Exploring the Linear-Response Regime with Real-Time TDDFT

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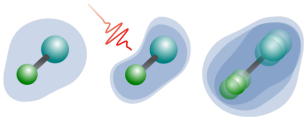
Project B02 – Ab-initio Simulation of Electronic Excitation and Relaxation



Motivation

Generally:

Simulating dynamical response of matter to external stimuli

Requirements:

Treatment of linear and nonlinear electronic response

Physical processes/techniques:

- Absorption spectroscopy
- High-harmonic generation
- Pump-probe excitation
- Ion bombardment

Approach

Density Functional Theory (DFT): good compromise between efficiency & accuracy → Real-Time Time-Dependent DFT for dynamics

- Localized-orbital RT-TDDFT efficient for molecules and low-dimensional systems
- RT-TDDFT scales better than conventional Linear-Response TDDFT for large systems

Implementation of Real-Time TDDFT functionality into the FHI-aims [1] code package (*done, official and operational*)

Code Assessment

- Proof of principle
- Implementation-specific characteristics

This study:

linear-response regime
(→ absorption spectroscopy)

Validation → Benchmarking

Benchmark-Set by Thiel [2]

- Quantum-chemistry molecular test set for excitations
- LR-TDDFT, DFT-MRCI, CASPT2, CC3
- 28 small-medium organic molecules:

1. Ethene	11. Pyrrole	21. p-Benzoquinone
2. E-Butadiene	12. Imidazole	22. Formamide
3. All-E-Hexatriene	13. Pyridine	23. Acetamide
4. All-E-Octatetraene	14. Pyrazine	24. Propanamide
5. Cyclopropene	15. Pyrimidine	25. Cytosine
6. Cyclopentadiene	16. Pyridazine	26. Thymine
7. Norbornadiene	17. s-Triazine	27. Uracil
8. Benzene	18. s-Tetrazine	28. Adenine
9. Naphtalene	19. Formaldehyde	
10. Furan	20. Acetone	

RT-TDDFT 1: Theory

Numerical solution of the time-dependent Kohn-Sham equation

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

$$\mathcal{H}^{\mathrm{KS}}[\rho(t),t] = \mathcal{H}^{\mathrm{KS}}[\rho(t)] + \mathcal{V}_{\mathrm{ext}}(t)$$

[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] M. R. Silva-Junior, M. Schreiber, S. P. A. Sauer, W. Thiel, J. Chem. Phys. 129, 104103 (2008)

RT-TDDFT 2: Observables

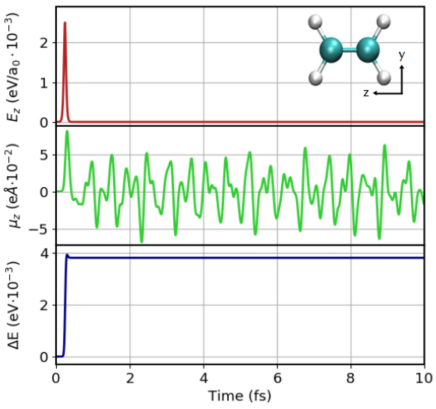
- Weak δ-kick field → linear response
- Polarizability → absorption spectrum
- Key observable: electronic dipole moment

$$\boldsymbol{\mu}(t) = \sum_n f_n \langle \Psi_n^{\mathrm{KS}} | \hat{\mathbf{r}} | \Psi_n^{\mathrm{KS}} \rangle$$

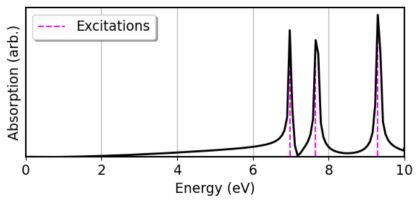
FT

$$\alpha_{ij}(\omega) = \frac{\tilde{\mu}_i(\omega)}{\tilde{E}_j(\omega)}$$

$$S(\omega) = \frac{4\pi\omega}{3c}\mathrm{Im}\Big\{\mathrm{Tr}[\alpha(\omega)]\Big\}$$



Post-processing → Analysis, FT & fitting



Linear-Response TDDFT

- Perturbative approach

$$\delta\rho(\mathbf{r},t) = \int\int \chi_{\mathrm{KS}}(\mathbf{r},t,\mathbf{r}',t') \times \delta v_{\mathrm{KS}}(\mathbf{r}',t')\, d^3\mathbf{r}'\, dt'$$

- Exact density-density response function

$$\chi^{-1}(\mathbf{r},\mathbf{r}',\omega) = \chi_{\mathrm{KS}}^{-1}(\mathbf{r},\mathbf{r}',\omega) - \frac{1}{|\mathbf{r}-\mathbf{r}'|} - f_{\mathrm{XC}}(\mathbf{r},\mathbf{r}')$$

- Casida formulation:

$$\boldsymbol{\Omega}\mathbf{X}_n = \omega_n^2 \mathbf{X}_n$$

→ Excitation energies ω_n

→ Oscillator strengths $f_n = f_n(\mathbf{X}_n)$

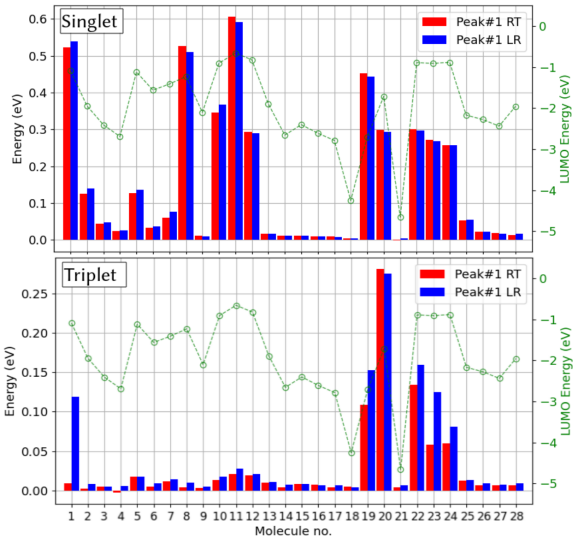
Results

$$\Psi^{\mathrm{KS}}(\mathbf{r},t) = \sum_j c_j(t)\phi_j(\mathbf{r}) \quad \leftarrow \quad \text{basis set } \{\phi_j\}$$

Basis set comparison:

Change of lowest excitation peak with respect to basis set: ‚tight' vs. ‚tight+aug2' (doubly augmented)

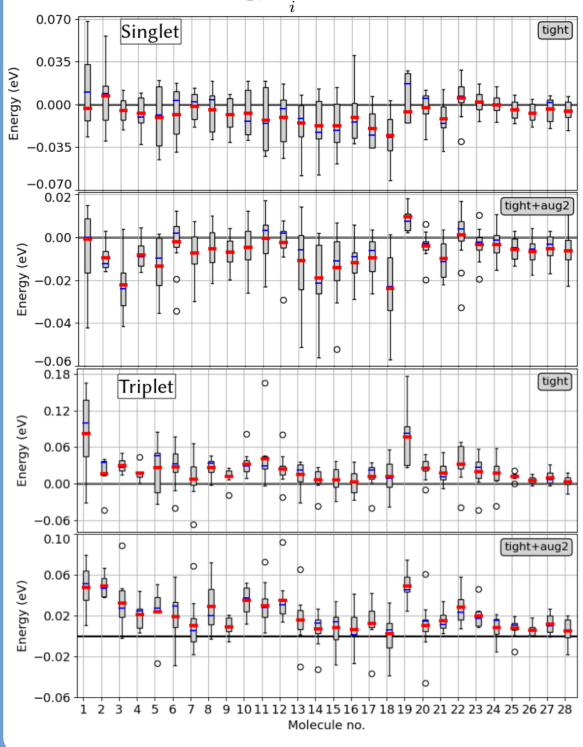
$$\Delta E_{1,\mathrm{mol}} = E_1(\text{tight}) - E_1(\text{tight + aug2})$$



Method comparison:

Avg. change of peak location between RT-TDDFT and LR-TDDFT for both basis sets:

$$\Delta E_{\mathrm{mol}} = \frac{1}{N}\sum_i^N (E_i(\mathrm{RT}) - E_i(\mathrm{LR}))$$



Conclusion & Outlook

- RT- and LR-TDDFT mostly agree very well
- Partially high sensitivity of excitation energy to basis set size/type (linked to electron affinity?)
- Singlet excitations in RT-TDDFT slightly lower relative to LR-TDDFT, vice versa for triplets