Computational study of optical and structural properties of an organic dye sensitized solar cell

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Overview

• Nanostructured photovoltaic devices (Grätzel cells)

• Application of TDDFT to such systems
  • computational approach
dry system
  including (explicit) solvent
  averaging over MD in presence of solvent

• Dye adsorption/desorption in presence of explicit solvent
Sensitized semiconductor surfaces as photovoltaic devices

Idea (Graetzel solar cells):

\[ \text{ENERGY} \]
\[ \text{e}^- \rightarrow \text{excited state} \]
\[ \text{hv} \]
\[ \text{ground state} \]
\[ \text{conduction band} \]
\[ \text{valence band} \]

\text{semiconductor TiO}_2

\text{surface complex}
Functioning of a Grätzel cell

*Figure 3* Schematic of operation of the dye-sensitized electrochemical photovoltaic cell. The photoanode, made of a mesoporous dye-sensitized semiconductor, receives electrons from the photo-excited dye which is thereby oxidized, and which in turn oxidizes the mediator, a redox species dissolved in the electrolyte. The mediator is regenerated by reduction at the cathode by the electrons circulated through the external circuit. Figure courtesy of P. Bonhôte/EPFL-LPL.

Various dyes


Figure 3. Spectral response curve of the photocurrent for the DYS sensitized by N3 and the black dye. The incident photon to current conversion efficiency is plotted as a function of wavelength.
Our system: Squaraine on TiO$_2$ slab

Slab geometry:
1x4 TiO2 anatase slab, Exposing (101) surface

PBE functional, PW basis set (Quantum-ESPRESSO code)

Shown here: minimum energy configuration
TiO2 slab with squaraine dye

PDOS

Fermi Energy

Energy [eV]
TDDFT treatment of model system

• Adiabatic PBE functional

• Recursive Lanczos algorithm for TDDFT:
  Ideally suited for
  • large systems
  • broad spectral region,
  • large basis set
Linear response formalism in TDDFT:

\[
\omega \delta \psi^+_v(r) = \left( H_{KS}^0 - \epsilon^0_v \right) \delta \psi^+_v + \hat{P}_c \left( \delta V_{SCF}^+(r) + V_{pert}(r) \right) \psi^0_v(r)
\]

\[
-\omega \delta \psi^-_v(r) = \left( H_{KS}^0 - \epsilon^0_v \right) \delta \psi^-_v + \hat{P}_c \left( \delta V_{SCF}^-(r) + V_{pert}(r) \right) \psi^0_v(r)
\]

Now define the following linear combinations:

\[
x_v(r) = \frac{1}{2} (\delta \psi^+_v(r) + \delta \psi^-_v(r))
\]

\[
y_v(r) = \frac{1}{2} (\delta \psi^+_v(r) - \delta \psi^-_v(r))
\]
\[(\omega - \mathcal{L}) |x, y\rangle = |0, v\rangle\]

\[
\mathcal{L} = \begin{pmatrix}
0 & D \\
K & 0
\end{pmatrix}
\]

With the following definitions:

\[
D |x\rangle = \left\{ (H_{KS}^0 - \epsilon_i) x_i(r) \right\}
\]

\[
K |x\rangle = \left\{ (H_{KS}^0 - \epsilon_i) x_i(r) + \psi_i^0(r) \sum_j \int dr' f_{Hxc}(r, r') \psi_j^0(r') x_i(r') \right\}
\]

\[
\begin{pmatrix}
0 & D \\
K & 0
\end{pmatrix}
\begin{pmatrix}
x \\
y
\end{pmatrix}
= \omega
\begin{pmatrix}
x \\
y
\end{pmatrix}
\]
Consider an observable $A$:

$$A(t) = \sum_i \left( \langle \delta \psi_i(t) | \hat{A} | \psi_i^0 \rangle + \langle \psi_i^0 | \hat{A} | \delta \psi_i(t) \rangle \right)$$

Its Fourier transform is:

$$\tilde{A}(\omega) = \sum_i \left( \langle \psi_i^0 | \hat{A} | \delta \psi_i^-(\omega) \rangle + \langle \psi_i^0 | \hat{A} | \delta \psi_i^+(\omega) \rangle \right)$$

$$= \sum_i 2 \langle \psi_i^0 | \hat{A} | x_i(\omega) \rangle$$

$$= 2 \langle \alpha, 0 | x, y \rangle$$
\[ \tilde{A}(\omega) = \sum_i \left( \langle \psi_i^0 | \hat{A} | \delta \psi_i^-(\omega) \rangle + \langle \psi_i^0 | \hat{A} | \delta \psi_i^+(\omega) \rangle \right) \]
\[ = 2 \sum_i \langle \psi_i^0 | \hat{A} | x_i(\omega) \rangle \]
\[ = 2 \langle a, 0 | x, y \rangle \]

Recall: \( (\omega - \mathcal{L}) | x, y \rangle = | 0, \nu \rangle \)

Therefore:

\[ \tilde{A}(\omega) = 2 \langle a, 0 \mid (\omega - \mathcal{L})^{-1} \mid 0, \nu \rangle \]

Thus in order to calculate the spectrum, we need to calculate one given matrix element of \((\omega - \mathcal{L})^{-1}\).
Use a recursion to represent \( L \) as a tridiagonal matrix:

\[
L = \begin{pmatrix}
    a_1 & b_1 & 0 \\
    c_1 & a_2 & b_2 \\
    0 & c_2 & a_3 & b_3 \\
    & & \ddots & \ddots & \ddots & b_{N-1} \\
    & & & & c_{N-1} & a_N
\end{pmatrix}
\]

And the response can be written as a continued fraction!

\[
\tilde{A}(\omega) = 2 \langle a, 0 \mid (\omega - L)^{-1} \mid 0, v \rangle = \frac{1}{\omega - a_1 + b_2 \frac{1}{\omega - a_2 + \cdots + c_2}}
\]
Convergence of the TDDFPT spectrum

Isolated squaraine molecule

![Graph showing convergence of the TDDFPT spectrum](image_url)
Charge response at main absorption peak:
Main features:

Recursive Lanczos technique allows to compute TDDFT spectra:

• Rather fast (even in large systems)
• Over broad spectral region
• No virtual KS states required
• Allows to analyze particular features of a spectrum

(use of this "turboTDDFT" code will be part of next week's hands-on tutorial)
Experimental and TDDFT absorption spectra

(a)

I(ω)

Energy [eV]

Experiment

(b)

I(ω)

Energy [eV]

Computation
Analyzing the various transitions
A more realistic system: Including the solvent
TDDFT calculation of optical spectra and related quantities

Various challenges:

• System is large (429 atoms, 1.666 electrons, 181.581 PWs, resp. 717.690 PWs)
• Broad spectral region of interest
• Many excited states in spectral region

Computational tool:

• Recursive Lanczos algorithm for TDDFT
TDDFT optical spectrum: dry system

\[\text{Im } \alpha_{zz}(\omega)\]

- \(\omega_1\)
- \(\omega_2\)
- \(\omega_3\)
- \(\omega_4\)

Energy [eV]
TDDFT optical spectrum including solvent

\[ \text{Im } \alpha_{zz}(\omega) \]

- Squaraine on TiO\(_2\) in vacuum
- Squaraine on TiO\(_2\) in water

\[ \omega_1, \omega_2, \omega_3, \omega_4 \]

Energy [eV]
Including the solvent in MD and TDDFT computations

• Solvent is treated at the same level of theory as molecule and surface slab

• **Solvent changes electrostatic conditions (dielectric constant …)**

• Solvent participates actively:
  - in formation surface dipoles, etc.
  - hydrogen bonding networks
  - is essential for geometry of solute
Squaraine on \( \text{TiO}_2 \)

Simulation in explicit water

Absorption vs. energy [eV]
Squaraine on TiO$_2$
Simulation in explicit water

Absorption vs. energy [eV]

- Black line: MD averaged simulation
- Red line: experiment
Squaraine on TiO$_2$

Simulation in explicit water

Absorption vs. energy [eV]

- Black line: MD averaged simulation
- Red line: experiment
- Green line: no MD average
Energy level fluctuations and electron injection driving force

![Graph showing energy level fluctuations over time with specific energy values marked: 0.55, 0.67, 1.38, and 1.29.](image)
Squaraine adsorption on TiO$_2$
Dye desorption steps:
Conclusions

• TD-DFT study of squaraine dye adsorbed on TiO$_2$ slab

  Fair agreement with experiment in absence of solvent in computation

• Including the solvent explicitly

  Improvement of computed spectrum, but important features are not reproduced (shoulders, etc.)

• Molecular dynamics of dye sensitized slab with explicit solvent

  Averaging of optical properties over many configurations leads to a description of optical properties in good agreement with experiment

• Very efficient implementation of TD-DFT for large systems/basis sets

  Recursive Lanczos TDDFT based on time-dependent DFPT for a system composed of 429 atoms and described by $\approx 200,000$ PWs
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To know more: