Real-time approaches to x-ray and optical spectra

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Real-time Approaches for Optical and X-ray Spectra

**Goal:** Real-time linear and non-linear response

**Talk:**

- **I.** Linear and Nonlinear Optical Response  \( \text{RT-TDDFT} \)
- **II.** Real-time core-level XAS
- **III.** Many-body Effects
I. Real-Space & Real-Time Linear and Non-linear Optical Response

- Difficulty: frequency-space is computationally demanding too-many excited states
- Solution: RT-TDDFT - extension of SIESTA*

Real-Time-TDDFT*

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

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(Received 11 July 2007; accepted 4 September 2007; published online 19 October 2007)

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-(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.

Real time Linear Response

\[ \delta p(t) = p(t) - \bar{\mu}_0 \]
\[ \delta p_i(t) = \int dt' \chi_{ij}^{(1)}(t - t') E_j(t') \]
\[ \chi_{ij}^{(1)}(\omega) = \delta p_i(\omega) / E_j(\omega) = \alpha_{ij}(\omega) \]

Induced Dipole Moment

Linear Response Function

Linear Dielectric Function

Optical Absorption
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**:

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

Sometimes 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

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

- 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
Example: CO Linear Response

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

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

\[ p_z^{\text{delta}}(t) \]

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

\[ p_z^{\text{step}}(t) \]

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

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

Ground state without field

Evolution for $t>0$

Ground state with constant field

Evolution for $t>0$
Real time Nonlinear Response

- The nonlinear expansion in field strength
- Accounting for time lag in system response

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

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

¿ How can we invert the equation to get nonlinear response function?
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, …. 

• Quadratic response \( \chi^{(2)} \) is then

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

- Sine wave enveloped by another sine wave or Gaussian

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

SHG

Linear and Nonlinear response of CO
Example pNA: Nonlinear SHG

- Comparison with other methods
II. Real-time core-level XAS

Time-correlation function approach

\[
\mu(\omega) = \frac{1}{\pi} \text{Re} \int_0^\infty dt \, e^{i\omega t} G_c(t) \langle \psi(t) | \psi(0) \rangle \theta(\omega + \epsilon_c - E_F).
\]  

\[ |\psi(0)\rangle = d |b\rangle \]
XANES with time-dependent DFT

Goal:
- Time-dependent x-ray response
- Include core hole dynamics

Why use a real-time approach?
- New experimental pulsed sources (XFEL, LCLS)
- Pump-probe experiments
- Increased interest in time-dependent (TD) response
RTXS: The cartoon view

$|c\rangle$

Atom GS

\[ |\psi(0)\rangle = d|c\rangle \quad |\psi(t)\rangle = U(t, 0)|\psi(0)\rangle \]

PAPW

SCF

Init

CH PP

Screened CH

TD
RTXS equations

XAS Absorption (FGR, ΔSCF, FSR)
\[ \mu(\omega) = \sum_k |\langle c | d | k \rangle|^2 \delta_\Gamma(\omega + \varepsilon_c - \varepsilon_k) \theta(E - E_F) \]

FT
\[ \mu(\omega) = \frac{1}{\pi} \text{Re} \int_0^\infty dt e^{i\omega t} G_c(t) \langle \psi(t) | \psi(0) \rangle \theta(\omega + \varepsilon_c - E_F) \]

Core Hole Green’s Function
\[ G_c(t) = i \exp[i(\varepsilon_c + i \Gamma)t] \]

\[ \langle \psi(0) | \psi(t) \rangle \]
\[ \langle \psi(0) \rangle = d |c \rangle \]
\[ |\psi(t)\rangle = U(t, 0) |\psi(0)\rangle \]

Autocorrelation Function
\[ \langle \psi(t) | \psi(0) \rangle = \sum_{jj'} \langle c | d^\dagger | j \rangle U_{jj'}(t, 0) \langle j' | d | c \rangle \]

Crank-Nicolson
\[ \bar{t} = t + \Delta/2 \]
\[ U(t + \Delta, t) = \frac{1 - S^{-1} H(\bar{t}) \Delta/2}{1 + S^{-1} H(\bar{t}) \Delta/2} \]

\[ H_{jj'} = \langle j | h_H + v_{ch} + \Sigma | j' \rangle \]
Physical interpretation

Projected density of states p-DOS given by autocorrelation function for Seed state of p-symmetry:

\[
\rho_\psi(\omega) = -\frac{1}{\pi|\psi|^2} \text{Im} \int_0^\infty dt \ e^{i\omega t} \langle \psi(t)|\psi(0) \rangle
\]
Connection with Fermi golden rule agrees in limit $t \to \infty$

$$G(\omega) = \int_0^{\infty} dt \, e^{i\omega t} U(t, 0) \quad G(E) = [E - H + i\Gamma]^{-1}$$

$$\mu(\omega) = -\frac{1}{\pi} \text{Im} \langle c| d^\dagger G(E) d| c \rangle \theta(E - E_F)$$

$$\mu(\omega) = \sum_k |\langle c| d| k \rangle|^2 \delta \Gamma(\omega + \epsilon_c - \epsilon_k) \theta(E - E_F)$$
Check: C K-edge of CO

Decomposed projected pDOS (from TD)

Decomposed projected pDOS (Exact)

Time-Correlation Function
Example: C K-edge XES of Benzene
C K-Edge XAS of Diamond (C_{47}H_{60} cluster)
III. Many-body effects: Intrinsic losses

Cumulant expansion for core-hole Green’s function*

\[ G_c^+(t) = e^{i\epsilon_c t} e^{C(t)} \theta(t) \]

Particle-hole cumulant approach for inelastic losses in x-ray spectra

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\[ \tilde{G}_K(t) = \tilde{G}_K^0(t)e^{\tilde{C}_K(t)} \]

\[ \tilde{C}_K(t) = \int d\omega \gamma_K(\omega)(e^{i\omega t} - i\omega t - 1) \]

\[ \tilde{C}_K(t) = C_c(t) + C_k(t) + C_{ck} \]

All losses in particle-hole spectral function \( A_K \)

\[ \mu(\omega) = \int d\omega' \tilde{A}_K(\omega')\mu_K(\omega - \omega') \]

NiO

Intrinsic losses: real-time TDDFT cumulant

Real-time cumulant approach for charge-transfer satellites in x-ray photoemission spectra

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Langreth cumulant in time-domain*

\[ C(t) = \sum_{q,q'} V_q^* V_{q'} \int d\omega S(q,q',\omega) \frac{e^{i\omega t} - i\omega t - 1}{\omega^2} = \int d\omega \beta(\omega) \frac{e^{i\omega t} - i\omega t - 1}{\omega^2} \]

\[ \beta(t) = \frac{d^2C(t)}{dt^2} = \int d^3r V(r) \delta \rho(r,t) \]

Real-space interpretation: RT-TDDFT cumulant explains intrinsic excitations in TiO₂

**Interpretation**: satellites arise from oscillatory charge density fluctuations between ligand and metal at frequency $\sim \omega_{CT}$ due to turned-on core-hole
High-resolution valence and core excitation spectra of solid C_{60}

via first-principles calculations and experiment

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RT-TDDFT cumulant

Particle-hole cumulant

XPS

EELS

NBSE

XPS
X-ray Edge Singularities

Low energy particle-hole excitations in cumulant explain edge singularities in XPS and XAS of metals

\[ \beta_{ph}(\omega) = \alpha \omega e^{-\omega/\omega_p} \]

\[ C_{ph}(t) = -i \alpha \omega_p t - \alpha \ln(1 - i \omega_p t) \]

\[ A_{ph}(\omega) = e^{-a_p} \frac{e^{-\omega/\omega_p}}{\Gamma(\alpha)} \frac{\omega_{p}^{-\alpha}}{\tilde{\omega}^{1-\alpha}} \]
Question: Does the cumulant method work for correlated systems?

Hedin’s answer * MAYBE

“Calculation similar to core case … but with more complicated fluctuation potentials …

\[ V_n \rightarrow -\text{Im} \varepsilon^{-1}(\omega_n, q_n) \]

… not question of principle, but of computational work…”

Particle-hole cumulant for CeO$_2$

Ce 5s XPS of CeO$_2$

Spectral function

Ce $L_3$ XAS of CeO$_2$

Spectral weights
Real-time approach for x-ray Debye-Waller factors

X-ray absorption Debye-Waller factors from *ab initio* molecular dynamics

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(Received 30 August 2011; revised manuscript received 11 January 2012; published 25 January 2012)

An *ab initio* equation of motion method is introduced to calculate the temperature-dependent mean-square vibrational amplitudes $\sigma^2$ which appear in the Debye-Waller factors in x-ray absorption, x-ray scattering, and related spectra. The approach avoids explicit calculations of phonon modes, and is based instead on calculation of the displacement-displacement time correlation function from *ab initio* density functional theory molecular dynamics simulations. The method also yields the vibrational density of states and thermal quantities such as the lattice free energy. Illustrations of the method are presented for a number of systems and compared with other methods and experiment.
Conclusions

Efficient RT-TDDFT approach for frequency dependent nonlinear optical response –

Accuracy comparable to frequency-domain methods for small systems; also applicable to large systems

Similar real-time approaches can be applied to dynamic structure, Debye-Waller factors, etc.
Acknowledgments:

Supported by DOE BSE DE-FG02-97ER45623

Thanks to

J.J. Kas
J. Vinson
T. Fujikawa
S. Story
M. Verstraete
et al.

L. Reining
K. Gilmore
F. Vila
S. Biermann
J. Sky Zhou
et al.

G. Bertsch
L. Campbell
E. Shirley
M Guzzo
C. Draxl

& especially the ETSF
Conclusions

Particle-hole cumulant theory yields reasonable approximation for inelastic losses in XPS & XAS

\[
\mu(\omega) = \int d\omega' \tilde{A}_K(\omega')\mu_K(\omega - \omega')
\]

All losses (intrinsic, extrinsic and interference) in spectral function \(A_K(\omega)\) – can be added ex post facto

Interference terms explain mysteries in amplitudes and energy dependence: adiabatic- sudden transition

Theory also applicable to some \(d\)- and \(f\)-systems.
Many-body amplitudes $S_0^2(\omega)$ in XAS

- Many-body XAS $\approx$ Convolution

$$\mu(\omega) = \int_0^\infty d\omega' \tilde{A}(\omega, \omega') \mu_{qp}(\omega - \omega')$$

$$\equiv \langle \mu_{qp}(\omega) \rangle \approx \mu_{qp}(\omega) S_0^2(\omega)$$

- Explains crossover: \textbf{adiabatic} $S_0^2(\omega) = 1$

\textbf{to sudden transition} $S_0^2(\omega) \approx 0.9$

$$|g_q|^2 = |g_q^{\text{ext}}|^2 + |g_q^{\text{intrinsic}}|^2 - 2 g_q^{\text{ext}} g_q^{\text{intrinsic}}$$

Interference reduces loss!
Dynamic core-hole screening algorithm

PHYSICAL REVIEW B 73, 075402 (2006)

Dynamical core-hole screening in the x-ray absorption spectra of graphite, C_{60}, and carbon nanotubes: A first-principles electronic structure study

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(Received 14 September 2005; revised manuscript received 23 November 2005; published 1 February 2006)

\[
\Delta(t) = i \text{Tr} V \int_0^t dt_1 \int_{-\infty}^{\mu} \frac{d\epsilon}{\pi} \text{Im} g^R(\epsilon) \tilde{\varphi}(\epsilon, t_1),
\]
where \( \tilde{\varphi}(\epsilon, t) \) can be found from the matrix integral equation

\[
\tilde{\varphi}(\epsilon, t) = 1 + V \int_{\mu}^{\infty} \frac{d\epsilon_1}{\pi} \text{Im} g^R(\epsilon_1) L^+(\epsilon, \epsilon_1, t) \tilde{\varphi}(\epsilon_1, t),
\]

\[
I(\omega) \sim \text{Re} \int_0^\infty dt \int_{\mu}^{\infty} \frac{d\epsilon}{\pi} e^{i(\omega - s + \epsilon)} + \Delta(-t)
\]
\[
\times \sum_{ij} t_{ij} [\text{Im} g^R(\epsilon) \tilde{\varphi}(\epsilon, t)] t^j_{ij},
\]

\[
\text{I}(\epsilon, t) = 1 + V \int_{-\infty}^{\mu} \frac{d\epsilon_1}{\pi} e^{i(s - \epsilon_1)\chi - 1} \text{Im} G^R(\epsilon_1).
\]

alá Nozieres & De Dominicis

Extrinsic losses and Interference

XAS of Al

Satellite strengths

Particle-hole cumulant explains **cancellation** of extrinsic and intrinsic losses at threshold and crossover: **adiabatic** to **sudden** approximation.
Extension to: *Extrinsic and Intrinsic losses*

**Quasi-boson Model**

Interference between extrinsic and intrinsic losses in x-ray absorption fine structure

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**Energy Dependent Spectral Function** \(A(k,\omega)\)

**Question:** How to extend theory to real-time approach?
Interference: Quasi-Boson Approach*

Excitations - plasmons, electron-hole pairs ... are bosons

Many-body Model: $|e^-, h, \text{bosons}\rangle$

- Excitations: $H_v = \sum_n \omega_n a^\dagger_n a_n$
- Electrons: $h' = \sum_k \epsilon_k c^\dagger_k c_k$
- e-boson coupling $V_{pv} = \sum_{nkk'} [V_{kk'} a^\dagger_n (V_{kk'}^*) a_n] c^\dagger_k c_{k'}$
- Core-hole-boson coupling: $V_{vc} = -\sum_n V_{bb}^n (a^\dagger_n + a_n)$

“GW++” Same ingredients as GW self-energy

$V^n \rightarrow -\text{Im} \varepsilon^{-1}(\omega_n, q_n)$ fluctuation potentials

Many-pole Self-energy Algorithm* 

-\text{Im} \varepsilon^{-1}(\omega) \quad \text{Many-pole} \text{ Dielectric Function} \quad \sim \sum_i g_i \delta(\omega - \omega_i) 

\rightarrow \text{Many-pole GW self-energy} \Sigma(E) 

* J. Kas et al. PRB 76, 195116(2008)
Effective $GW^{++}$ Green’s Function $g_{\text{eff}}(\omega)$


g_{\text{eff}}(\omega) = e^{-\alpha} \left[ g'(\omega) + \sum_n \left( \frac{V^2_{bb}}{\omega_n} \right)^2 g'(\omega - \omega_n) - 2 \sum_n \frac{V_{bb}^2}{\omega_n} g'(\omega - \omega_n) V^n g'(\omega) \right]

Extrinsic + Intrinsic - 2 x Interference

Damped $qp$ Green’s function $g'(\omega) \equiv [\omega - h' - \Sigma(\omega) + i\gamma]^{-1}$

Spectral function: $A(\omega) = -(1/\pi) \text{Im} \ g_{\text{eff}}(\omega)$
That's all folks