Calculations of X-ray Spectra in Real-space and Real-time

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Time (s)

X-Ray Science in the 21st Century

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Calculations of X-ray Spectra in Real-space and Real-time

Goals: Real-space & Real-time response beyond linear response & harmonic approx

Talk: Two approaches:

• **I.** Linear & Non-linear Response RT-TDDFT

• **II.** Real space & time XAS of non-equilibrium system
  Finite Temperature DFT/MD + Real-Space Green’s Function XAS
``If I can't calculate it,
I don't understand it.``

R.P. Feynman
I. Real-Space & Real-Time

*Linear and Non-linear Response*

• **Difficulty:** frequency-space is computationally demanding - *too-many* excited states

• **Strategy:** extend RT-TDDFT/ SIESTA approach*

Approach I: RT-TDDFT

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 quasi-monochromatic 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-(4-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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RT-TDDFT Formalism


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

- 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 \( \Delta H(t) = -E(t) \cdot x \).

- Optical properties determined from total dipole moment:

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

MORE EFFICIENT THAN FREQUENCY -SPACE METHODS!
Numerical Real-time Evolution

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

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

Coefficients of Orbitals

• Crank-Nicholson time-evolution: **unitary, time-reversible**

**Stable for long time-steps**!

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

• Adiabatic GGA exchange-correlation (PBE) functional
Real time Linear Response

\[ \delta p(t) = p(t) - \bar{\mu}_0 \quad \text{(Induced Dipole Moment)} \]

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

\[ \chi_{ij}^{(1)}(\omega) = \delta p_i(\omega)/E_j(\omega) = \alpha_{ij}(\omega) \quad \text{(Linear Response Function)} \]

\[ \epsilon_{ij}(\omega) = 1 + 4\pi N\alpha_{ij}(\omega) \quad \text{(Linear Dielectric Function)} \]

\[ \sigma(\omega) \sim \omega \langle \alpha(\omega) \rangle/E(\omega) \quad \text{(Optical Absorption)} \]
Example: CO Linear Response

\( p_z(t) \) response due to applied \( E_z(t) \)

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

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

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

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

Graphs showing time evolution and energy response for ground state and evolution for \( t>0 \).

\[ E(t) \]

Ground state without field

Evolution for \( t>0 \)

\[ \text{Dipole} \ (t) \text{ (a.u.)} \]

Graphs showing dipole response over time.

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

Ground state with constant field

Evolution for \( t>0 \)

\[ E(t) \]

Graphs showing energy evolution over energy for ground state.

\[ \alpha_{ij}(\omega) = \frac{p_i^{\text{step}}(0)/E_j - i\omega p_i^{\text{step}}(\omega)/E_j}{E_j} \]
Example: Small molecule p-Nitroaniline (pNA)

- **Linear absorption**

- **Sum rule**
  \[ \lambda_0 = 356 \text{nm} \]
  \[ \omega_0 = 3.49 \text{ eV} \]
  \[ \lambda_0^{\text{exp.}} = 347 \text{nm} \]
  (in chloroform)

\[ N_e = 51.8 \]

Total 52 valence electrons

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

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

- Second order nonlinearities

\[ \chi^{(2)}(-2\omega; \omega, \omega) \quad \text{Second Harmonic Generation (SHG)} \]

\[ \chi^{(2)}(0; -\omega; \omega) \quad \text{Optical Rectification (OR)} \]

\[ \chi^{(2)}(-\omega; 0; \omega) \quad \text{Electro-Optic effect (Pockel’s effect)} \]
Extraction of Static Nonlinear Polarizabilities

- Standard technique: static nonlinearity

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

Finite-difference or polynomial fitting \( p_i(E) \) e.g.,

\[ \beta_{ijj} = \left[ -p_i(-2E_j) + 16p_i(-E_j) - 30p_i(0) + 16p_i(E_j) - p_i(2E_j) \right]/24E_j^2 \]
Example: Static CHCl$_3$ Hyperpolarizability*

Difficult case: $\beta$ very small!

Basis-set effects on the hyperpolarizability of CHCl$_3$: Gaussian-type orbitals, numerical basis sets and real-space grids

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(Dated: October 26, 2009)


3 methods

All agree with large diffuse basis sets!
Local Response Densities

Note: Contributions from Cl and HC are of opposite sign – Explains smallness of $\beta$
Real time Dynamic Nonlinear Response

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

• Accounting for time lag in system response

\[
p_i(t) = \mu^0_i + \int dt_1 \chi^{(1)}_{ij}(t-t_1)E_j(t_1) + \int dt_1 \int dt_2 \chi^{(2)}_{ijk}(t-t_1, t-t_2)E_j(t_1)E_k(t_2) + \int dt_1 \int dt_2 \int dt_3 \chi^{(3)}_{ijkl}(t-t_1, t-t_2, t-t_3)E_j(t_1)E_k(t_2)E_l(t_3) + \cdots
\]

¿ How can we invert the equation to get nonlinear response function?
Dynamic Nonlinear Polarizabilities

• Set $E_j(t) = F(t)E_j$ and define expansion $p_i(t)$

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

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

• Quadratic response $\chi^{(2)}$

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

- Sine wave enveloped by another sine wave or Gaussian

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

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

Linear and Nonlinear response of CO

SHG

OR
Real time vs Frequency space
Nonlinear Response

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

• Memory cost $\mathcal{O}(N_{KS} N_{basis} N_{evolve} M_{steps} M_\omega)$
  – Sternheimer equation (frequency space)
  – Real time $\mathcal{O}((N_{occ} + N_{unocc}) N_{basis})$
    $\mathcal{O}(N_{occ} N_{basis})$
Example pNA: Nonlinear SHG

- Comparison with other methods
Extension to high fields:

High Harmonic Generation in Ar

![Graph showing dipole response and pulse shape for different electric fields](image)
RT-TDDFT High Harmonic Generation in Ar

Odd Harmonic Magnitude

Max. El. Field
- 0.06
- 0.07

Magnitude (Arb. units)

Energy (eV)
II. Real-space & Real-time calculations of X–ray Response*

Dynamic structure in supported Pt nanoclusters

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The nature of local atomic and electronic structure at the nano-scale is both of fundamental and technological importance. For example, supported metal nanoclusters exhibit a number of unusual phenomena including large structural disorder and bond-length contraction with increasing temperature. We investigate this behavior for a prototypical 10-atom Pt cluster supported on γ-alumina using temperature-dependent, real-time simulations based on density functional theory/molecular dynamics and x-ray spectroscopy theory. The simulations reveal a complex dynamical structure on multiple-time scales including librational motion of the center of mass and fluctuating bonding characteristics which explain many of the unusual properties.

Real-space Green’s Function theory

XAS, XES, IXS, XMCD…

**FEFF9**

JJR et al., Comptes Rendus Physique 10, 548 (2009)

*in Theoretical Spectroscopy*

L. Reining *(Ed)* (2009)
Paradigm shift:

Use Green’s functions *not* wave functions!

- Golden rule via Wave functions

\[ \mu(E') \sim \Sigma_f |\langle i| \hat{e} \cdot r |f \rangle|^2 \delta(E - E_f) \]

- Golden rule via Green’s functions  *Efficient!*

Theorem: \[ -\frac{1}{\pi} \text{Im} G(r', r, E) = \Sigma_f |f \rangle \delta(E - E_f) \langle f | \]

\[ \mu(E') \sim -\frac{1}{\pi} \text{Im} \langle i| \hat{e} \cdot r' G(r', r, E) \hat{e} \cdot r |i \rangle \]
Parallel calculation of electron multiple scattering using Lanczos algorithms

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**MPI:** “Natural parallelization”

Each CPU does few energies

Lanczos: Iterative matrix inverse
Experiment vs Theory: Full spectrum X-ray Absorption Spectra (XAS)

theory vs expt

fcc Al

arXiv:cond-mat/0601242
http://leonardo.phys.washington.edu/feff/opcons

Phonon energy (eV)
Example: Finite T Nano-scale Pt Clusters

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

- Negative thermal expansion,
- Large disorder, ...

**Goals:** Understand structure

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

*Alternative to conventional paradigm!*
Experimental Observations (X-ray Absorption Expt)*

**1 H bond expansion**

**2 NTE**

**3 Enhanced $\sigma^2$**

**4 Red shift**

**4 Anomalies**

Calculation – Finite-\textit{T} DFT/MD

Non-equilibrium Finite temperature

Mean nn distance $R_{Pt-Pt}$

2500 3 fs steps

$\sim 10^4$ cpu-hrs (VASP)

10 atom Pt/ $\gamma$-Al$_2$O$_3$

time-elapsed rendering
Prototypical Pt\textsubscript{10} cluster on [110] surface of \(\gamma\)-Al\textsubscript{2}O\textsubscript{3}

**DFT/MD**

- VASP
- PBE Functional
- 396 eV Cutoff
- 3 fs Step
- 3 ps Equilibration
- 5 ps Runs (3)
- 165 K & 573 K

**XAS**

- FEFF8
- Full Multiple Scattering
- 32 Configurations from MD
- 7 Å Clusters (\(~150\) atoms)
Bond expansion in H₂ atmosphere

Adding H increases bond lengths
Negative Thermal Expansion

2.585 Å

2.596 Å

-0.011 Å

(-0.027 Å expt)
Morse-potential Fits to PDFs

\[ g(r) = Ae^{-\Phi(r)} \]

Note: increased low r width at HT implies PDF is \textit{non-vibrational}. 

\[ \Phi(r) = \beta D \left[ e^{-\alpha(r-r_0)} - 1 \right]^2 \]
High Pt-Pt Disorder

- $5 \times 10^{-3} \text{ Å}^2$ (8 $\times 10^{-3} \text{ Å}^2$)
- $10 \times 10^{-3} \text{ Å}^2$ (10 $\times 10^{-3} \text{ Å}^2$)
Physical Interpretation

Librational motion of center of mass

Period \(\sim 2\) ps
Amplitude \(\sim 1\) Å

Hindered Brownian motion
Librational motion: long time-scale fluctuations of the center of mass
Cluster footprint @ 573 K
Increased intensity and redshift at high T

Pt L$_3$ XANES

32 configuration average over last 5.5 ps
Interpretation of **red shift**: Charge fluctuations due to transient bonding

**Fermi energy vs time**

Surface Pt-O bonds & charge fluctuate!
Conclusions

1. RT-TDDFT explains linear and non-linear response & high harmonic generation
   
   **Challenge:** extension to core-XAS
   
   *(e.g. time-correlation function methods - in progress ... )*

2. RT-DFT/MD + RSGF XAS explains dynamic structure & experimental XAS of Pt nanoclusters
   
   **Novel nano-scale behavior:** Brownian-like motion

   **Challenge:** Extension to Faster, Hotter, Denser ...
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That’s all folks