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

J. J. Rehr
Calculations of X-ray Spectra in Real-space and Real-time

**Goal:** Real-space, real time Theory of XAS

**Talk:** Mostly real-time

- I. RT-TDDFT and XAS
- II. Many-body effects – $S_0^2$ and satellites
- III. Vibrational & non-equilibrium properties
"The real-time formalism is a gift of god"

W. Kohn
Why real-time?

XFEL pulsed x-ray sources (FLASH, LCLS)

Pump-probe experiments

Interest in time-dependent response

Non-equilibrium systems
Theoretical challenge: many length & time-scales

- BSE
- RSGF
- "True" Crystals
- Molecular Crystals
- DFT/MD
- RT-TDDFT
- Molecules
- Clusters
- Liquids
- IR, V/UV, X-Rays
- Real-time - Real-space
- ns, ps, fs, as
A. Real-time approach for XAS

Time-correlation function formalism

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

Equivalent to single-particle Fermi golden rule
Real-time time-dependent density functional theory approach for frequency-dependent nonlinear optical response in photonic molecules

Y. Takimoto, F. D. Vila, and J. J. Rehr
Department of Physics, University of Washington, Seattle, Washington 98195, USA
(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.


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

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

• 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**:

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

Can be more powerful and more EFFICIENT than Frequency space
Numerical Real-time Evolution

\[ |\psi(t)\rangle = \sum_j |j\rangle c_j(t) \equiv c(t) \]

- 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!

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

- Adiabatic GGA exchange-correlation (PBE) functional
Example: CO molecule Linear Response

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

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

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

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

\[ E(t) \]

Ground state without field

Evolution for $t>0$

Example: CO molecule Linear Response
Shaped pulses and non-linear response

- Nonlinear expansion in field $E(t)$ including time lag in response

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

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

¿ How to invert the equation for nonlinear response ́?
• Define $E_j(t) = F(t)E_j$ and response $p_i(E)$

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

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

• Quadratic response function $\chi^{(2)}$

$$p_{ijk}^{(2)}(t) = \int dt_1\int dt_2 \chi_{ijk}^{(2)}(t - t_1, t - t_2)F(t_1)F(t_2)$$
Shaped pulses and non-linear response $F_\delta(t)$

- Sine wave enveloped by another sine wave or Gaussian

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

\[
\chi^{(2)}_{ijk}(0; -\omega_0, \omega_0) = \frac{\pi p^{(2)}_{ijk}(0)}{\int_{-\Delta}^{\Delta} d\omega' F^*(\omega_0 + \omega') F(\omega_0 + \omega')} \quad \text{(OR)}
\]
Example: non-linear SHG in pNA

- Comparison with other methods
XAS Absorption Fermi golden rule, 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
\[ G_c(t) = i \exp[i(\varepsilon_c + i\Gamma)t] \]
\[ \langle \psi(0) | \psi(t) \rangle = d |c\rangle \]
\[ |\psi(t)\rangle = U(t,0) |\psi(0)\rangle \]

Autocorrelation Function
\[ \langle \psi(t) | \psi(0) \rangle = \sum_{j,j'} \langle c | d^\dagger | j \rangle U_{j,j'}(t,0) \langle j' | d | c \rangle \]
\[ U(t,0) = T \exp \left[ -i \int_0^t dt H(t) \right] \]

Crank-Nicolson RT-TDDFT
\[ \tilde{t} = t + \Delta/2 \]
\[ U(t + \Delta, t) = \frac{1 - S^{-1}H(\tilde{t})\Delta/2}{1 + S^{-1}H(\tilde{t})\Delta/2} \]
\[ \langle j | \psi(t) \rangle = \sum_j \langle j | c_j(t) \rangle \]
\[ \Pi_{j,j'} = \langle j | h_H + v_{ch} + \Sigma | j' \rangle \]
Interpretation of correlation function

\[ \rho_{\psi}(\omega) = -\frac{1}{\pi|\psi|^2} \text{Im} \int_{0}^{\infty} dt \, e^{i\omega t} \langle \psi(t) | \psi(0) \rangle \]

\[ |\psi_{+}(0)\rangle \equiv \mathcal{P} |\psi(0)\rangle = \mathcal{P} d(x)|c\rangle \]
C K-edge of CO
Example: C K-edge XAS of Diamond cluster
B. Real-time approach for many-body effects

1. Intrinsic losses - due to sudden core-hole

Formalism: Cumulant expansion for core-hole Green’s function

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

Many body effects implicit in “cumulant” \( C(t) \)

Reviews and references


On correlation effects in electron spectroscopies and the GW approximation

Lars Hedin
Department of Theoretical Physics, Lund University, Sölvegatan 14A, 223 62 Lund, Sweden


Dynamical effects in electron spectroscopy

Jianqiang Sky Zhou,1,2,a) J. J. Kas,2,3 Lorenzo Sponza,4 Igor Reshetnyak,1,2 Matteo Guzzo,5 Christine Giorgetti,1,2 Matteo Gattl,1,2,6 Francesco Sottile,1,2 J. J. Rehr,2,3 and Luca Reining1,2

1Laboratoire des Solides Irradiés, École Polytechnique, CNRS, CEA-DSM-IRAMIS, Université Paris-Saclay, F-91128 Palaiseau, France
2European Theoretical Spectroscopy Facility (ETSF)
3Department of Physics, University of Washington, Seattle, Washington 98195-1560, USA
4Department of Physics, King’s College London, London WC2R 2LS, United Kingdom
5Institut für Physik und IRIS Adlershof, Humboldt-Universität zu Berlin, D-12489 Berlin, Germany
6Synchrotron SOLEIL, L’Orme des Merisiers, Saint-Aubin, BP 48, F-91192 Gif-sur-Yvette, France
Cumulant expansion properties

\[ G_k(t) = e^{i\epsilon_0 t} e^{C(t)} \]

\[ C(t) = \int d\omega' \beta(\omega') \frac{e^{i\omega' t} - i\omega' t - 1}{\omega'^2} \]

Landau formula for \( C(t) \)

Excitation spectra

\[ \beta_k(\omega) = \frac{1}{\pi} |\text{Im} \Sigma_k(\omega + \epsilon_k)| \]

GW\_\Sigma

Spectral Function

\[ A_k(\omega) = \int \frac{dt}{2\pi} e^{i(\omega - \epsilon_k) t} \exp \left\{ \int d\omega' \beta(\omega') \frac{e^{i\omega' t} - i\omega' t - 1}{\omega'^2} \right\} \]

*For diagrammatic expansion of higher order terms, see e.g. O. Gunnarsson et al., Phys. Rev. B 50, 10462 (1994)*
Intrinsic losses: CT excitations RT-TDDFT cumulant

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

J. J. Kas, F. D. Vila, J. J. Rehr, and S. A. Chambers

1Department of Physics, University of Washington, Seattle, Washington 98195-1560, USA
2Physical Sciences Division, Pacific Northwest National Laboratory, Richland, Washington 99352, USA

Langreth cumulant in time-domain*

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

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


\( \text{TiO}_2 \)
Interpretation: satellites arise from oscillatory charge density fluctuations between ligand and metal at frequency $\omega_{CT}$ due to turned-on core-hole.
C. Real-time approach for vibrations and non-equilibrium systems

1. XAS Debye-Waller factors

2. DFT/MD approach for nanocatalysts
1. Real-time EXAFS Debye-Waller factors

X-ray absorption Debye-Waller factors from \textit{ab initio} molecular dynamics

F. D. Vila, V. E. Lindahl, and J. J. Rehr

\textit{Department of Physics, University of Washington, Seattle, Washington 98195, USA}

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

An \textit{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 calculations of the displacement-displacement time correlation function from \textit{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.

\begin{equation}
\sigma^2_r(T) = \frac{\hbar}{\mu_R \pi} \int_0^{t_{\text{max}}} dt \langle Q_R(t)|Q_R(0) \rangle \times \ln \left( 2 \sinh \frac{\pi t}{\beta \hbar} \right)^{-1} e^{-\beta t^2}
\end{equation}
2. Non-equilibrium systems

A theoretical horror story

Starring

Fernando Vila &
Anatoly Frenkel

with

J. Kas, S. Bare & S. Kelly

Directed by J. J. Rehr

a DOE CSGB Production
Theoretical Challenge: Anomalous properties of $\text{Pt}_{10}/\gamma\text{Al}_2\text{O}_3$

- Pt-Pt nn
  Negative Thermal Expansion & Bond expansion in $\text{H}_2$

- Anomalous Pt-Pt disorder

NOT bulk-like!
More Anomalous properties* Pt_{10}/γAl_{2}O_{3}

- Increased edge intensity
- Redshift of XANES with increasing T (charge effects)
- Standard theory fails!
What’s going on?

Breakthrough: DFT-MD

Blob footprint @ 573 K

The BLOB

Cluster center of mass
Dynamic structure in supported Pt nanoclusters: Real-time density functional theory and x-ray spectroscopy simulations

F. Vila,1 J. J. Rehr,1,* J. Kas,1 R. G. Nuzzo,2 and A. I. Frenkel3
1Department of Physics, University of Washington, Seattle, Washington 98195, USA
2Department of Chemistry, University of Illinois at Urbana-Champaign, Urbana, Illinois 61801, USA
3Department of Physics, Yeshiva University, New York, New York 10016, USA
(Received 24 July 2008; published 11 September 2008)

Fuzzy “structure”
Decomposition into Vibrational and Disorder components

Vibrational – Normal behavior (THz - 200-400 fs periods)

Dynamic disorder – Large, chaotic, sub THz
Real-time, real-space formalism - powerful alternative to frequency and $k$-space methods

- Linear and non-linear optical and x-ray response to monochromatic and pulsed sources
- Many-body effects: multi-electron excitations, plasmon and charge-transfer satellites
- Vibrational and non-equilibrium effects
Acknowledgments

Supported by DOE BSE DE-FG02-97ER45623

Thanks to
J.J. Kas    L. Reining    G. Bertsch
J. Vinson   K. Gilmore   L. Campbell
T. Fujikawa F. Vila      E. Shirley
S. Story    S. Biermann  M. Guzzo
M. Verstraete J. Sky Zhou C. Draxl