Recent and ongoing developments and applications of TDDFT for large molecular and materials systems

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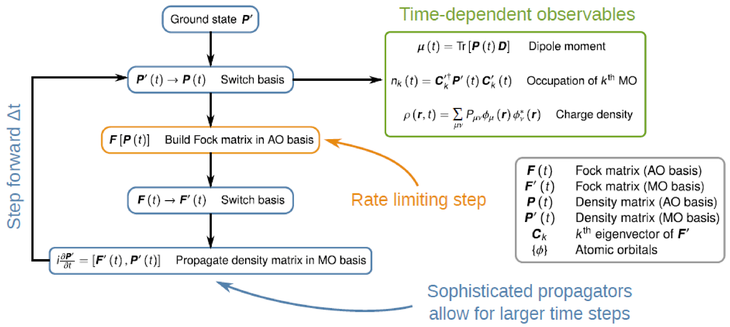
SciDAC Scientific Discovery through Advanced Computing

Real-Time (RT) TDDFT Approach

Explicit propagation of the time-dependent Kohn-Sham (KS) equations in time.



The second order Magnus propagator:

$$\mathbf{P}'(t+\Delta t) = e^{-i\mathbf{F}'(t+\Delta t/2)\Delta t}\mathbf{P}'(t)e^{i\mathbf{F}'(t+\Delta t/2)\Delta t}$$

All electronic modes are induced simultaneously with a narrow Gaussian electric field kick

$$\mathbf{E}(t) = \kappa \exp\left[\frac{-(t-t_0)^2}{2w^2}\right]\hat{d}$$

The applied field excites the system through a dipole coupling term added to the Fock matrix

$$\mathbf{V}_{\mu\nu}^{\mathrm{app}}(t) = -\mathbf{D}_{\mu\nu}\cdot\mathbf{E}(t)$$

$$\mathbf{D}_{\mu\nu}^{x} = \int \phi_\mu^*(\mathbf{r}) x \phi_\nu(\mathbf{r}) d\mathbf{r}$$

Pros:
+ Efficient implementation of a wide range of functionals within RT-TDDFT scheme
+ Only requires first derivatives of the exchange-correlation functionals
+ Can be used as a diagnostic for potential-driven DFT
+ Wide range absorption spectrum and for spectra involving high density of states
+ Non-linear optical properties
+ Real-time dynamics
+ Resonant excitation simulations
+ Efficient for large systems

Cons:
- Time consuming for small systems

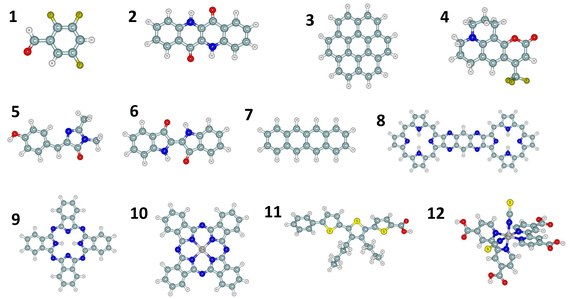
Computational Details

NWChem 6.3/dev and **Gaussian 09 (linear response results for meta functionals)**
8 density functionals were tested
3 local functionals: BLYP, M06L and M11L with dual-range DFT exchange;
3 global hybrid functionals: B3LYP, M06 and M06-2X with 20, 27 and 54% of Hartree-Fock (HF) exchange, respectively;
2 range-separated hybrid functional CAM-B3LYP and M11, comprising 19 and 42.8% HF exchange in the short-range and 65 and 100% in the long-range, respectively.

Ground state DFT calculations: tight density convergence to avoid numerical error accumulation: RMS difference less than 10^{-9}.
Geometry optimization at B3LYP/6-31G* for dyes **1**-**10,** P3B2 and f-coronene
BHLYP-D3/def2-SVP (**11**) and B3LYP/def2-SVP (**12**)

Real-time TDDFT simulations: B3LYP/6-31G*
Δt = 0.2 au = 0.0048 fs, t=1000 au = 24.2 fs or N=5000 time steps. δ-kick with κ=2·10^{-5} au = 10 mV/nm, peaks were broadened by artificially damping the time signal by $e^{-t/t}$, where τ= 200 au = 6 fs before taking the Fourier transform.

Dye Benchmark



2,3,5-trifluorobenzaldehyde (**1**), dibenzonaphthyridindione (**2**), coronene (**3**), coumarin 153 (**4**), 4′-hydroxybenzylidene-2,3-dimethylimidazoline (**5**), indigo (**6**), naphtacene (**7**), oligoporphyrin dimer (**8**), phtalocyanine (**9**), zinc phthalocyanine (**10**), 3′,4′-dibutyl-2-phenyl-2,2′:5′,2″-terthiophene-5″-carboxylic acid (**11**), *cis*-[Ru(4,4′-COOH-2,2′-bpy)$_2$(NCS)$_2$] complex or N3 (**12**).

	BLYP*	B3LYP	CAM-B3LYP	M06l	M06	M06-2X	M11L	M11
1	**3.75**	**4.31**	**4.69**	**4.04**	**4.40**	**4.83**	**4.15**	**4.88**
	3.73	4.30	4.69	4.03	4.38	4.81	4.15	4.87
2	**2.70**	**3.11**	**3.55**	**2.89**	**3.23**	**3.53**	**2.86**	**3.74**
	2.69	3.10	3.53	2.89	3.22	3.52	2.86	3.67
3	**3.75**	**4.15**	**4.66**	**3.95**	**4.20**	**4.63**	**3.87**	**4.91**
	3.74	4.15	4.65	3.94	4.19	4.63	3.87	4.91
4	**2.95**	**3.36**	**3.78**	**3.16**	**3.43**	**3.76**	**3.11**	**3.98**
	2.94	3.36	3.76	3.15	3.44	3.76	3.13	3.91
5	**3.25**	**3.54**	**3.79**	**3.47**	**3.57**	**3.78**	**3.42**	**3.87**
	3.25	3.54	3.79	3.46	3.58	3.78	3.42	3.86
6	**2.04**	**2.32**	**2.61**	**2.21**	**2.41**	**2.58**	**2.18**	**2.66**
	2.04	2.30	2.59	2.20	2.40	2.57	2.18	2.64
7	**2.21**	**2.49**	**2.84**	**2.32**	**2.50**	**2.86**	**2.24**	**3.06**
	2.20	2.49	2.85	2.32	2.49	2.86	2.23	3.06
8	**2.07**	**2.41**	**3.06**	**2.16**	**2.46**	**3.02**	**2.13**	**3.28**
	2.05	2.40	3.04	2.17	2.44	3.00	2.09 2.15	3.11 3.28
9	**1.99**	**2.08**	**2.07**	**2.05**	**2.02**	**2.11**	**1.99**	**1.98**
	1.96 1.99	2.06 2.09	1.99 2.05	2.04 2.06	2.00 2.02	2.07 2.12	1.98 1.99	1.91 2.00
10	**1.99**	**2.10**	**2.06**	**2.07**	**2.02**	**2.11**	**1.99**	**1.99**
	1.99	2.09	2.04	2.06	2.02	2.11	1.99	1.98
11	**2.75**	**3.23**	**3.70**	**2.94**	**3.31**	**3.72**	**2.78**	**3.93**
	2.74	3.22	3.70	2.93	3.31	3.71	2.88	3.94
12	**1.55**	**1.76**	**-**	**1.69**	**1.90**	**1.96**	**1.52**	**-**
	1.55	1.77	-	1.65	1.91	1.96	1.54	-

*Numbers in bold and regular forms are RT and LR-TDDFT results, correspondingly.

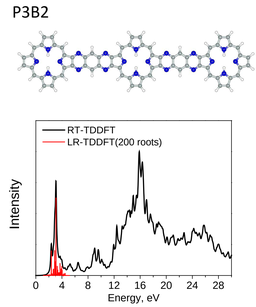
-Excellent agreement between LR- and RT-TDDFT calculated vertical singlet excitation energies was achieved. The largest deviation does not exceed 0.07 eV, corresponding to ≈ 2%.
-Efficient calculation of the wide range absorption spectrum of a large dye molecule (more than 1000 basis functions) employing RT-TDDFT.

Wide Excitation Spectra of Large Dye Molecules

Porphyrins – building blocks of molecular wires

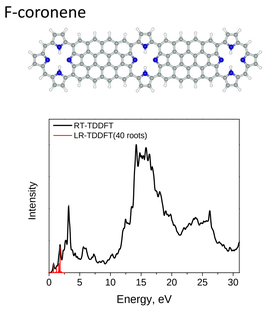
Spectral resolution of the RT approach is limited by the time step $\omega_{\max} = \pi/\Delta t_{\max}$

P3B2



Absorption spectrum of P3B2, 130 atoms, **1364 basis functions (6-31G*),** B3LYP

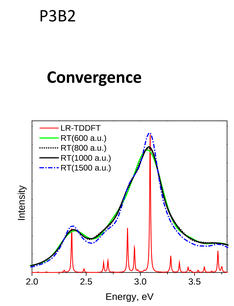
F-coronene



Absorption spectrum of f-coronene, 162 atoms, **1764 basis functions (6-31G*),** B3LYP

P3B2

Convergence



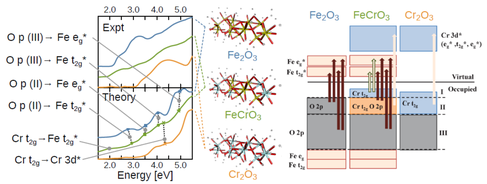
Fragment of the absorption spectrum of P3B2 for different (**600**, **800**, **1000** and **1500** a.u.) total simulation times.

$(Fe_{1-x}Cr_x)_2O_3$ Solid Solutions

Finite QM embedded cluster approach
- Host environment → non-polarizable point charge
- Infinite Ewald consistent electrostatic potential
- ~100 atoms, ~700 electrons, ~1200 basis functions
- Anti-ferromagnetic system
- Very high DOS

Linear-response (frequency domain) TDDFT
- Span ~5.5 eV: ~5000 roots
- Windowing procedure is not clear cut

Real-time TDDFT
- Delta-function electric field (x,y,z)
- Three simulations per cluster
- Simultaneously excites all the modes
- Full absorption spectrum
- Weak electric field
- Time step 0.005 fs (total time ~12 fs)



▸ Optical band gap in $FeCrO_3$ (~ 2 eV): Cr t_{2g} → Fe t_{2g}^*

Chamberlin, et al , J. Phys.: Condens. Matter **25** 392002 (2013)
Wang et al, J. Phys. Chem C, DOI: 10.1021/jp407496w (2013)

Projected Conjugate Gradient Method for Casida Eigenvalue Problem in Linear-Response (LR) TDDFT

$$H_{LR} = \begin{pmatrix} A & B \\ -B & -A \end{pmatrix}, A^T = A, B^T = B,$$

- $A \pm B$ positive definite
- Structured eigenpairs: if λ is an eigenvalue with eigenvector $(x^T\ y^T)^T$, then $-\lambda$ is also an eigenvalue with eigenvector $(y^T\ x^T)^T$
- A special class of Hamiltonian eigenvalue problem
- Only need to compute (positive) half of the eigenvalues
- Matrix available through matrix-vector multiplication subroutines only

Equivalent Formulation

$$\begin{pmatrix} 0 & K \\ M & 0 \end{pmatrix}\begin{pmatrix} x \\ y \end{pmatrix} = \lambda\begin{pmatrix} x \\ y \end{pmatrix},$$

- $K = A - B, M = A + B$;
- $KMy = \lambda^2 y$ and $MKx = \lambda^2 x$;
- $\min_{x^T y = 1} x^T K x + y^T M y$

Projected Conjugate Gradient

- Current approximation $X = (x_1, x_2, \dots, x_k)$
- Projected gradient: $R = (I - XX^T)(AX - X(X^T AX) = (r_1, r_2, \dots, r_k)$
- $\hat{x}_i = \mathrm{argmin}_{x\in\{x_i, r_i, p_i\}} x^T Ax$
- Project $\hat{X} = (\hat{x}_1, \hat{x}_2, \dots, \hat{x}_k)$ onto the orthonormality constraint