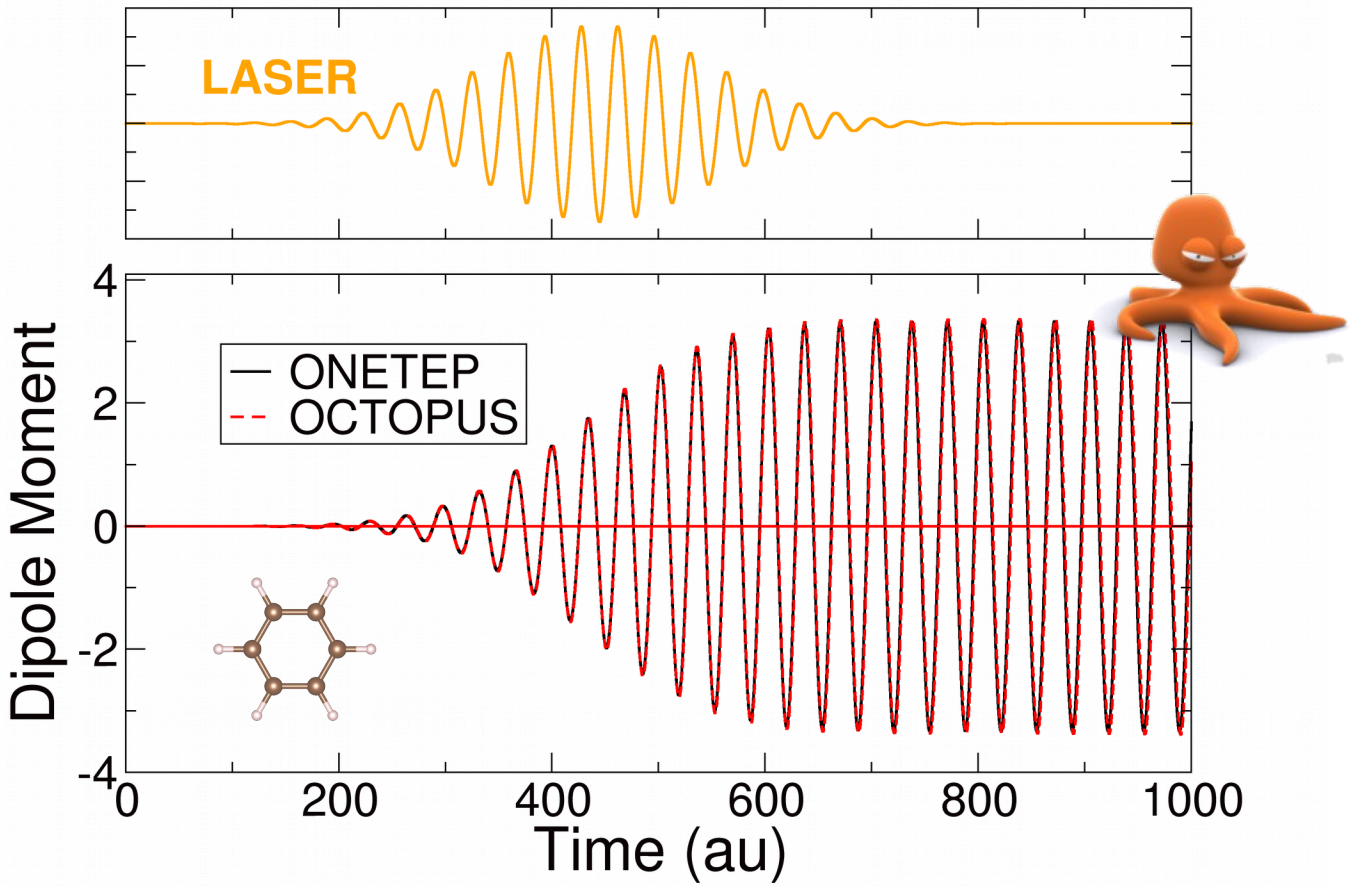


Aluminium (108 atoms)



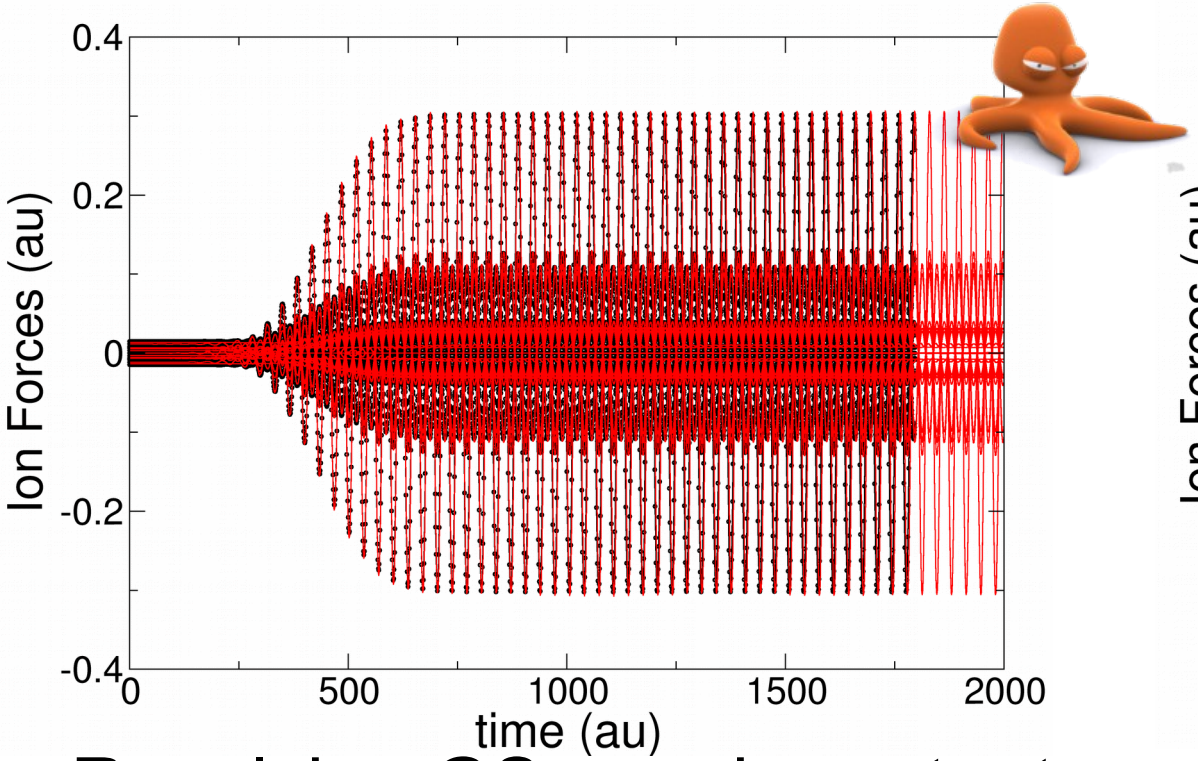
ELK: elk.sourceforge.io
O(N^3) (but larger timestep possible)

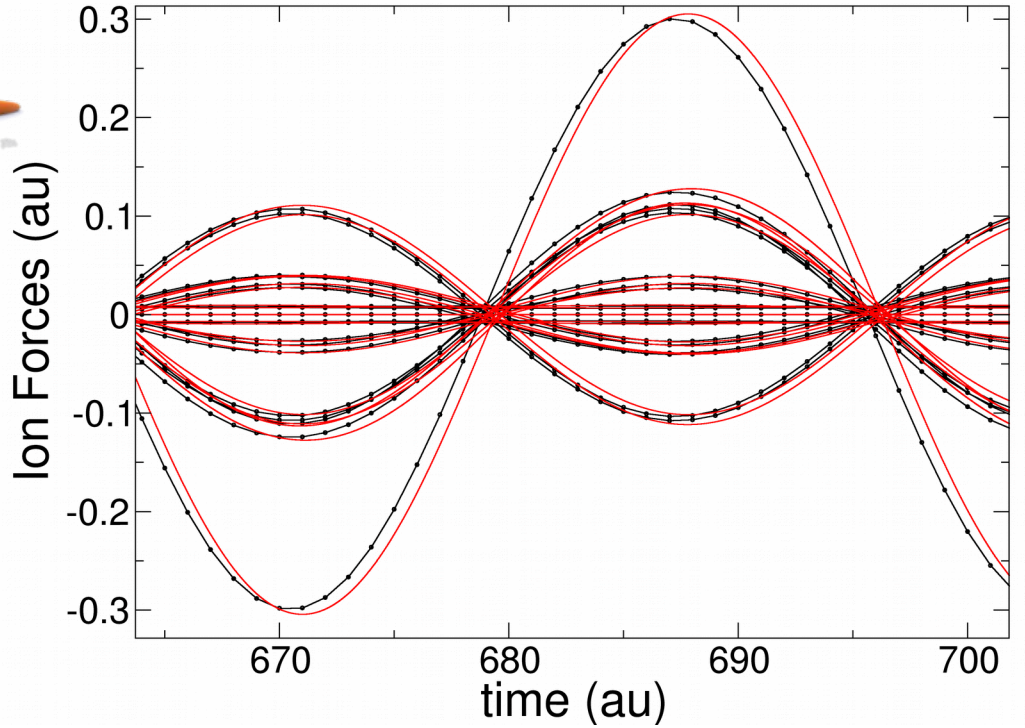
Benzene+Strong Pulse



TDDFT+Forces

- Forces: ion-ion, local pseudopotential, non-linear pseudopotential, non-linear core correction, pulay, and ion-laser





- Resolving GS very important

TDDFT+MD

- **Molecular Dynamics: TDDFT+Ehrenfest**
  - TDDFT for electronic motion
  - Coupled to classical ions, with forces from TDDFT
  - Non-adiabatic, beyond Born-Oppenheimer
- Allows access to:
  - Phonons
  - Dissipation
  - Energy scales from IR->visible->UV->XUV
  - Longer time scales

ToDo

- Internal check: LR-TDDFT & RTLR-TDDFT should agree
- Demonstrate linear-scaling – e.g. hBN-nanoribbon
- Understand bottlenecks – density+XCpot_ngwf
  - Fast density,fast_locpot_int for joint basis?
  - GPU for density

- Compatible with more functionals
  - Hybrids (excitons)
  - DFT+U

ToDo

- Non-collinear spin + spin current
  - Magnons
  - SOC, e.g. Spin-hall effect (and inverse-SHE)
- Solvant effects with embedding
- Spatially dependent A(r,t)
  - Excite in one regions, see current flow (energy dissipation, interface transport)
  - Vortex light
- TDDFT+Ehrenfest MD

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Thank You For Attention

Ehrenfest I

$$\dot{\mathbf{K}} = -i(\mathbf{S}^{-1}(\mathbf{H} - i\mathbf{B})\mathbf{K} - \mathbf{K}(\mathbf{H} + i\mathbf{B})\mathbf{S}^{-1})$$

$$\mathbf{B} = \sum_{\gamma} \dot{\vec{R}}_{\gamma}(t) \cdot \vec{\boldsymbol{\mathcal{B}}}_{\gamma}$$

$$\vec{\mathcal{B}}_{\gamma,\alpha\beta} = \langle \vec{\nabla}_{R_\gamma} \phi_\alpha | \phi_\beta \rangle = -\langle \phi_\alpha | \vec{\nabla} | \phi_\beta \rangle$$

Ehrenfest II

$$M_\gamma \ddot{\vec{R}}_\gamma = -\vec{\nabla}_{R_\gamma} U[\{\vec{R}\}] + Z_\gamma \vec{E}(t) - \int d^3r\; n(\mathbf{r},t)\vec{\nabla}_{R_\gamma} v_{\text{ext}}(\mathbf{r},t)$$

$$- \text{Tr}[\mathbf{K}(\vec{\boldsymbol{\mathcal{H}}} - \vec{\boldsymbol{\mathcal{S}}})]$$

$$v_{\text{ext}}(\mathbf{r},t) = \sum_\gamma \frac{-Z_\gamma}{|\mathbf{r} - \mathbf{R}_\gamma(t)|}$$

$$\vec{\mathcal{H}}_{\alpha\beta} = \langle \vec{\nabla}_{R_\gamma} \phi_\alpha | \hat{H}_\text{S} | \phi_\beta \rangle + \langle \phi_\alpha | \hat{H}_\text{S} | \vec{\nabla}_{R_\gamma} \phi_\beta \rangle$$

$$\vec{\boldsymbol{\mathcal{S}}} = \vec{\boldsymbol{\mathcal{B}}}_\gamma \mathbf{S}^{-1}\mathbf{H} + \mathbf{H}\mathbf{S}^{-1}\vec{\boldsymbol{\mathcal{B}}}_\gamma^\dagger$$

Ehrenfest III

$$\vec{F}_J^{\mathrm{PULAY}} = \sum_{\alpha\beta} \langle \vec{\nabla}_J \phi_\alpha | \sum_{\gamma\delta} S^{-1}_{\beta\gamma} H_{\gamma\delta} K_{\delta\alpha} - K_{\beta\alpha} \hat{H}_{\mathrm{S}} | \phi_\beta \rangle + c.c$$

$$= -\sum_{\alpha} \langle \vec{\nabla}_J \phi_\alpha | g_\alpha \rangle + c.c = \sum_{\alpha} \int d^3r \; g_\alpha(\vec{r}) \vec{\nabla} \phi_\alpha(\vec{r}) + c.c \text{ if } \alpha \text{ on atom J}$$

Ehrenfest IV

$$|g_\alpha\rangle = \sum_\beta \left(K_{\beta\alpha}\hat{H}_\mathrm{S} - \sum_{\gamma\delta} S^{-1}_{\beta\gamma} H_{\gamma\delta} K_{\delta\alpha} \right) |\phi_\beta\rangle$$

$$= \sum_\beta \left(K_{\beta\alpha}\hat{H}_\mathrm{S} - Q_{\beta\alpha} \right) |\phi_\beta\rangle$$

$$\mathbf{Q} = \mathbf{S}^{-1}\mathbf{H}\mathbf{K}$$