Real-time TDDFT for linear and nonlinear optical response

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Motivation: Polymeric Electro-optic devices for integrated photonics

The electro-optic coefficient
(the change of the refractive index induced by applying an electric voltage)

\[ r_{33} = 2N\beta_{zzz}(-\omega; 0, \omega)\langle\cos^3 \theta\rangle \frac{g(\omega)}{n(\omega)^4} \]

NOTE: The best EO coefficient of organic polymer is about 450 pm/V, more than 15x higher than the best inorganic materials!
Acknowledgments

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- the CMSN [JJR]
Outline

- Objectives

- Approach: Real-time Time-dependent Density Functional Theory (RT-TDDFT)

- Results: small and LARGE molecules

- X-ray Spectra: real-time real-space methods

- Conclusions
Objective and Motivation

- Applications to *Organic-based photonics*

- Need: *non-linear* optical response in large organic molecular systems

- Difficulty: frequency-space is computationally difficult - too-many excited states

- **Strategy**: extend linear RT-TDDFT/ SIESTA approach
  
Reference: Real space, real time linear and non-linear optical response*


Real-time time-dependent density functional theory approach for frequency-dependent nonlinear optical response in photonic molecules

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We present *ab initio* calculations of frequency-dependent linear and nonlinear optical responses based on real-time time-dependent density functional theory for arbitrary photonic molecules. This approach is based on an extension of an approach previously implemented for a linear response using the electronic structure program SIESTA. Instead of calculating excited quantum states, which can be a bottleneck in frequency-space calculations, the response of large molecular systems to time-varying electric fields is calculated in real time. This method is based on the finite field approach generalized to the dynamic case. To speed the nonlinear calculations, our approach uses Gaussian enveloped quasimonochromatic external fields. We thereby obtain the frequency-dependent second harmonic generation \(\beta(-2\omega;\omega,\omega)\), the dc nonlinear rectification \(\beta(0;\omega,\omega)\), and the electro-optic effect \(\beta(-\omega;\omega,0)\). The method is applied to nanoscale photonic nonlinear optical molecules, including p-nitroaniline and the FTC chromophore, i.e., 2-[3-Cyano-4-(2-[5-[2-(diethylamino-phenyl)-vinyl]-thiophen-2-yl]-vinyl)-5,5-dimethyl-5H-furan-2-ylidene]-malononitrile, and yields results in good agreement with experiment. © 2007 American Institute of Physics.

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Nonlinear Polarizabilities

\[ P = \chi^{(1)} E + \chi^{(2)} E^2 + \chi^{(3)} E^3 + \ldots \]

- Second order nonlinearities

\[ \chi^{(2)}(2\omega; \omega, \omega) \quad \text{Second Harmonic Generation (SHG)} \]
\[ \chi^{(2)}(0; -\omega; \omega) \quad \text{Optical Rectification (OR)} \]
\[ \chi^{(2)}(-\omega; 0; \omega) \quad \text{Electro-Optic effect (Pockel’s effect)} \]
Real time TDDFT


\[ \frac{i}{\hbar} \frac{\partial \Psi}{\partial t} = H(t) \Psi \]

\[ H = \frac{-1}{2} \nabla^2 + V_{\text{ext}}(r, t) + V_H[\rho](r, t) + V_{xc}[\rho](r, t) \]

- Direct numerical integration of TD Kohn-Sham equations

\[ \Psi(t) = T \exp \left( -i \int_0^t H(t') dt' \right) \Psi(0) \]

- The response to external field is determined by applying a time-dependent electric field \( \Delta H(t) = -E(t) \cdot \hat{r} \).

- Optical properties are determined from the total dipole moment:

\[ p(t) = \int \rho(r, t) r \, d^3r \]

MORE EFFICIENT THAN EIGENSTATE METHODS!
Calculation of $\Psi(t)$ at each time step based on: SIESTA*

- Self-consistent DFT Ground State Code with LDA or GGA exchange/correlation
  - Ab-initio
- LCAO and confined basis functions using pseudo potential
  - Scalable
- Projects the electron wavefunctions and density onto a real-space grid
  - Flexible
- Multiple zeta basis definition
  - Accurate

*Spanish Initiative for Electronic Simulations with Thousands of Atoms
Numerical Real time Evolution

- Ground state density $\rho_0$, overlap matrix $S$, and $H(t)$ at each time-step evaluated with SIESTA

$$i \frac{\partial c(t)}{\partial t} = S^{-1}H(t)c(t)$$

- Crank-Nicholson time-evolution: accurate, stable

$$c(t + \Delta t) = \frac{1 - iS^{-1}H(t)\Delta t/2}{1 + iS^{-1}H(t)\Delta t/2}c(t) + \mathcal{O}(\Delta t^2)$$

- Adiabatic GGA exchange-correlation (PBE) functional used for all of our calculations
Review: Real time Linear Response

Well known relations...

\[ \delta p(t) = p(t) - \bar{\mu}_0 \]

\[ \delta p_i(t) = \int dt' \chi^{(1)}_{ij}(t - t') E_j(t') \]

\[ \chi^{(1)}_{ij}(\omega) = \delta p_i(\omega)/E_j(\omega) = \alpha_{ij}(\omega) \]

\[ \epsilon_{ij}(\omega) = 1 + 4\pi N \alpha_{ij}(\omega) \]

\[ \sigma(\omega) \sim \omega \langle \alpha(\omega) \rangle/E(\omega) \]
Example: Linear Response

Carbon Monoxide (CO), $p_z(t)$ response due to applied $E_z(t)$

- **Delta Function**
  (Unit Impulse at $t=0$)

- **Step Function**
  (Turn-off Constant $E$ at $t=0$)

\[
\alpha_{ij}(\omega) = \frac{p_i^{\text{delta}}(\omega)}{E_j}
\]

\[
\alpha_{ij}(\omega) = \frac{p_i^{\text{step}}(0) / E_j - i\omega p_i^{\text{step}}(\omega) / E_j}{E_j}
\]

- **Ground state without field**
- **Evolution for $t>0$**
Example: Small molecules

\( p \)-Nitroaniline (pNA)

- Linear absorption
  \( \lambda_0 = 356 \text{ nm} \)
  \( \omega_0 = 3.49 \text{ eV} \)
  \( \lambda_0^{\exp.} = 347 \text{ nm} \) (in chloroform)

- Sum rule

\[ \int_0^\infty d\omega \, S(\omega) = \lim_{\omega \to \infty} f_{\text{sum}}(\omega) = \sum_i f_i = N_e, \]

\( f_{\text{sum}} \) Electron Counts

Total 52 valence electrons

Absorption (au)
Large Photonic molecules

YLD156

Linear response, yields linear absorption spectra \( \sigma(\omega) \) or the polarizability \( \alpha(\omega) \), which is related to the refractive index though the Lorentz-Lorentz relation

\[
\frac{4\pi}{3} N \alpha(\omega) = \frac{n^2(\omega) - 1}{n^2(\omega) + 2}
\]

The figure below is the calculation of refractive index \( n(\omega) \) from the linear polarizability calculation of RT-TDDFT for the YLD156 chromophore developed by the Dalton group (UW).
Real time Nonlinear Response

- The nonlinear expansion in field strength
  \[ P = \chi^{(1)} E + \chi^{(2)} E^2 + \chi^{(3)} E^3 + \ldots \]

- Accounting for time lag in system response
  \[
  p_i(t) = \mu_i^0 + \int dt_1 \chi_{ij}^{(1)}(t - t_1) E_j(t_1) \\
  + \int dt_1 \int dt_2 \chi_{ijk}^{(2)}(t - t_1, t - t_2) E_j(t_1) E_k(t_2) \\
  + \int dt_1 \int dt_2 \int dt_3 \chi_{ijkl}^{(3)}(t - t_1, t - t_2, t - t_3) E_j(t_1) E_k(t_2) E_l(t_3) \\
  + \ldots
  \]

How can we invert the equation to get nonlinear response function?
Extraction of Static Nonlinear Polarizabilities

- Usual technique: fits to static expansion

\[ p_i = \mu_i^0 + \alpha_{ij} E_j + \beta_{ijk} E_j E_k + \gamma_{ijkl} E_j E_k E_l + \cdots \]

Either finite-difference or fitting \( p_i(E) \) to a polynomial

Example:

\[ \beta_{ijj} = \left[ -p_i(-2E_j) + 16p_i(-E_j) - 30p_i(0) + 16p_i(E_j) - p_i(2E_j) \right]/24E_j^2 \]
Extraction of Dynamic Nonlinear Polarizabilities

- Set $E_j(t) = F(t)E_j$, and define expansion $p_i(E)$

$$p_i(t) = \mu_i^0 + p_{ij}^{(1)}(t)E_j + p_{ijk}^{(2)}(t)E_jE_k + \cdots$$

where $p^{(1)}$ yields linear response, $p^{(2)}$ first non-linear quadratic response, ….

- The quadratic response $\chi^{(2)}$ is then given by

$$p_{ijk}^{(2)}(t) = \int dt_1 \int dt_2 \chi_{ijk}^{(2)}(t - t_1, t - t_2)F(t_1)F(t_2)$$
Dynamic Nonlinear Response with Quasi-monochromatic Field $F_\delta(t)$

- Sine wave enveloped by another sine wave or Gaussian

\[ \chi_{ijk}^{(2)}(-2\omega_0; \omega_0, \omega_0) = \frac{2\pi p_{ijk}^{(2)}(2\omega_0)}{\int_{-\Delta}^{\Delta} d\omega' F(\omega_0 - \omega') F(\omega_0 + \omega')} \]

\[ \chi_{ijk}^{(2)}(0; -\omega_0, \omega_0) = \frac{\pi p_{ijk}^{(2)}(0)}{\int_{-\Delta}^{\Delta} d\omega' F^*(\omega_0 + \omega') F(\omega_0 + \omega')} \]

SHG

OR

Linear and Nonlinear response of CO
Real time vs Frequency space
Nonlinear Response

- **Operation cost**
  - Sternheimer equation (frequency space)
    $$\mathcal{O}(N_{KS}^2 N_{basis} M_{iterations} M_\omega)$$
  - Real time
    $$\mathcal{O}(N_{KS} N_{basis} N_{evolve} M_{steps} M_\omega)$$

- **Memory cost**
  - Sternheimer equation (frequency space)
    $$\mathcal{O}((N_{occ} + N_{unocc}) N_{basis})$$
  - Real time
    $$\mathcal{O}(N_{occ} N_{basis})$$
Example: CO: Nonlinear Second Harmonic Generation (SHG)

- Comparison with other methods

\[ \beta_\parallel = \frac{1}{5} \sum_i (\beta_{iiz} + \beta_{izi} + \beta_{zii}) \]

\[ \Gamma = \gamma + \frac{\mu_0 \beta_\parallel}{3kT} \]

H$_2$O: Nonlinear
Second Harmonic Generation (SHG)

- Comparison with other methods

![Graph showing comparison of different methods for nonlinear second harmonic generation](image.png)
$\text{H}_2\text{O}$: Nonlinear Optical Rectification (OR)

- Resonant Frequencies

Chloroform (CHCl$_3$)

- **Static calculation comparison**

<table>
<thead>
<tr>
<th></th>
<th>PBE</th>
<th>B3LYP</th>
<th>HF</th>
<th>MP2</th>
<th>CCSD</th>
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<td>$\mu_z$</td>
<td>0.40</td>
<td>0.43</td>
<td>0.48</td>
<td>0.43</td>
<td>0.43</td>
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<tr>
<td>$\alpha$</td>
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<td>58.52</td>
<td>54.50</td>
<td>57.35</td>
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<td>-5.58</td>
<td>-3.22</td>
<td>-4.02</td>
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<tr>
<td>$\beta_{zz}$</td>
<td>11.35</td>
<td>10.04</td>
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<td>8.64</td>
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<td>$\beta_k$</td>
<td>-0.88</td>
<td>-0.68</td>
<td>0.21</td>
<td>0.36</td>
<td>+0.10</td>
</tr>
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</table>

This Work

Gaussian03

23

Gaussian03
**CHCl₃: Effect of basis**

- *Nonlinear* calculation require “large” basis (especially for a small molecules)

<table>
<thead>
<tr>
<th></th>
<th>DZP (default)</th>
<th>5Z4P</th>
<th>5Z4P</th>
<th>5Z4P</th>
<th>5Z4P</th>
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<td>r_s(C)</td>
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<td>10.48</td>
<td>13.80</td>
<td>14.88</td>
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<tr>
<td>r_s(Cl)</td>
<td>3.83</td>
<td>6.15</td>
<td>7.15</td>
<td>8.95</td>
<td>9.41</td>
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### Linear

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<th>μ</th>
<th>z</th>
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<th>β</th>
<th>k</th>
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<th>β</th>
<th>k</th>
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<td></td>
<td>0.26</td>
<td>0.41</td>
<td>0.40</td>
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<td></td>
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<tr>
<td>α</td>
<td>44.39</td>
<td>60.18</td>
<td>60.39</td>
<td>60.15</td>
<td>60.09</td>
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<td>β zzz</td>
<td>-16.40</td>
<td>3.98</td>
<td>9.39</td>
<td>11.35</td>
<td>11.28</td>
<td></td>
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<tr>
<td>β k</td>
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<td>-3.59</td>
<td>-1.86</td>
<td>-0.88</td>
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</table>
$\rho$NA: Nonlinear (SHG)

- Comparison with other methods

```
<table>
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<tr>
<th>Method</th>
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<td>Real-time S24P</td>
<td>PBE</td>
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<td>Real-time DZDP</td>
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<td>EFISHG in 1,4-dioxane</td>
<td></td>
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<tr>
<td>EFISHG in gas phase</td>
<td></td>
</tr>
<tr>
<td>TDDFT OCTOPUS</td>
<td></td>
</tr>
<tr>
<td>B3LYP TDDFT</td>
<td></td>
</tr>
<tr>
<td>CCSD</td>
<td></td>
</tr>
<tr>
<td>TDCP HF</td>
<td></td>
</tr>
</tbody>
</table>
```

![Graph showing comparison of different methods with experimental data](image-url)
\( \beta_{k}(-2\omega,\omega,\omega) \) (au)

Energy (eV)

- 28/35
NLO Molecule

- **YLD156 chromophore**

![Molecule Structure]

**Experimental Absorption peak of YLD_156 in Chloroform solution**

$$\omega_0 = 1.65 \text{ eV} \quad (\lambda_0 = 753\text{nm})$$

**Real-time Absorption peak of YLD_156 (GAS)**

$$\omega_0 = 1.72 \text{ eV} \quad (\lambda_0 = 721\text{nm})$$
YLD156

- Nonlinear results

\[ \beta_{\parallel}(0; -\omega; \omega) \quad \text{OR} \quad \beta_{\parallel}(-2\omega; \omega, \omega) \quad \text{SHG} \]
YLD_156
Hyper-Rayleigh Scattering (HRS) Experiment ($<\beta^2>$)

- **HRS measurement** (in solution)

<table>
<thead>
<tr>
<th>Energy (eV)</th>
<th>λ</th>
<th>Relative value</th>
<th>This Work</th>
<th>Expt.</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.65 eV</td>
<td>1.9 μm</td>
<td>0.65 eV</td>
<td>446</td>
<td>5150</td>
</tr>
<tr>
<td>1.24 eV</td>
<td>1.0 μm</td>
<td>1.24 eV</td>
<td>980</td>
<td>10190</td>
</tr>
</tbody>
</table>
Solvent Effects – HRS Experiment

\[
\frac{8 \pi \rho N_A (\epsilon - 1)(n^2 + 2)}{3 M_w (2 \epsilon + n^2)} \times 10^{23} \text{ esu}
\]

<table>
<thead>
<tr>
<th>solvent</th>
<th>( \beta_{\text{solute}} /10^{-30} \text{ esu} )</th>
<th>( \lambda_{\text{max}} /\text{nm} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>chloroform</td>
<td>16.80 ± 0.50</td>
<td>347</td>
</tr>
<tr>
<td>p-dioxane *</td>
<td>16.90 ± 0.40</td>
<td>352</td>
</tr>
<tr>
<td>tetrahydrofuran (THF)</td>
<td>19.90 ± 1.00</td>
<td>363</td>
</tr>
<tr>
<td>ethyl acetate (EtAc)</td>
<td>20.50 ± 0.70</td>
<td>356</td>
</tr>
<tr>
<td>acetonitrile (MeCN)</td>
<td>23.30 ± 1.00</td>
<td>364</td>
</tr>
<tr>
<td>methanol (MeOH)</td>
<td>22.40 ± 0.90</td>
<td>356</td>
</tr>
<tr>
<td>dimethyl sulfoxide (DMSO)</td>
<td>24.70 ± 1.00</td>
<td>388</td>
</tr>
<tr>
<td>N,N-dimethylformamide (DMF)</td>
<td>26.60 ± 0.80</td>
<td>381</td>
</tr>
</tbody>
</table>

* Reference value for HRS, measured by EFISH

“Local” Solvent Effect

- Study of local contact with methanol (polar) or chloroform (non-polar)

Adjusted Expt. Values.
Appendix B
REAL TIME TDDFT PROGRAM MANUAL

B.1 Quick Start Guide

Real time TDDFT consists of following sets of files and you will find directories after unpacking the source distribution:

- rt-tddft/examples
- rt-tddft/patch
- rt-tddft/utils

Script for pre-process and post-process:
- utils/preprocess : TDDFT preparation script (Perl script)
- utils/hypfits : TDDFT post process script (Octave script)

The directory 'patch' contains the patch 'diff' file tddft-current.diff to modify the original SIESTA source code for version 2.0.1.

Optional scripts to help running a set of jobs:
- utils/submit_jobs : Script for running multiple jobs (require to edit)
- utils/submit_to_queue : Used in together with the script above

The other utility scripts may be used for analysis that will be explained later.

B.1.1 Compilation

Create a working directory and untar SIESTA source code siesta-2.0.1.tgz.

$ tar xzf siesta-2.0.1.tgz

Unpack the Real time TDDFT distribution rt-tddft****.tar.gz where '****' is the version control number.

$ tar xzf rt-tddft****.tar.gz

*If interested, please contact ytakimot@u.washington.edu or jjr@phys.washington.edu
Conclusions

- Efficient RT-TDDFT approach for frequency dependent nonlinear optical response – extension of RT-SIESTA
- Accuracy comparable to frequency-domain methods for small systems
- Efficient on large systems (HPC ready)
- Can treat solvent effects etc.
Part II: X-ray Spectra – DFT/MD - Dynamic Structure in Supported Pt nanoclusters*

**MYSTERY:** Unusual thermal properties of Pt\(_{10}\) /\(\gamma\)-Al\(_2\)O\(_3\)

NTE, disorder, redshift in XAS

**Approach:** Real-time DFT/MD

Calculation - VASP + $10^4$ cpu-hrs

Calculation 10 atom Pt/γ-Al$_2$O$_3$

Mean nn distance $R_{\text{Pt-Pt}}$

NTE

2500 3 fs steps

time-elapsed rendering
Librational motion: long time-scale fluctuations of the center of mass

Fluxional behavior in tetrahedral clusters with carbonyl ligands

$\text{Co}_4(\text{CO})_{12}$

That’s all folks
Results: Test case: p-nitroaniline (pNA)

Applied quasi-monochromatic field

\[ F(t) = \sin(\omega_0) \exp(-\gamma(t - t_0)^2) \]

Linear response

First nonlinear response