Implementation of Real-Time Simulation of Quantum Dynamics based on Density Functional Theory

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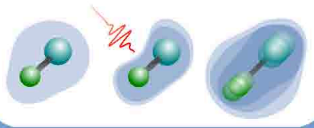
Project B02 – Ab-initio Simulation of Electronic Excitation and Relaxation



Motivation

Generally:
Simulating dynamical response of matter to external stimuli

Requirements:
Treatment of linear and nonlinear response / weak and strong perturbations of the system (electrons and nuclei)

Processes of interest:
- Photochemistry: Light-induced switching of atomic coordination and spin state of Fe-containing molecular complexes (Project A05)
- Ion bombardment: Excitation of 2D materials graphene or MoS_2 (Project C05)
- Higher Harmonic Generation
- Light harvesting
- Transport

Approach

Density Functional Theory (DFT) offers good compromise between efficiency and accuracy

Implementation of
- Real-Time Time-Dependent DFT
- Semiclassical Mean-Field Nuclear Motion

into the FHI-aims [1] code package

RT-TDDFT 1: Theory

Integrating the time-dependent Kohn-Sham equation

$$i\hbar\,\partial_t \Psi^{\mathrm{KS}}(\mathbf{r},t) = \mathcal{H}^{\mathrm{KS}}(t)\Psi^{\mathrm{KS}}(\mathbf{r},t)$$

$$\mathcal{H}^{\mathrm{KS}}(t) = \mathcal{H}_0^{\mathrm{KS}} + \mathcal{V}_{\mathrm{ext}}(t)$$

by applying the time-evolution operator:

$$\mathcal{U}(t',t) = \mathcal{T}\exp\left[-i\hbar\int_t^{t'} d\tau\,\mathcal{H}^{\mathrm{KS}}(\tau)\right]$$

$$\Psi^{\mathrm{KS}}(\mathbf{r},t') = \mathcal{U}(t',t)\Psi^{\mathrm{KS}}(\mathbf{r},t)$$

RT-TDDFT 2: Implementation

Current implementation status
- Full MPI-parallelism and scalability
- Efficient and accurate numerical linear algebra (Sca-) LAPACK support
- Periodic and finite systems
- Support for LDA, GGA and hybrid functionals
- Python-based postprocessing interface

Upcoming:
- Accelerated state-of-the-art time propagation schemes
- Integration of optimized external linear algebra framework ELSI

Ehrenfest 1: Theory

Integrating nuclear equations of motion

$$M_I\,\ddot{\mathbf{R}}_I = \mathbf{F}_I = -\frac{d}{dt}\langle\Psi^{\mathrm{KS}}|\mathcal{H}^{\mathrm{KS}}|\Psi^{\mathrm{KS}}\rangle$$

where nuclei feel average electronic potential. Forces include non-adiabatic coupling:

$$\mathbf{F}_I = \mathbf{F}_I^{\mathrm{coupl}} + \mathbf{F}_I^{\mathrm{DFT}}$$

Time-dependent KS equation also gets coupling term:

$$i\hbar\left(\partial_t + \sum_I \dot{\mathbf{R}}_I\cdot\nabla_I\right)\Psi^{\mathrm{KS}}(\mathbf{r},t) = \mathcal{H}^{\mathrm{KS}}(t)\Psi^{\mathrm{KS}}(\mathbf{r},t)$$

Ehrenfest 2: Implementation

Current implementation status
- Currently LAPACK (serial) support
- Finite systems
- Velocity Verlet nuclei propagation scheme
- Non-adiabatic couplings & forces

Upcoming:
- Full MPI-parallelism via ScaLAPACK/ELSI
- Wave function/density matrix extrapolation for speedup & accuracy

Functionality

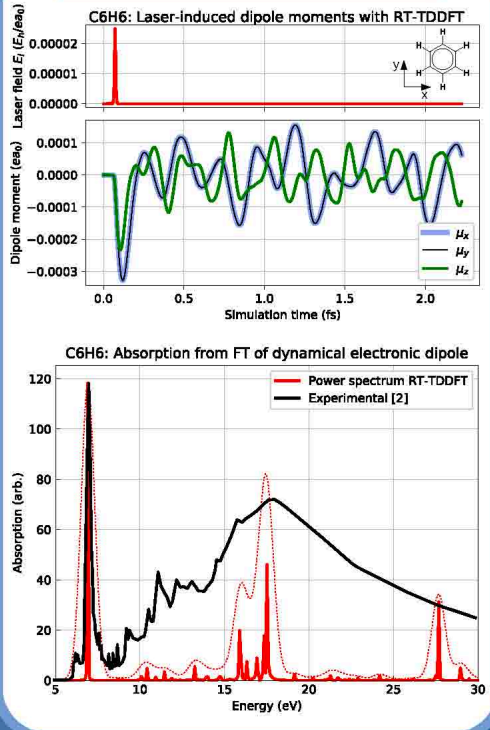
RT-TDDFT
Electron dynamics

Non-adiabatic coupling

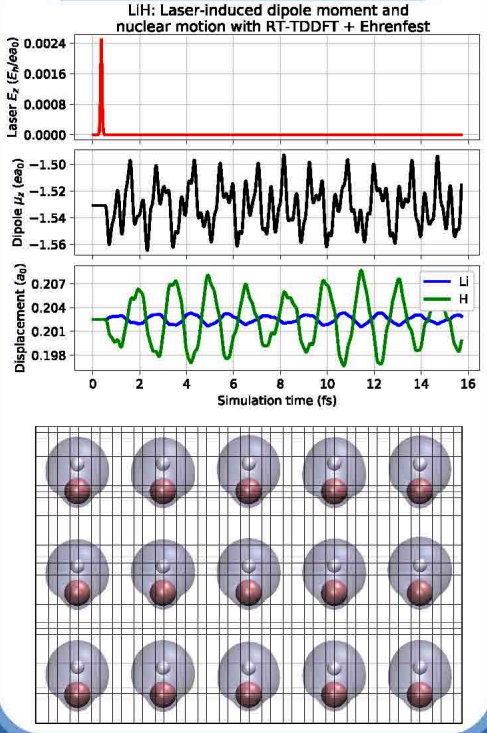
Semiclassical EOM
Nuclear dynamics

Ehrenfest Dynamics
Coupled electron-nuclear motion

RT-TDDFT 3: Results



Ehrenfest 3: Results



[1] V. Blum, R. Gehrke, F. Hanke, P. Havu, V. Havu, X. Ren, K. Reuter, M. Scheffler, Comp. Phys. Comm. 180, 2175-2196 (2009)

[2] C. O'Rourke, D. R. Bowler, J. Chem. Phys. 143, 102801 (2015)