New and ongoing developments and applications in real-time and linear-response TDDFT in NWChem

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Real-Time (RT) TDDFT

- Band gap engineering: Drive absorption into the visible
- Light harvesting, photocatalysis, etc
- Doping, solid solutions, etc
- Inexpensive, abundant, environmentally friendly materials
- Computing optical (excited state) properties with TDDFT
- Bulk-mimicking finite clusters
- Embedding with capping atoms and electrostatic potentials
- Band-like: many 1000’s of roots

Optical Excitations in Doped Metal Oxides

- Full response beyond perturbation limit
- Real-time: real-space \rightarrow full dynamical information
- Insight into ultrafast and nonlinear processes
- High harmonic generation
- Valence and core excitations

N-doped TiO₂ Rutile

Optical Band Gap (eV) vs. Energy (eV)

- TD-BLYP UV absorption
- Penta: bulk-like
- N-doped: electronic states
- But - potential of infinite periodic lattice
- 100 atoms, ~700 eV, ~1200 basis functions, open shell
- Linear-response (frequency domain) TDDFT
- Spectrum spanning 0–5 eV: 5000 roots (!!!)
- Painstaking “windowing” procedure
- Real-time TDDFT
- Three simulations \{x, y, z\} per cluster

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Optical Excitations in Doped Metal Oxides

- Fully compatible with all XC functionals in NWChem
- Optimized version released in NWChem 6.3 (May 2013)
- Gradients in development

Modeling Above Ionization Excitations

- Range-separated functionals: Fix incorrect DFT exchange-correlation asymptote by splitting exchange into short (DFT) and long range (Hartree-Fock) terms
- But how to pick γ? E.g., Want: enforce Koopmans’ Theorem to minimize object function:

\[
\min_{\gamma} \left\{ \sqrt{\langle \hat{H} | \hat{\rho} \rangle} - \gamma \langle \hat{\rho} \rangle \right\}
\]
- “First principles” tuning (no inputs from experiment)
- Typically brings Koopmans’ IP and SCF IP within ±1 eV, and within ±5% of experimental IP

Imaginary Absorbing Potentials

\[
\langle \rho_1 | \exp\{i \hat{H} \} | \rho_0 \rangle = \exp\{i \hat{\rho} \} | \rho_0 \rangle
\]
- Natural for planewaves or grids
- Atom-centered basis sets \X

Molecular Orbital-Based Absorb. Potential

- Instead build \D directly in the MO space:

- \( \beta \) : phenomenological damping parameter for the \( \nu \) MO
- Project onto TDD-Fock matrix via TD eigenvectors \( D^{(\nu)} \)
- Exponential damping acting on MOs in the continuum:

\[
\beta \leq \alpha \leq \omega
\]
- \( \alpha \): energy of \( \nu \) MO above vacuum cutoff energy \( \omega \)
- Virtually irrelevant in DFT, but “use “relaxed” orbitals (e.g., electron affinities)

Implementation of Analytic LR-TDDFT Gradients

Optical Dyes

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SciDAC-3 PI Meeting