Introduction

Dye-sensitized solar cells [1] are currently attracting widespread academic and commercial interest for the conversion of sunlight into electricity because of their low cost and high efficiency. In these cells, unluminescent dyes and the nanoparticles such as TiO₂ or ZnO represent the key components for high power conversion efficiencies. In this poster we present a recently started project on ab-initio Time Dependent Density Functional Theory (TDDFT) [2].

Work in progress

1. Introduce a scheme to systematically account for solvent effect. Continuum solvent models appear to be the first step toward this goal

2. Investigate more metal-free dyes such as indolines

3. Study the evolution of absorption spectrum in the exciton-allowed states 

Dye-sensitized Solar Cells (DSSC)

Solar cells built with N3-sensitized TiO₂ provide:
- Broad range of visible light absorption
- Good match with TiO₂ conduction band
- High thermal stability
- Environmentally friendly (metal-free dyes)
- Low cost production
- DSSC efficiency can reach up to 11%

Which dye?
Many! For instance:
- Quinacridones
- Perylenes
- Hemicyanines
- Boradiazaindacenes
- Triarylamines
- Coumarins
- Many! For instance:

Indoline D149 dye

Absorption spectroscopy with TDDFT

Time Dependent Density Functional Theory

At the one-electron level, the density matrix is a function of the time-dependent density and the external potential.

\[
\rho(t) = \int \frac{1}{\sqrt{2\pi}} e^{-i\omega t/\Delta \omega} \left| \psi(t) \right|^2 d\omega
\]

Excitation energies and linear response

At the first order in the perturbing field \( \mathbf{A} \), the fluctuation in the density is:

\[
\delta\rho(t) = \int \frac{1}{\sqrt{2\pi}} e^{-i\omega t/\Delta \omega} \left| \psi(t) \right|^2 d\omega
\]

The exchange kernel

\[
\rho_{ex}(\omega) = \frac{\rho_0(\omega)}{\omega^2}
\]

Polarizability tensor

\[
\alpha_{ij}(\omega) = -\int \frac{1}{\sqrt{2\pi}} e^{-i\omega t/\Delta \omega} \left| \frac{\partial^2 \psi(t)}{\partial x_i \partial x_j} \right|^2 d\omega
\]

Two possible ways to solve the linear response equations (finite systems)

Coulomb equation

Comparing the Lehman representation of the interacting response function \( \chi_{ij}(\omega) \) with the Khon-Sham response function \( \chi_{ij}(\omega) \), it is possible to derive the eigenvalue equation

\[
\int \frac{1}{\sqrt{2\pi}} e^{-i\omega t/\Delta \omega} \left( \rho_0(\omega) - \frac{1}{\Delta \omega} \chi_{ij}(\omega) \right) d\omega = \mu_{ij}
\]

Time propagation

- Apply a delta perturbation to the ground state of the system \( \rho_{0}(\omega) \)
- At \( t \to 0 \) the Khon-Sham orbitals are: \( \phi_{ij}(t=0) = \frac{\partial^2 \psi(t)}{\partial x_i \partial x_j} \)
- Propagate the KS orbitals for finite (long) time
- Obtain the dynamical polarizability from the states

References