Regional School on Physics at the Nanoscale:
Theoretical and Computational Aspects
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Computational approach to nanoscale photovoltaic devices

Ralph Gebauer

The Abdus Salam
International Centre for Theoretical Physics

United Nations
Educational, Scientific
and Cultural Organization

International Atomic
Energy Agency

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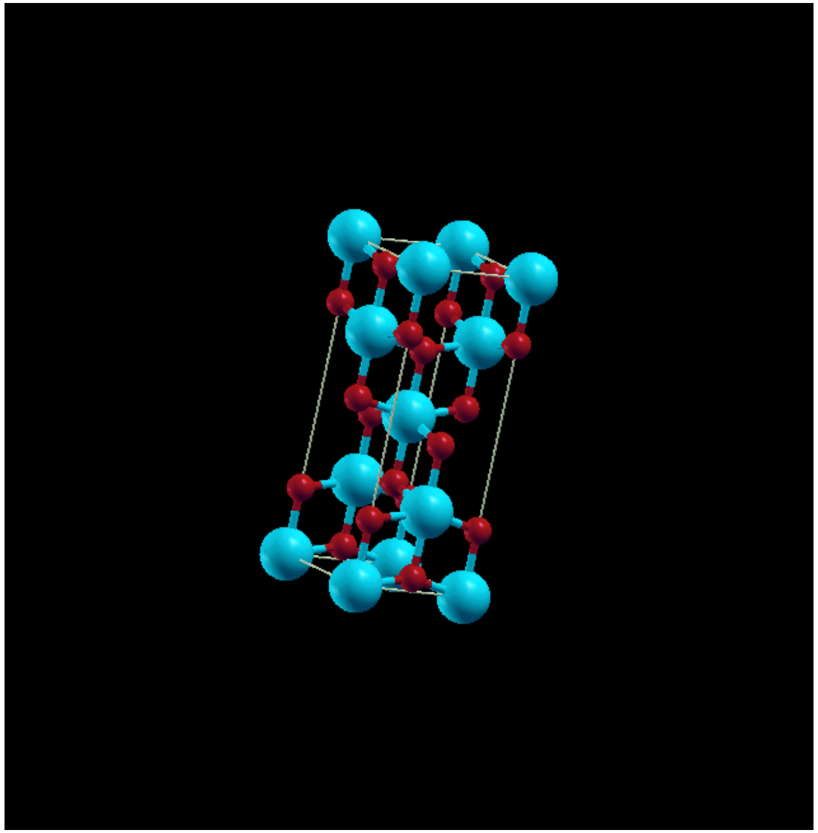
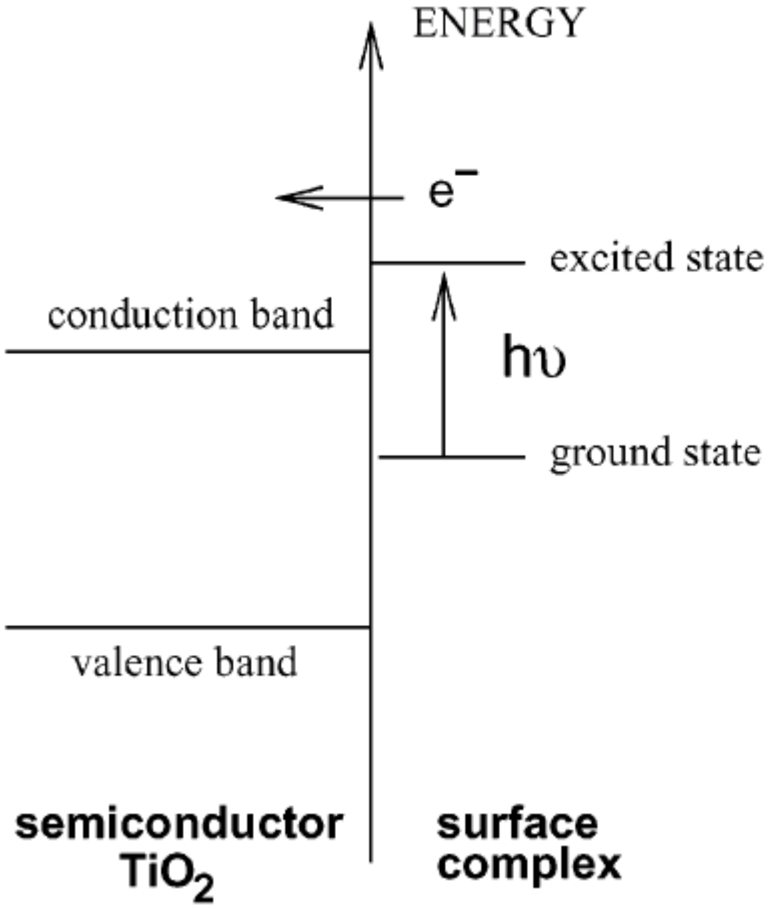
Overview

- Nanostructured photovoltaic devices (Grätzel cells)
- Research challenges
- Application of TDDFT to such systems
- Bringing together ab-initio molecular dynamics and TD-DFT
- Successes and failures for charge transfer energies

Electron transfer in sensitized semiconductor surfaces

Idea (Graetzel solar cells):





Nanostructured TiO_2 surface

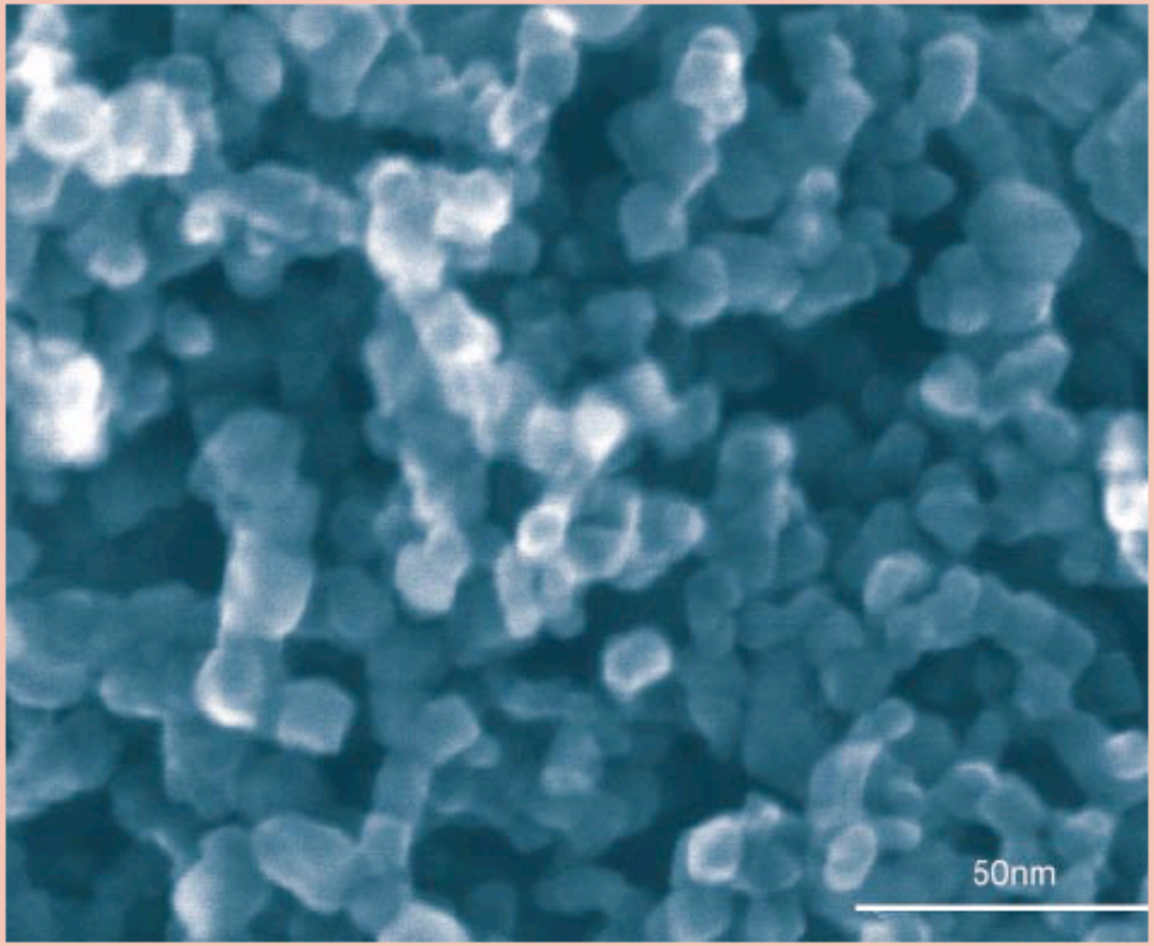


Figure 4 Scanning electron micrograph of the surface of a mesoporous anatase film prepared from a hydrothermally processed TiO_2 colloid. The exposed surface planes have mainly {101} orientation.

Source:
M. Grätzel, Nature **414**, 338 (2001)

Functioning of a Grätzel cell

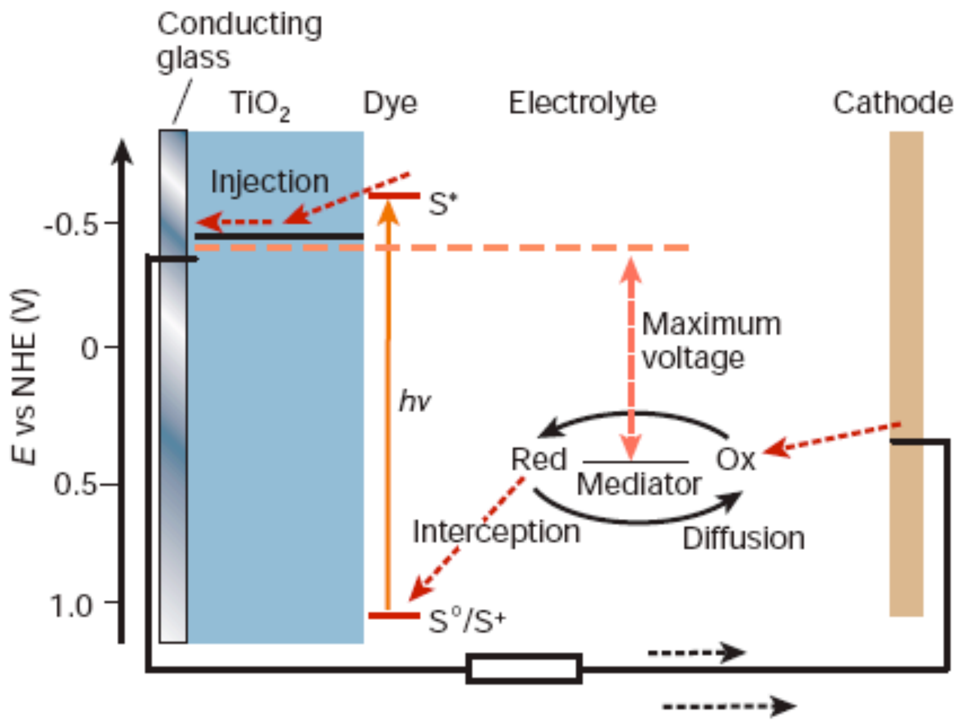


Figure 3 Schematic of operation of the dye-sensitized electrochemical photovoltaic cell. The photoanode, made of a mesoporous dye-sensitized semiconductor, receives electrons from the photo-excited dye which is thereby oxidized, and which in turn oxidizes the mediator, a redox species dissolved in the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

Source:
M. Grätzel, Nature **414**, 338 (2001)

Various dyes are extensively studied

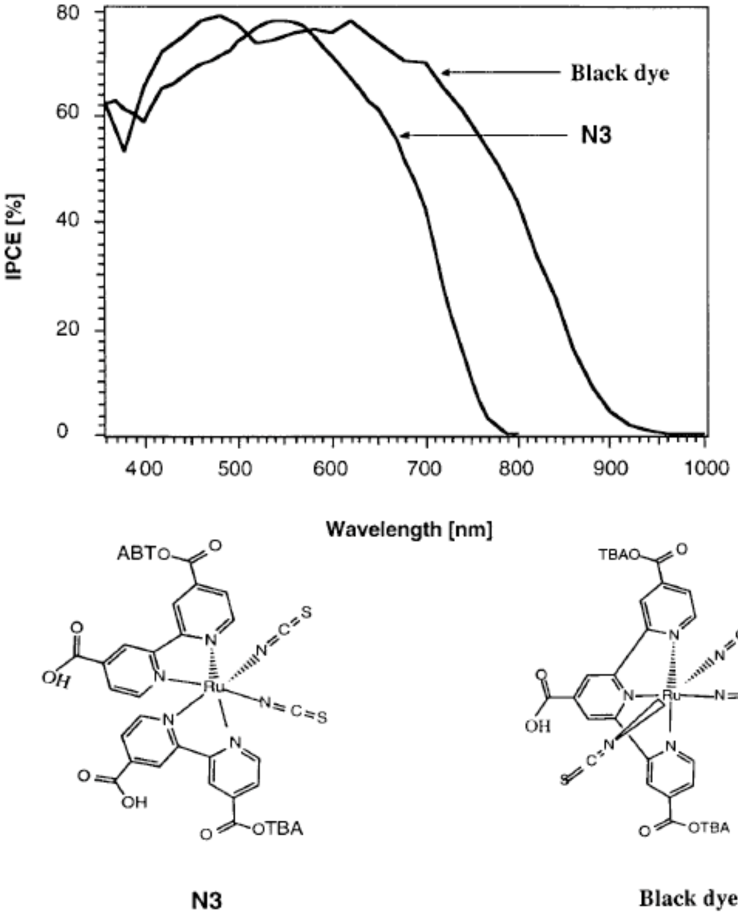
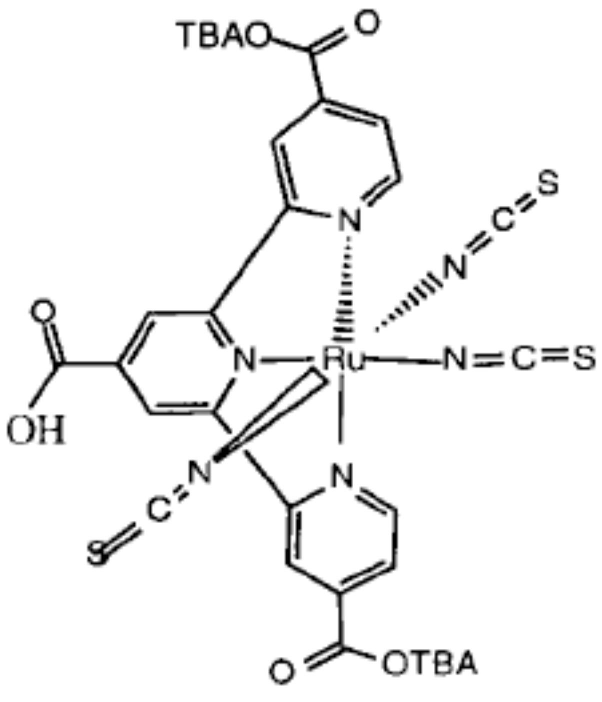


Figure 3. Spectral response curve of the photocurrent for the DYSC sensitized by N3 and the black dye. The incident photon to current conversion efficiency is plotted as a function of wavelength



Black dye

Source: M. Grätzel, Prog. Photovolt. Res. Appl. 8, 171-185 (2000)

Charge transfer dynamics

The science of dye sensitized solar cells contains many challenges:

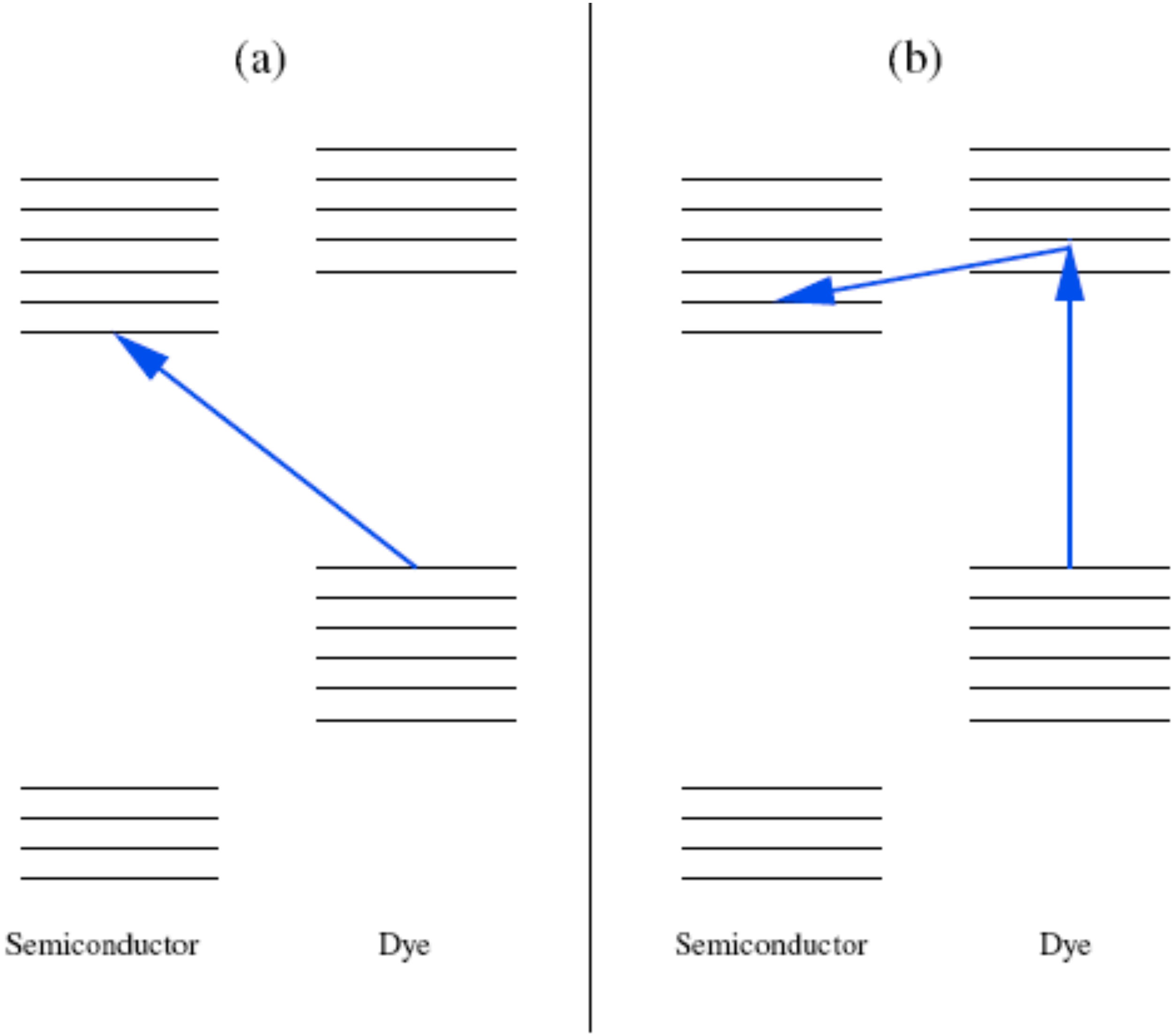
- Chemistry
- Materials science
- Surface science
- Physics

- Synthesis
- Stability
- Efficiency, Costs, etc.

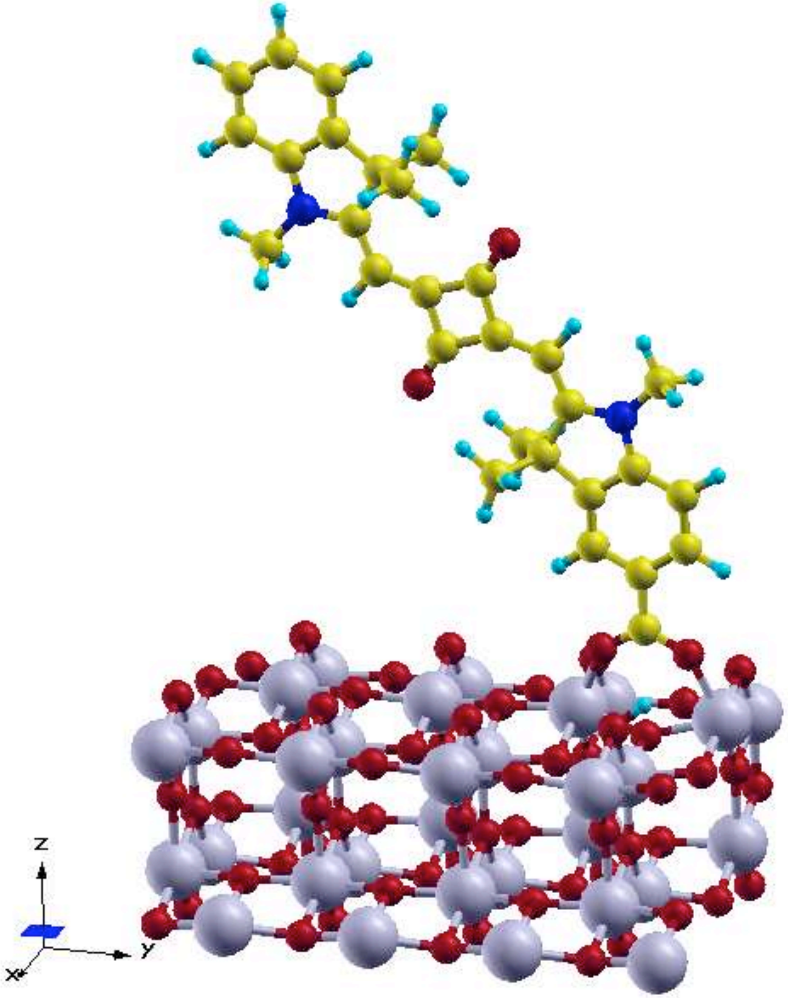
In this presentation: Concentrate on understanding of mechanisms of charge separation at dye/semiconductor interface

Electron transfer/ charge separation

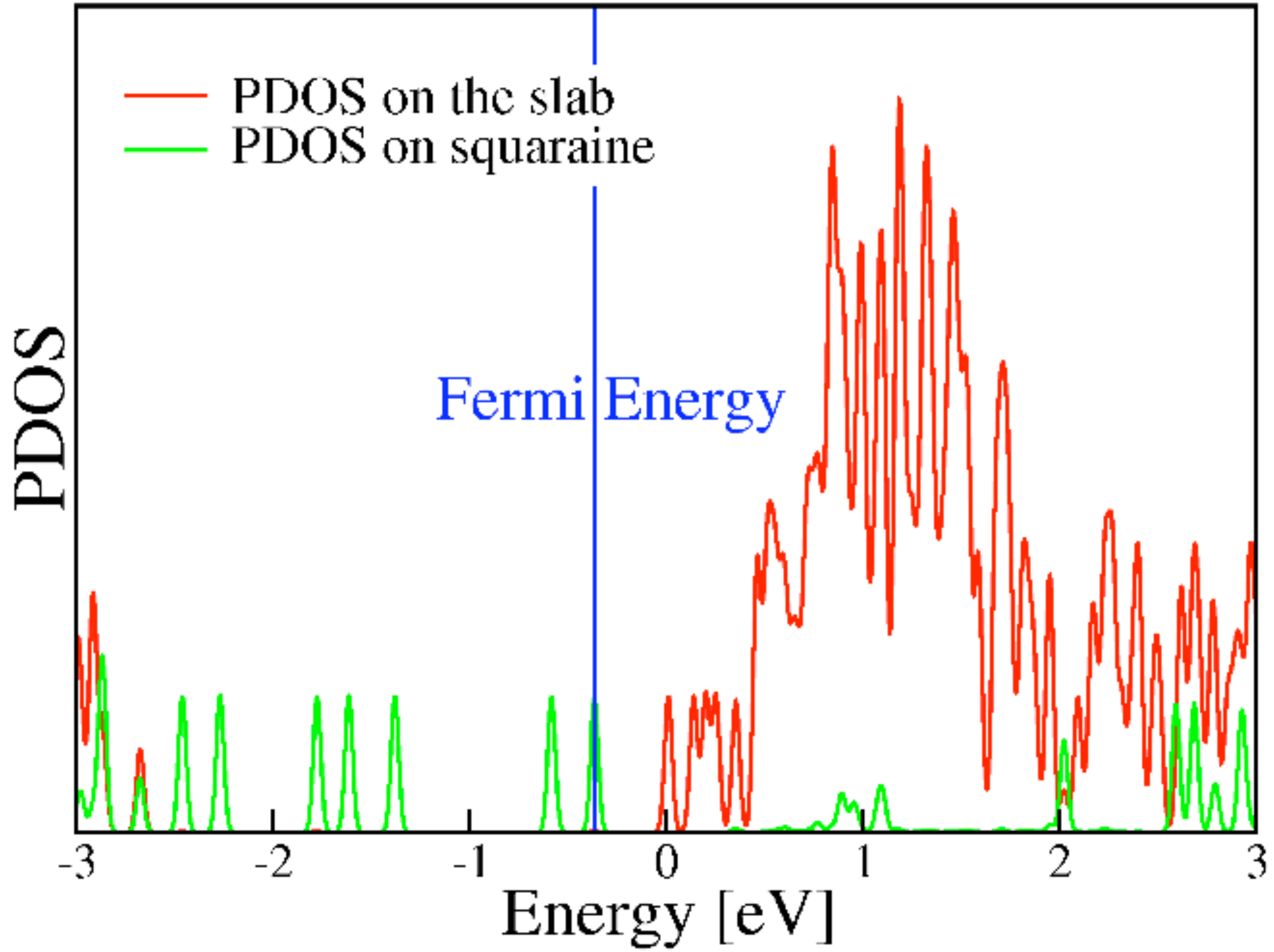
Direct versus indirect transitions:



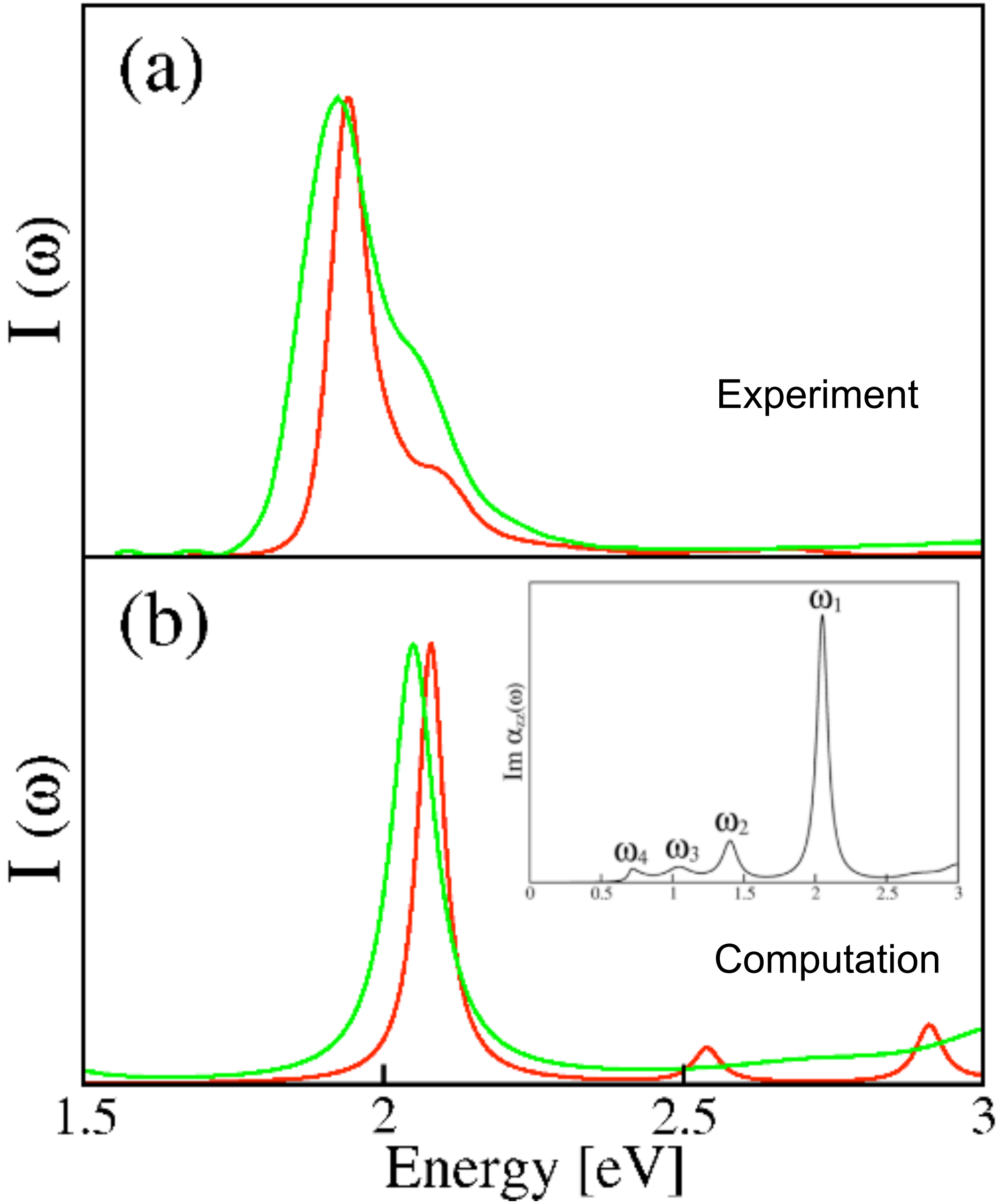
Our system: Squaraine on TiO2 nanoparticle



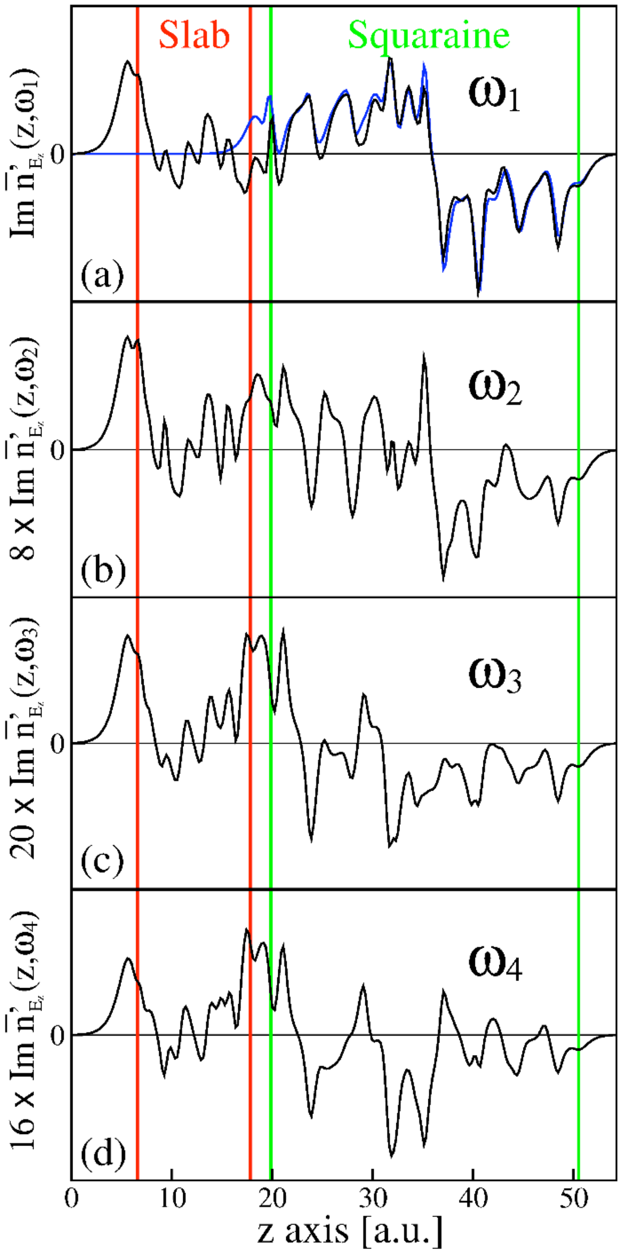
TiO2 particle with squaraine dye

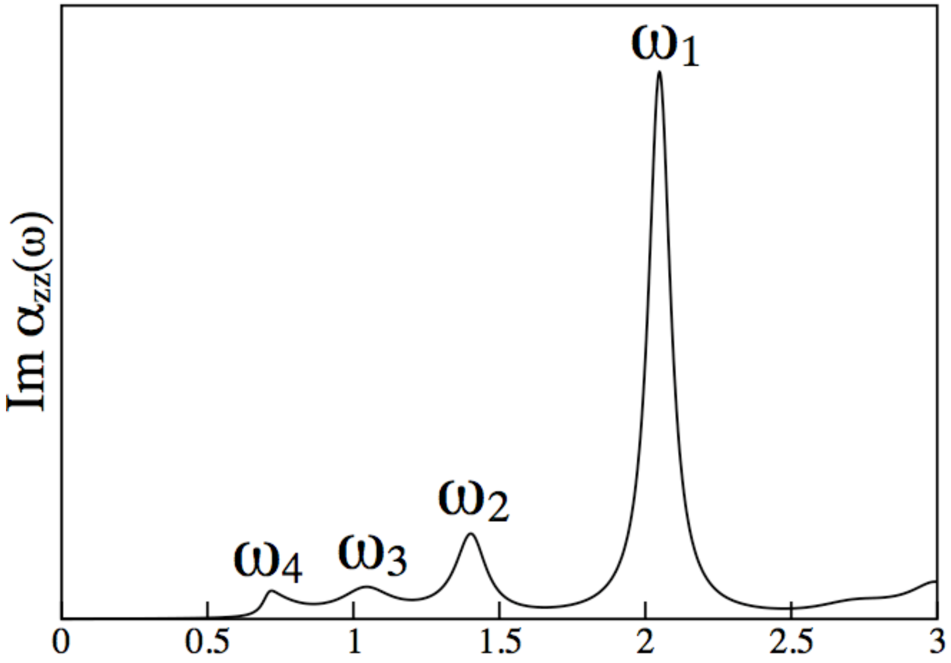


Experimental and TDDFT absorption spectra

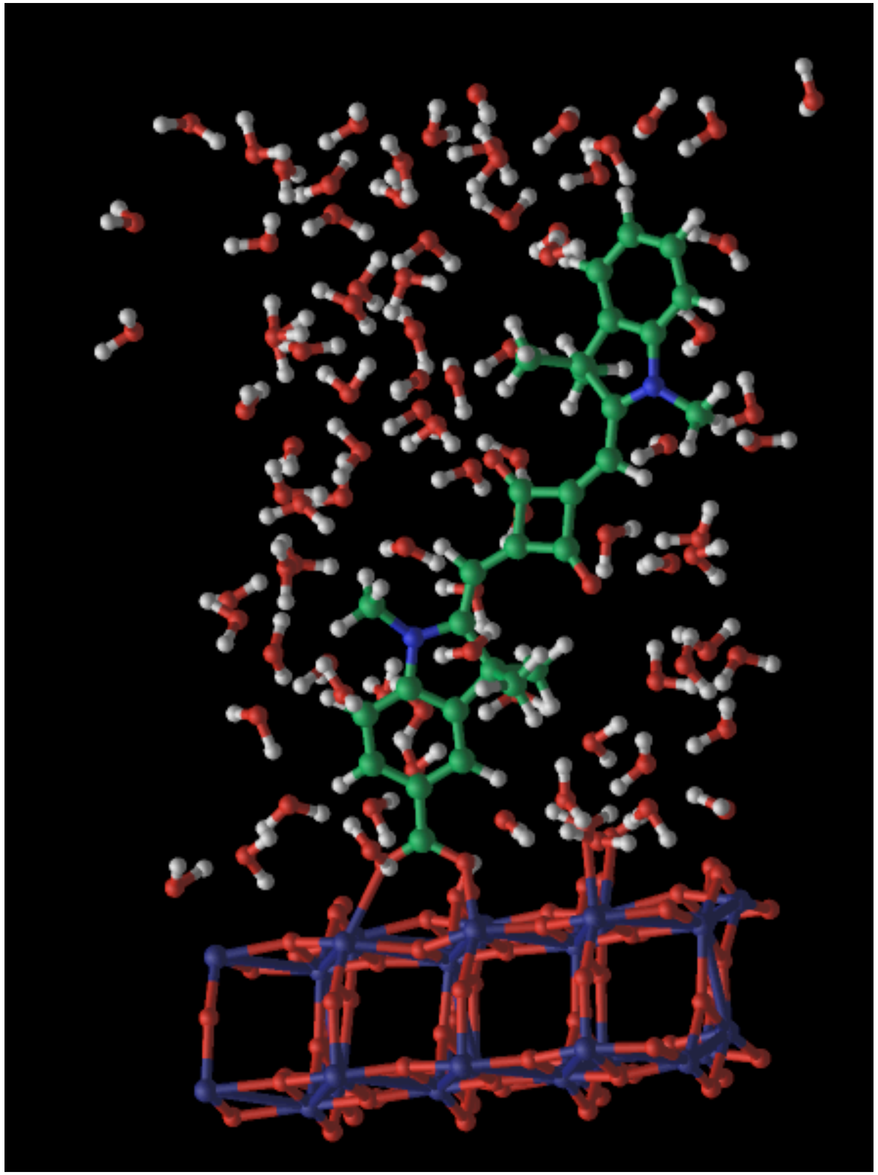


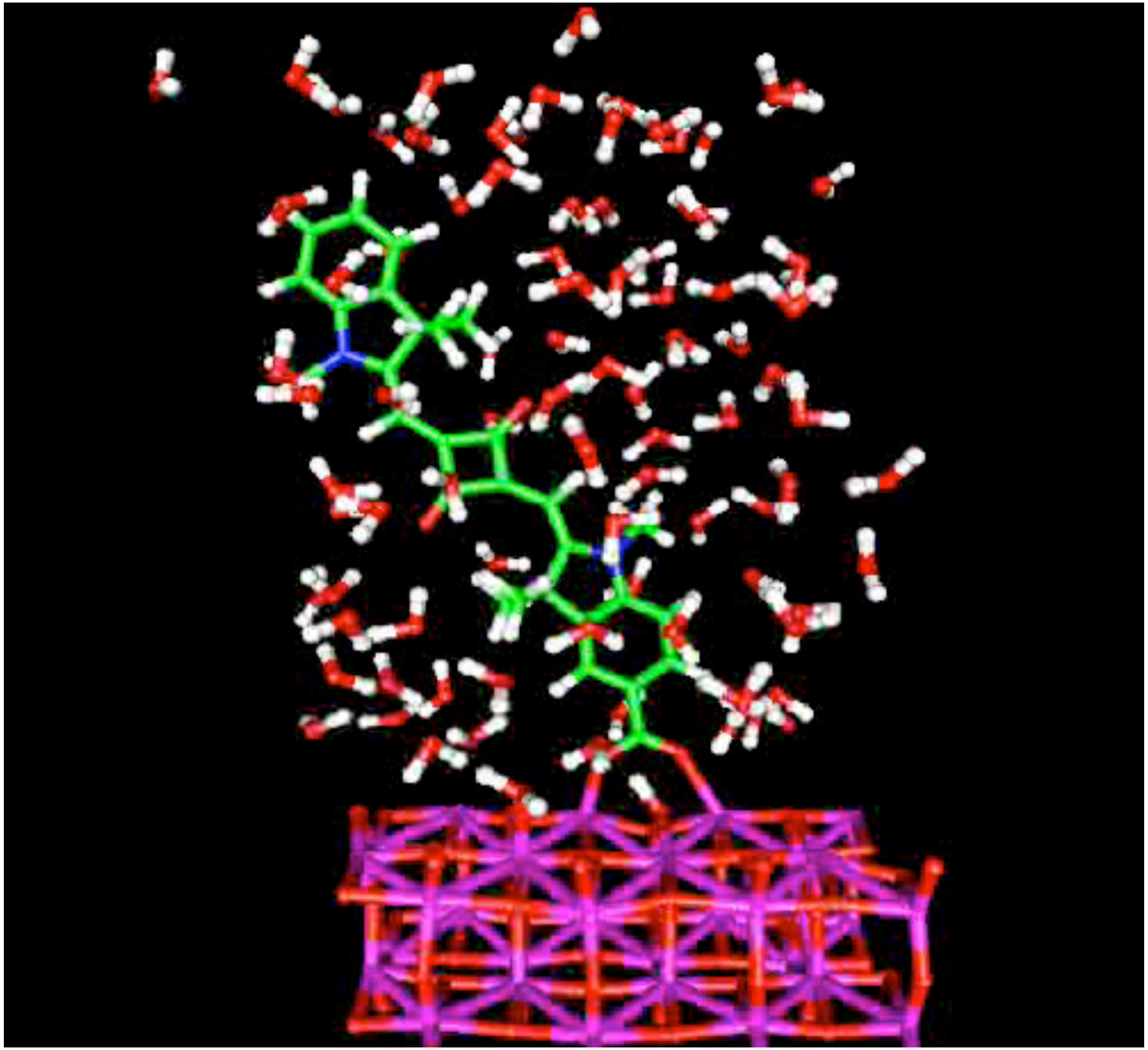
Analyzing the various transitions





A more realistic system: Including the solvent





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.
  - dissociates
  - is essential for geometry of solute

TDDFT calculation of optical spectra and related quantities

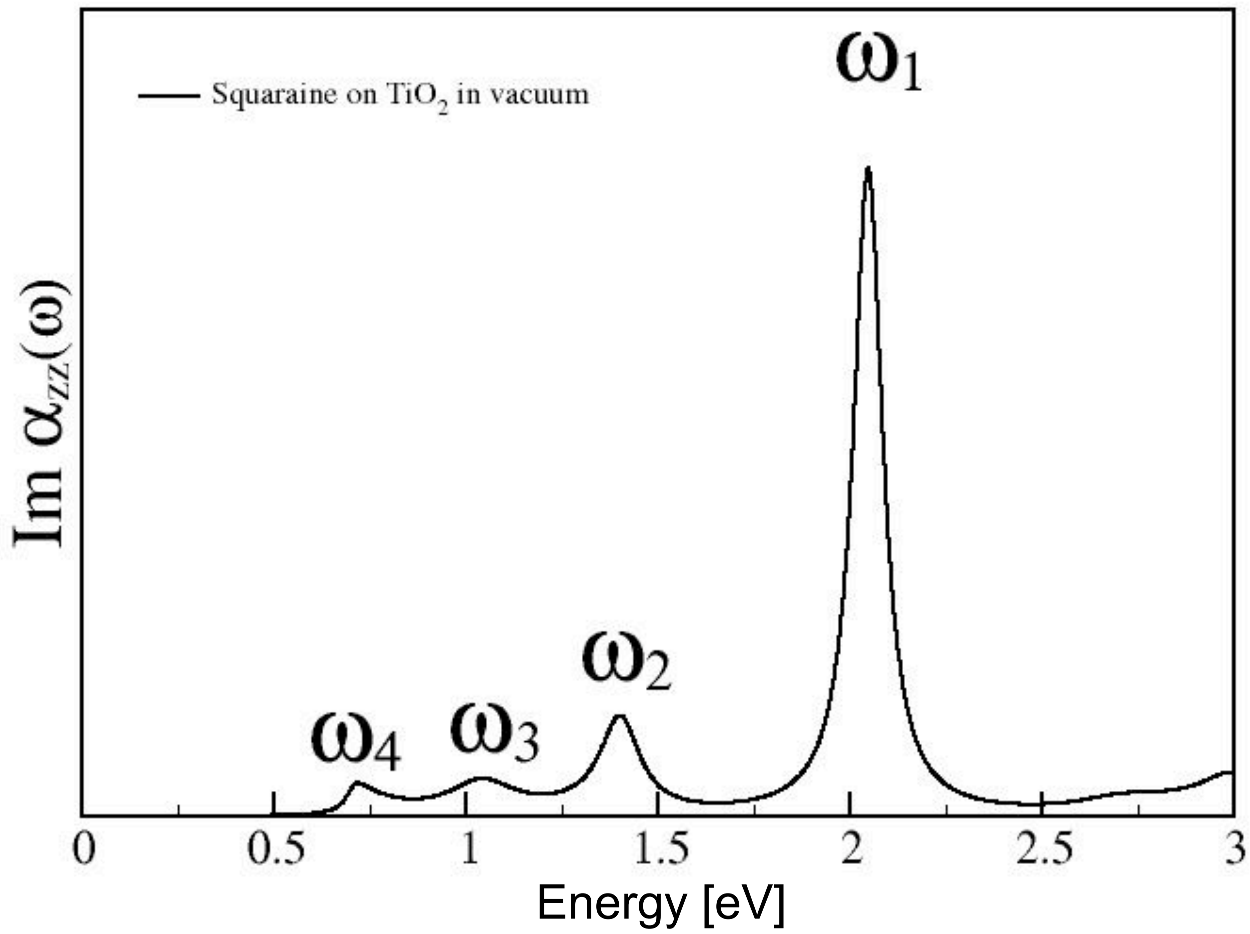
Various challenges:

- 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:

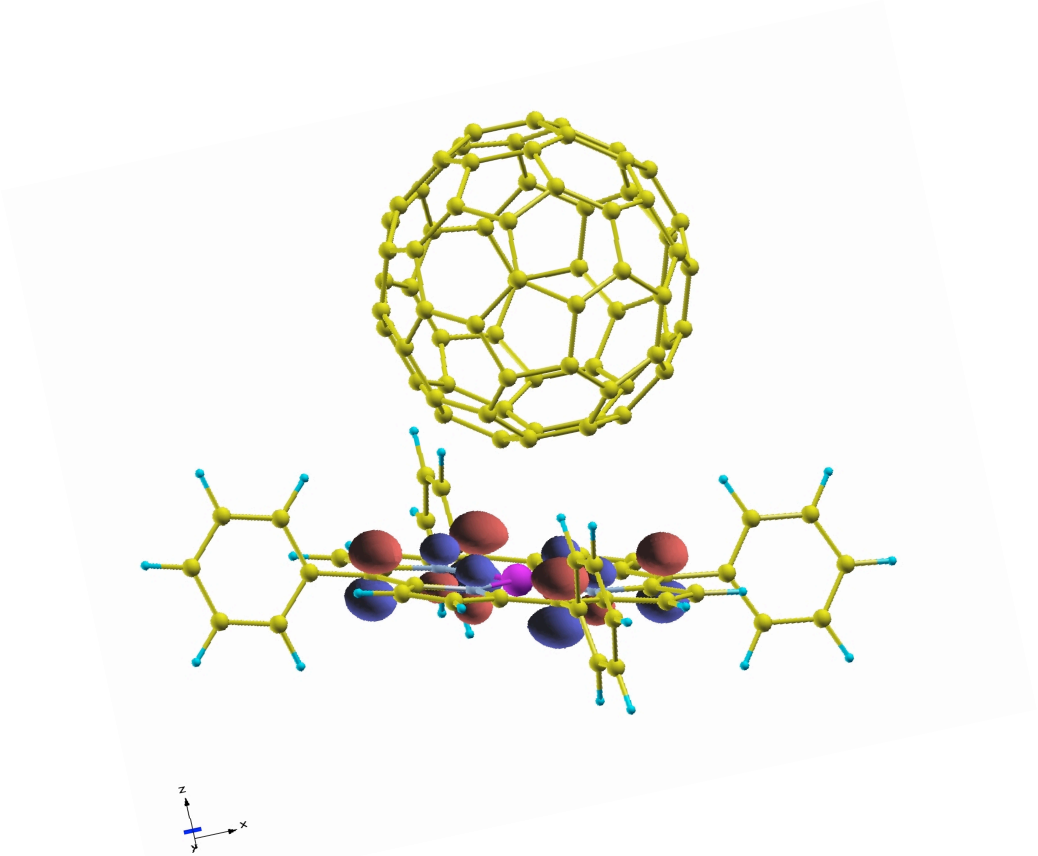
- Recursive Lanczos algorithm for TDDFT
- Ideally suited for large systems, broad spectral region with large basis set
- Here: Adiabatic GGA functional

Back to the optical spectra



Problematic aspects of using (TD)DFT in photovoltaic systems

Back to the previously studied system:

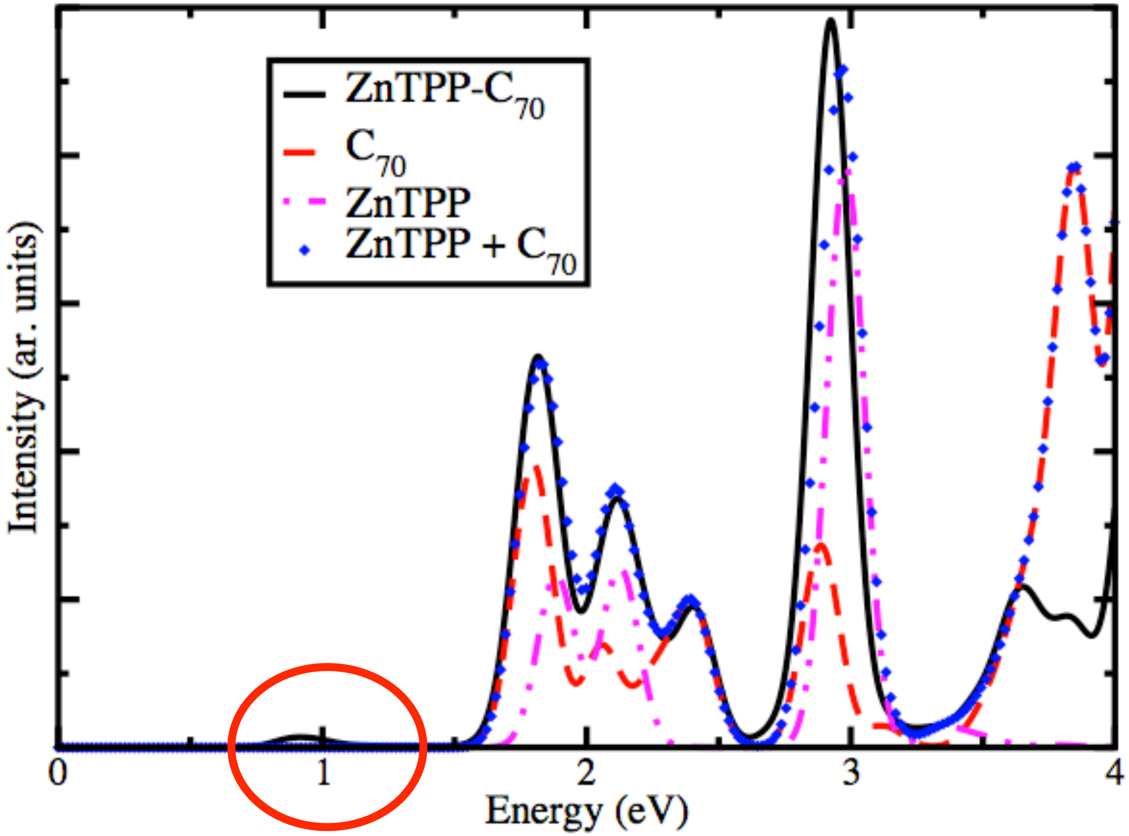


Donor-Acceptor Dyad

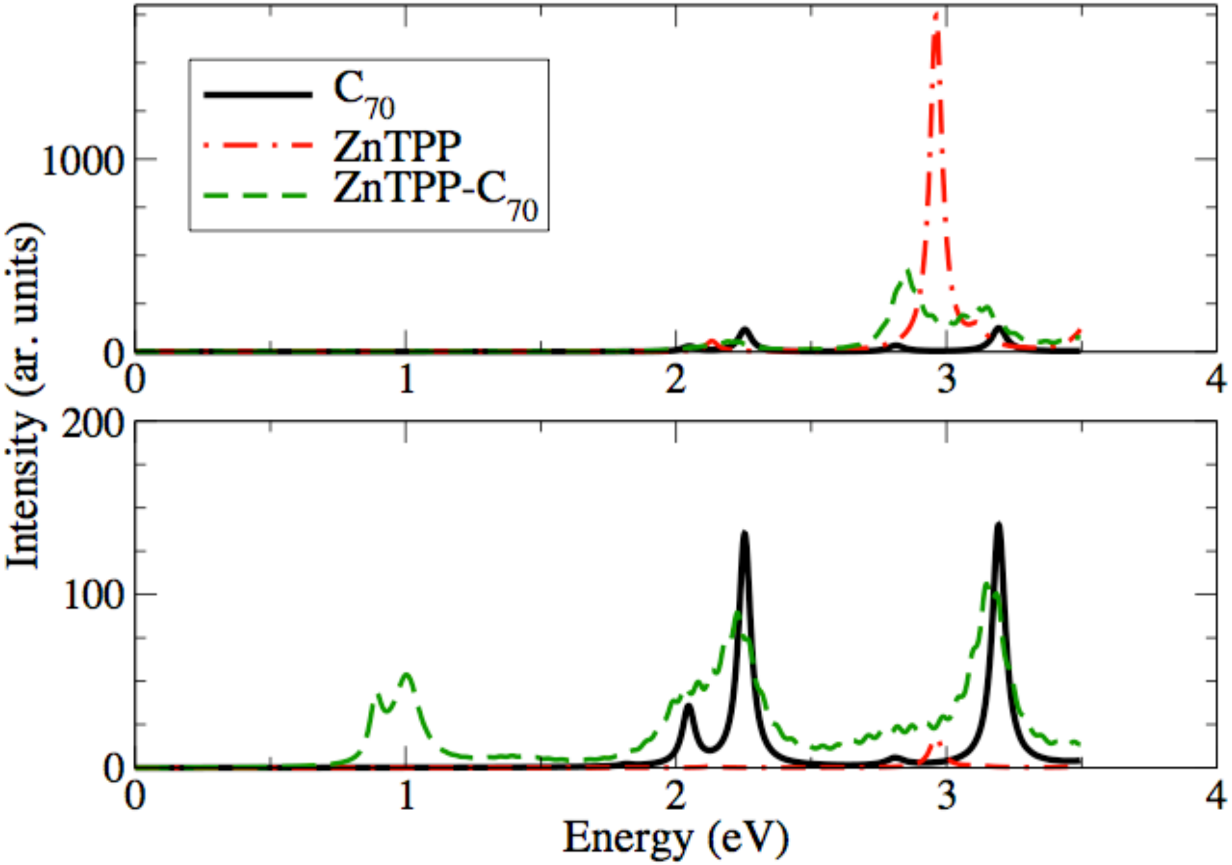
(ZnTPP-C_{70} complex)

Study the energy of the charge transfer excitation from donor to acceptor

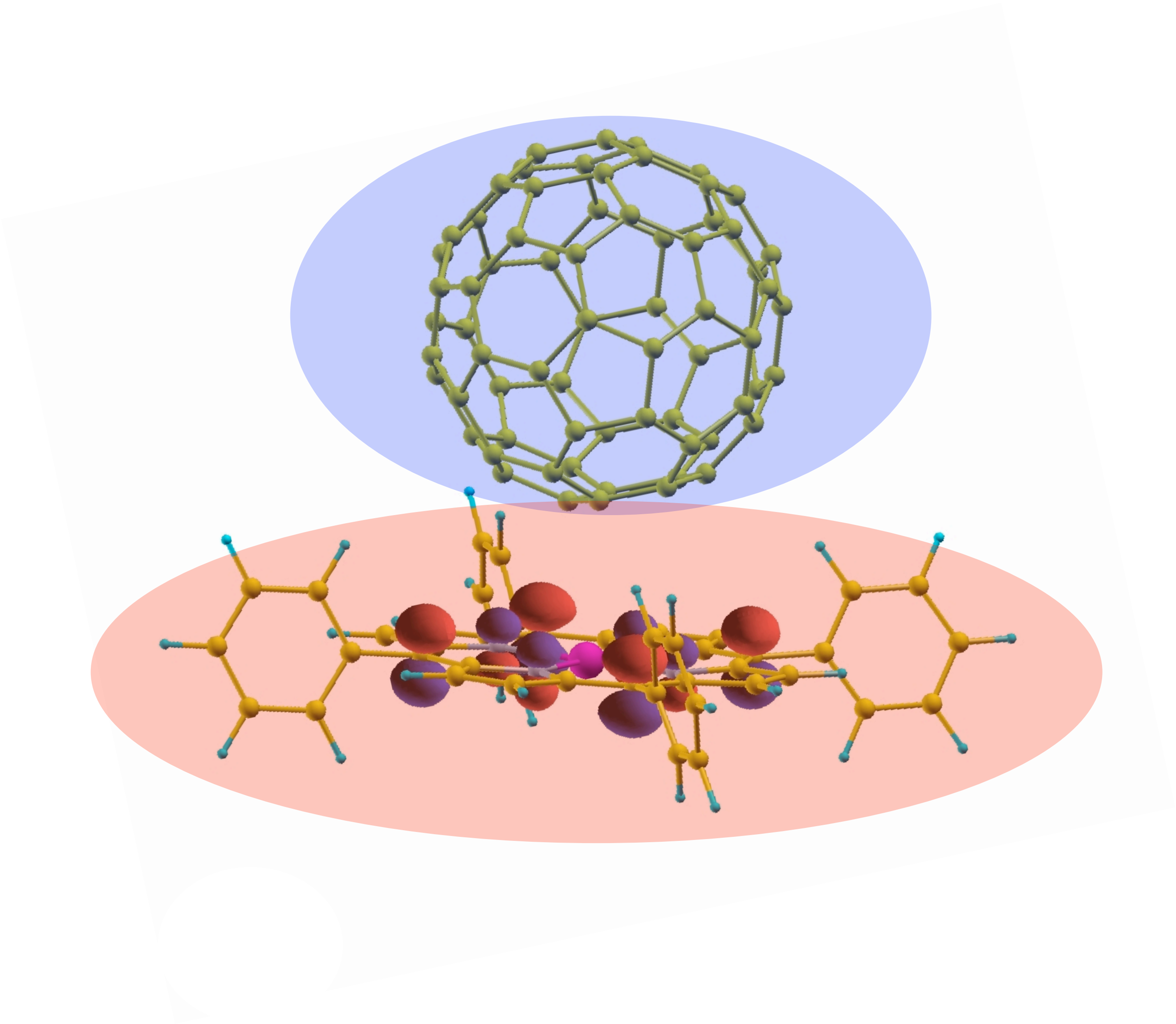
Basic DFT:



Can TDDFT do better?



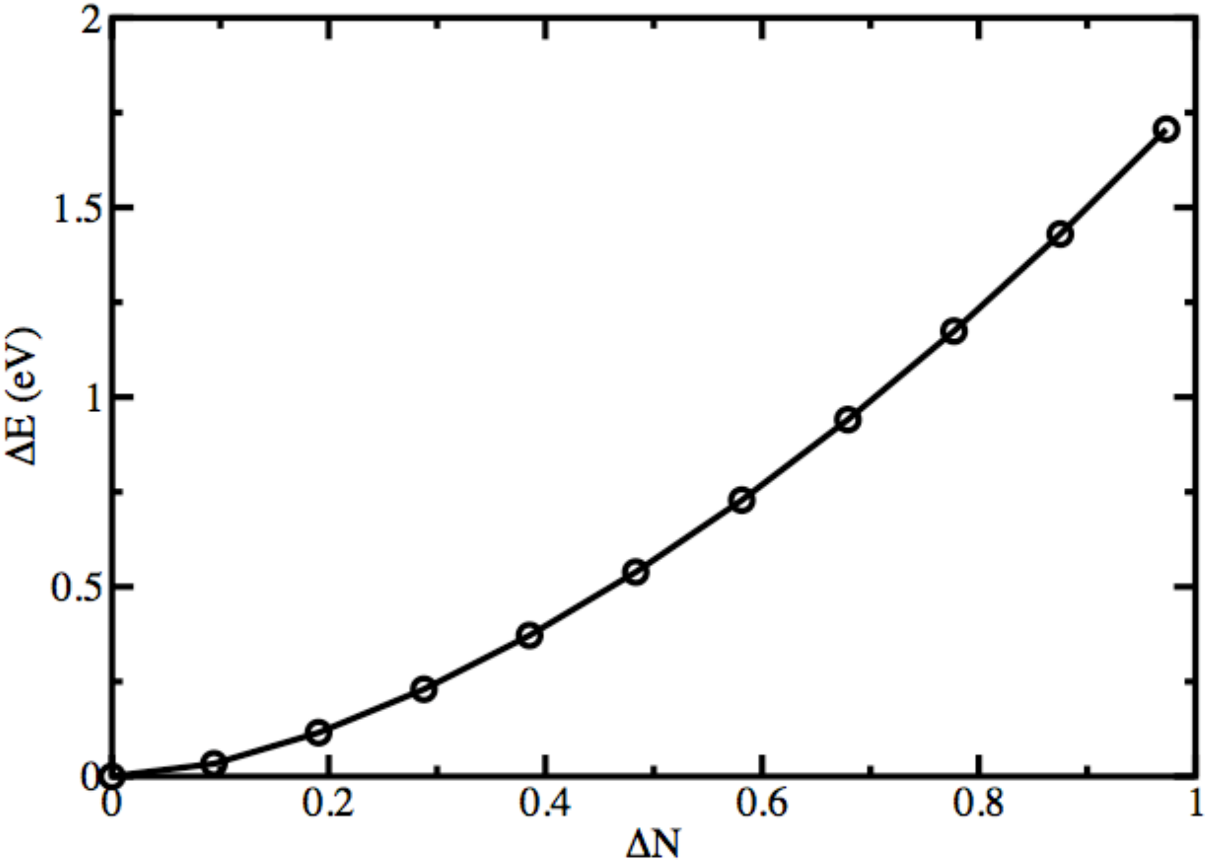
Solution is: CONSTRAINED DFT:



Acceptor region

Donor region

Solution is: CONSTRAINED DFT:



Conclusions on charge transfer excitations:

Both "basic DFT" and TD-DFT with the standard functionals *severely* underestimate the energy of a charge transfer excitation

Simple constrained DFT correctly predicts the energies

Problem: How can those two pictures be brought together?
(Necessary for a seamless description of sequetial charge transfer processes!)

Linear response formalism in TDDFT:

- Calculate the system's ground state using DFT
- Consider a monochromatic perturbation:

$$V_{pert}(\boldsymbol{r},t) = V_0(\boldsymbol{r})\left(\exp(i\omega t) + \exp(-i\omega t)\right)$$

- Linear response: assume the time-dependent response:

$$\psi_j(t) = e^{-i\epsilon_j t}\left(\psi_j^0 + \delta\psi_j^+ e^{i\omega t} + \delta\psi_j^- e^{-i\omega t}\right)$$

$$\delta n(\boldsymbol{r},t) = \delta n^+(\boldsymbol{r})e^{i\omega t} + \delta n^-(\boldsymbol{r})e^{-i\omega t}$$

$$\delta V(\boldsymbol{r},t) = V_{pert}(\boldsymbol{r},t) + \delta V_{SCF}^+(\boldsymbol{r})e^{i\omega t} + \delta V_{SCF}^-(\boldsymbol{r})e^{-i\omega t}$$

- Put these expressions into the TD Schrödinger equation

Linear response formalism in TDDFT:

$$\begin{aligned}
\omega\delta\psi_v^+(\boldsymbol{r}) &= \left(H_{KS}^0 - \epsilon_v^0\right)\delta\psi_v^+ + \hat{P}_v\left(\delta V_{SCF}^+(\boldsymbol{r}) + V_{pert}(\boldsymbol{r})\right)\psi_v^0(\boldsymbol{r}) \\
-\omega\delta\psi_v^-(\boldsymbol{r}) &= \left(H_{KS}^0 - \epsilon_v^0\right)\delta\psi_v^- + \hat{P}_v\left(\delta V_{SCF}^-(\boldsymbol{r}) + V_{pert}(\boldsymbol{r})\right)\psi_v^0(\boldsymbol{r})
\end{aligned}$$

Now define the following linear combinations:

$$\begin{aligned}
x_v(\boldsymbol{r}) &= \frac{1}{2}\left(\delta\psi_v^+(\boldsymbol{r}) + \delta\psi_v^-(\boldsymbol{r})\right) \\
y_v(\boldsymbol{r}) &= \frac{1}{2}\left(\delta\psi_v^+(\boldsymbol{r}) - \delta\psi_v^-(\boldsymbol{r})\right)
\end{aligned}$$

$$(\omega - \mathcal{L})\left|\boldsymbol{x}, \boldsymbol{y}\right\rangle = \left|\mathbf{0}, \boldsymbol{v}\right\rangle \qquad \mathcal{L} = \begin{pmatrix} 0 & D \\ K & 0 \end{pmatrix}$$

With the following definitions:

$$\begin{aligned} D\left|\boldsymbol{x}\right\rangle &= \left\{\left(H^0_{KS} - \epsilon_i\right) x_i(\boldsymbol{r})\right\} \\ K\left|\boldsymbol{x}\right\rangle &= \left\{\left(H^0_{KS} - \epsilon_i\right) x_i(\boldsymbol{r}) + \psi^0_i(\boldsymbol{r}) \sum_j \int d\boldsymbol{r}' \;\; f_{Hxc}(\boldsymbol{r}, \boldsymbol{r}')\psi^0_{i'}(\boldsymbol{r}') x_{i'}(\boldsymbol{r}')\right\} \end{aligned}$$

$$\begin{pmatrix} 0 & D \\ K & 0 \end{pmatrix} \begin{pmatrix} x \\ y \end{pmatrix} = \omega \begin{pmatrix} x \\ y \end{pmatrix}$$

Alternative methods
(if only the spectrum is nedded)

- Real-time propagation
- Recursions …

Remember: The photoabsorption is linked to the dipole polarizability $\alpha(\omega)$

$$d(t) = \int dt' \alpha(t - t') \mathcal{E}(t')$$

If we choose $\mathcal{E}(t') = \mathcal{E}_0 \delta(t')$, then knowing d(t) gives us α(t) and thus $\alpha(\omega)$.

Therefore, we need a way to calculate the observable d(t), given the electric field perturbation $\mathcal{E}_0 \delta(t)$.

Consider an observable A:

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

Its Fourier transform is:

$$\begin{aligned} \tilde{A}(\omega) &= \sum_i \left(\left\langle \psi_i^0 \left| \hat{A} \right| \delta\psi_i^-(\omega) \right\rangle + \left\langle \psi_i^0 \left| \hat{A} \right| \delta\psi_i^+(\omega) \right\rangle \right) \\ &= 2 \sum_i \left\langle \psi_i^0 \left| \hat{A} \right| x_i(\omega) \right\rangle \\ &= 2 \left\langle \boldsymbol{a}, 0 \left| \boldsymbol{x}, \boldsymbol{y} \right. \right\rangle \end{aligned}$$

$$\begin{aligned}\tilde{A}(\omega) &= \sum_i \left(\left\langle \psi_i^0 \middle| \hat{A} \middle| \delta\psi_i^-(\omega) \right\rangle + \left\langle \psi_i^0 \middle| \hat{A} \middle| \delta\psi_i^+(\omega) \right\rangle\right) \\ &= 2\sum_i \left\langle \psi_i^0 \middle| \hat{A} \middle| x_i(\omega) \right\rangle \\ &= 2\left\langle \boldsymbol{a}, 0 \middle| \boldsymbol{x}, \boldsymbol{y} \right\rangle\end{aligned}$$

Recall: $(\omega - \mathcal{L})\left|\boldsymbol{x}, \boldsymbol{y}\right\rangle = \left|\mathbf{0}, \boldsymbol{v}\right\rangle$

Therefore:

$$\tilde{A}(\omega) = 2\left\langle \boldsymbol{a}, \mathbf{0} \middle| (\omega - \mathcal{L})^{-1} \middle| \mathbf{0}, \boldsymbol{v} \right\rangle$$

Thus in order to calculate the spectrum, we need to calculate one given matrix element of $(\omega - \mathcal{L})^{-1}$.

In order to understand the method, look at the hermitean problem:

$$\langle v|\,(\omega - H)^{-1}\,|v\rangle$$

Build a Lanczos recursion chain:

$$\begin{aligned}
\phi_{-1} &= 0 \\
\phi_0 &= |v\rangle \\
b_{n+1}\phi_{n+1} &= (H - a_n)\phi_n - b_n\phi_{n-1} \\
\langle \phi_{n+1}|\phi_{n+1}\rangle &= 1 \\
a_n &= \langle \phi_n|H|\phi_n\rangle
\end{aligned}$$

$$H = \begin{pmatrix} a_0 & b_1 & 0 & \cdots & 0 \\ b_1 & a_1 & b_2 & 0 & \vdots \\ 0 & b_2 & a_2 & \ddots & 0 \\ \vdots & 0 & \ddots & \ddots & b_n \\ 0 & \cdots & 0 & b_n & a_n \end{pmatrix}$$

$$H = \begin{pmatrix} a_0 & b_1 & 0 & \cdots & 0 \\ b_1 & a_1 & b_2 & 0 & \vdots \\ 0 & b_2 & a_2 & \ddots & 0 \\ \vdots & 0 & \ddots & \ddots & b_n \\ 0 & \cdots & 0 & b_n & a_n \end{pmatrix}$$

$$(\omega - H) = \begin{pmatrix} \omega - a_0 & b_1 & 0 & \cdots & 0 \\ b_1 & \omega - a_1 & b_2 & 0 & \vdots \\ 0 & b_2 & \omega - a_2 & \ddots & 0 \\ \vdots & 0 & \ddots & \ddots & b_n \\ 0 & \cdots & 0 & b_n & \omega - a_n \end{pmatrix}$$

$$(\omega - H) = \begin{pmatrix} \omega - a_0 & b_1 & 0 & \cdots & 0 \\ b_1 & \omega - a_1 & b_2 & 0 & \vdots \\ 0 & b_2 & \omega - a_2 & \ddots & 0 \\ \vdots & 0 & \ddots & \ddots & b_n \\ 0 & \cdots & 0 & b_n & \omega - a_n \end{pmatrix}$$

$$(\omega - H)^{-1}_{00} = \cfrac{1}{\omega - a_0 + \cfrac{b_1^2}{\omega - a_1 + \cfrac{b_2^2}{\omega - a_2 + \cdots}}}$$

Back to the calculation of spectra:

Recall: $(\omega - \mathcal{L})\,|\boldsymbol{x},\boldsymbol{y}\rangle = |\mathbf{0},\boldsymbol{v}\rangle$

Therefore:

$$\tilde{A}(\omega) = 2\left\langle \boldsymbol{a},\mathbf{0}\middle|(\omega-\mathcal{L})^{-1}\middle|\mathbf{0},\boldsymbol{v}\right\rangle$$

Use a recursion to represent L as a tridiagonal matrix:

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

And the response can be written as a continued fraction!

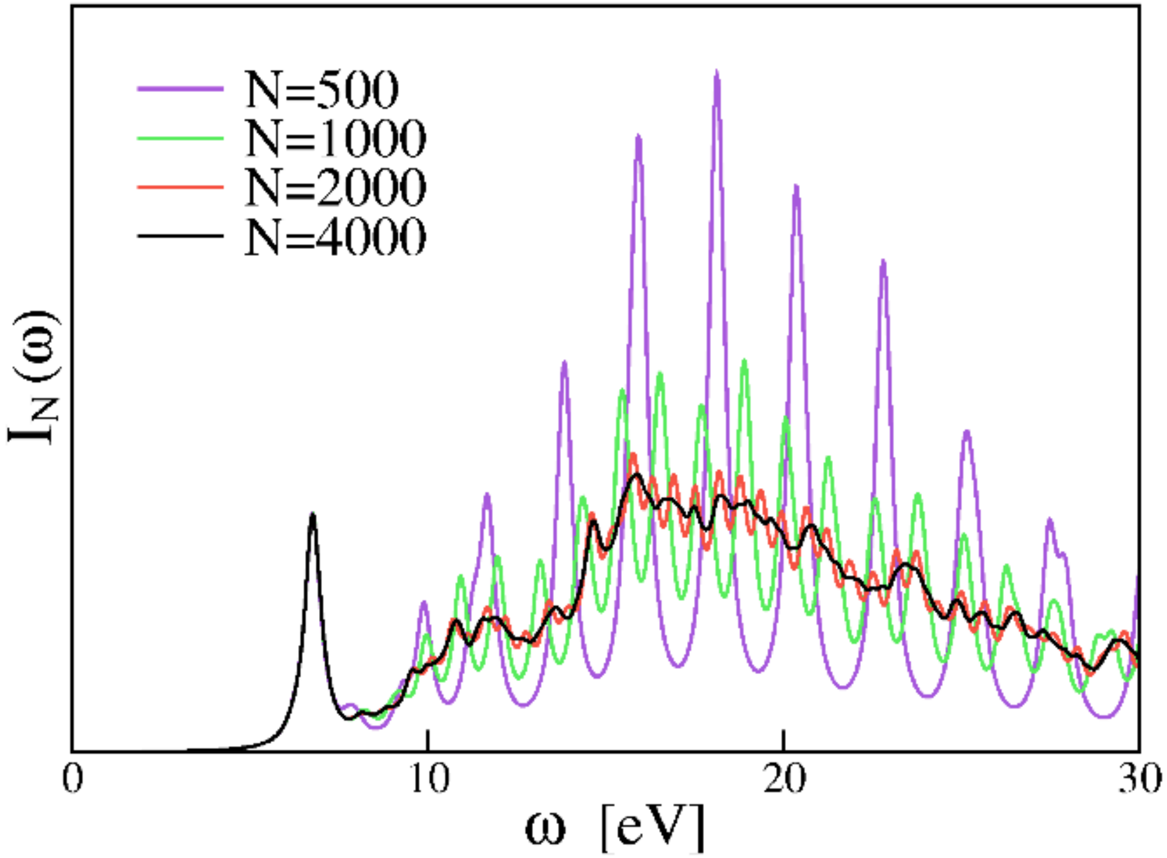
$$
\begin{aligned}
\tilde{A}(\omega) &= 2\left\langle \boldsymbol{a}, \boldsymbol{0} \middle| (\omega - \mathcal{L})^{-1} \middle| \boldsymbol{0}, \boldsymbol{v} \right\rangle \\
&= \frac{1}{\omega - a_1 + b_2 \frac{1}{\omega - a_2 + \cdots} c_2}
\end{aligned}
$$

Comparison with “traditional methods”

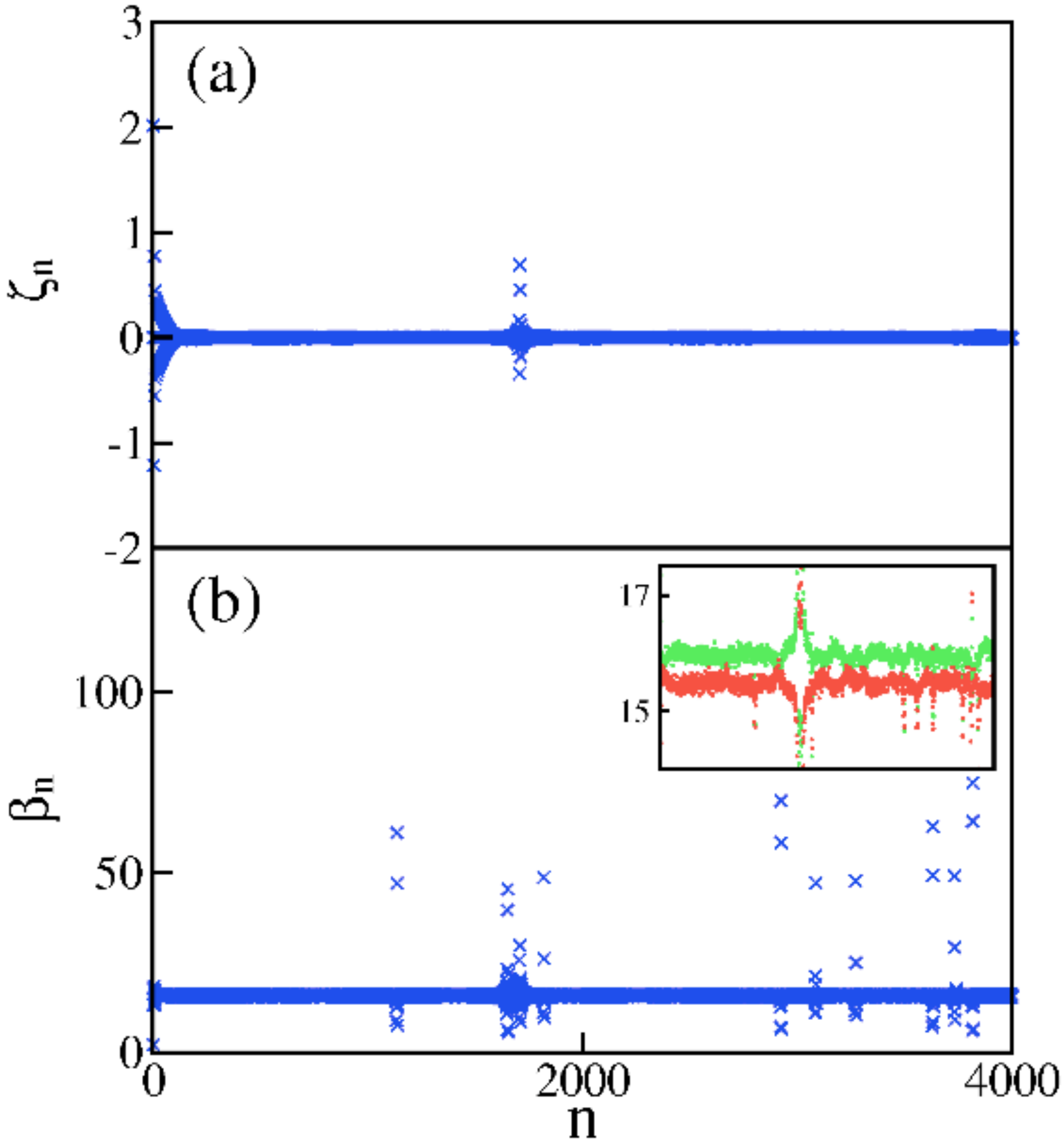
Here:	Other methods:
Virtual KS states not explicitly needed (similar to DFPT)	All (or many) virtual KS states needed
Main computation independent of frequency	Separate computation for each frequency
Whole spectrum is obtained "in one shot"	Some individual transitions in the low energy portion of the spectrum
No information about individual excitations	Excitation-eigenvectors can be used for further analysis
Ideally suited for large basis sets, large systems and for continuous spectra	Ideally suited for localized basis sets in smaller systems

How does is work?

Optical absorption in benzene:



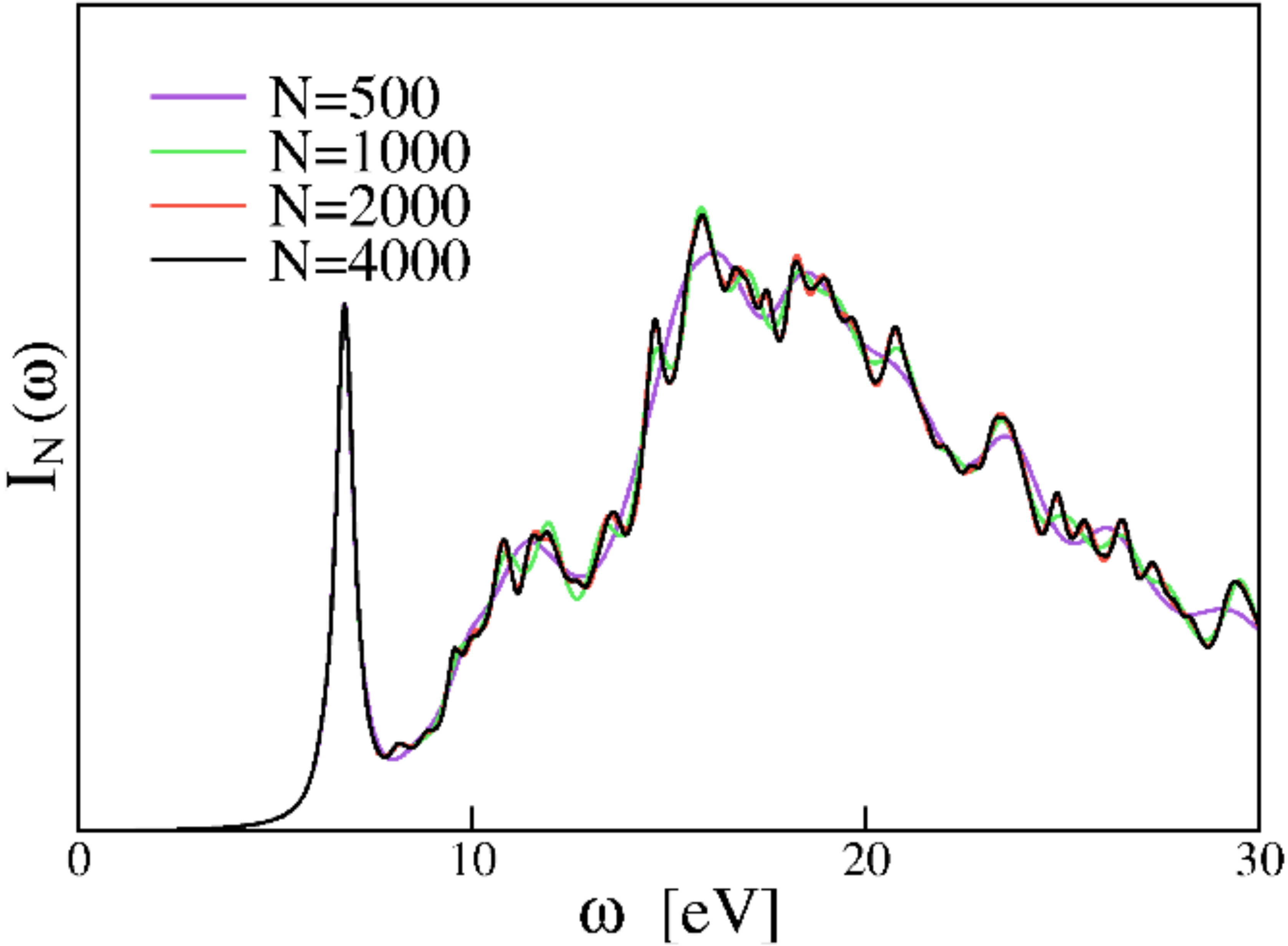
Speeding up: Look at the coefficients



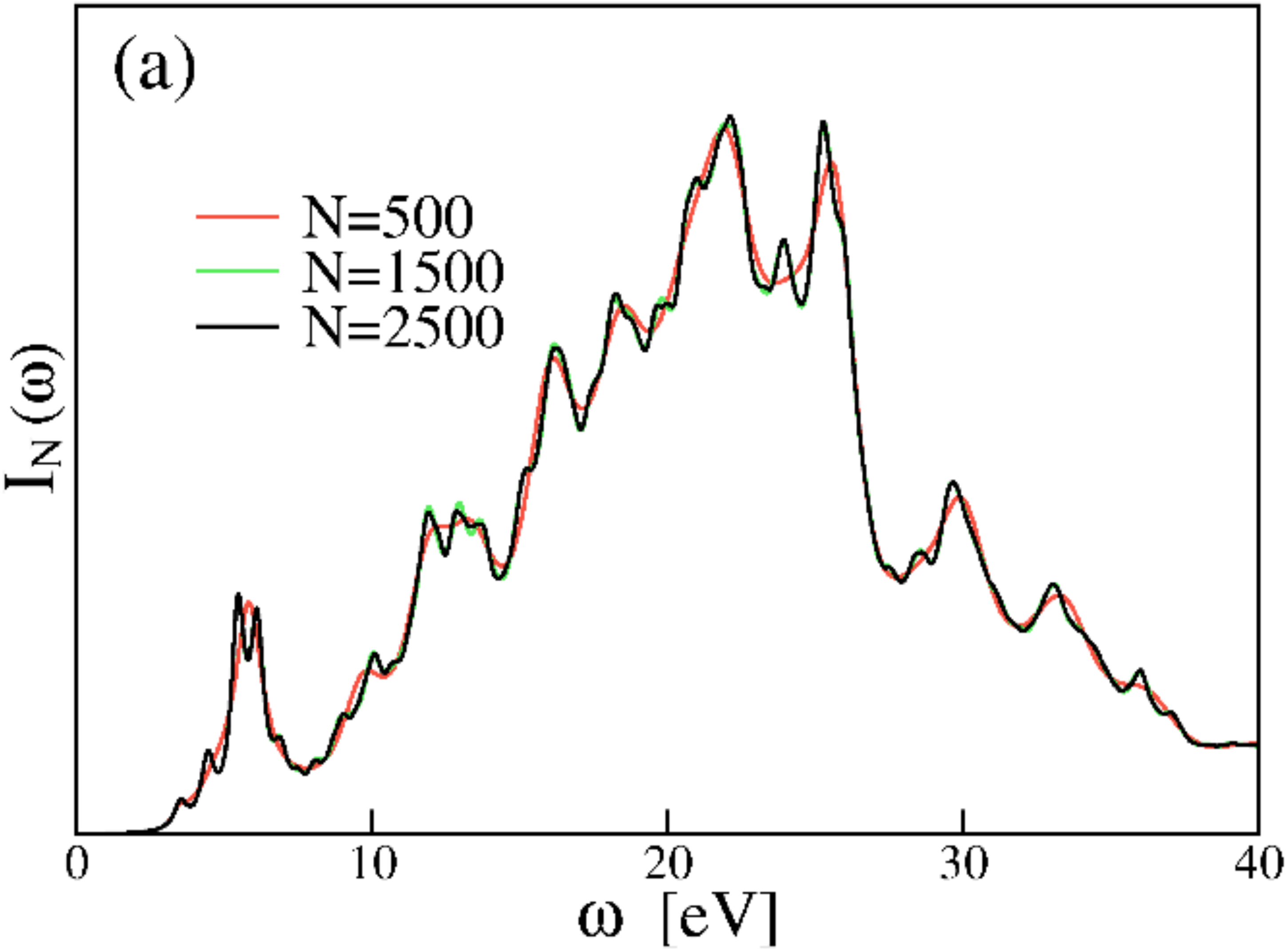
And the response can be written as a continued fraction!

$$\begin{aligned}\tilde{A}(\omega) &= 2\left\langle \boldsymbol{a}, \boldsymbol{0} \middle| (\omega - \mathcal{L})^{-1} \middle| \boldsymbol{0}, \boldsymbol{v} \right\rangle \\ &= \frac{1}{\omega - a_1 + b_2 \frac{1}{\omega - a_2 + \cdots} c_2}\end{aligned}$$

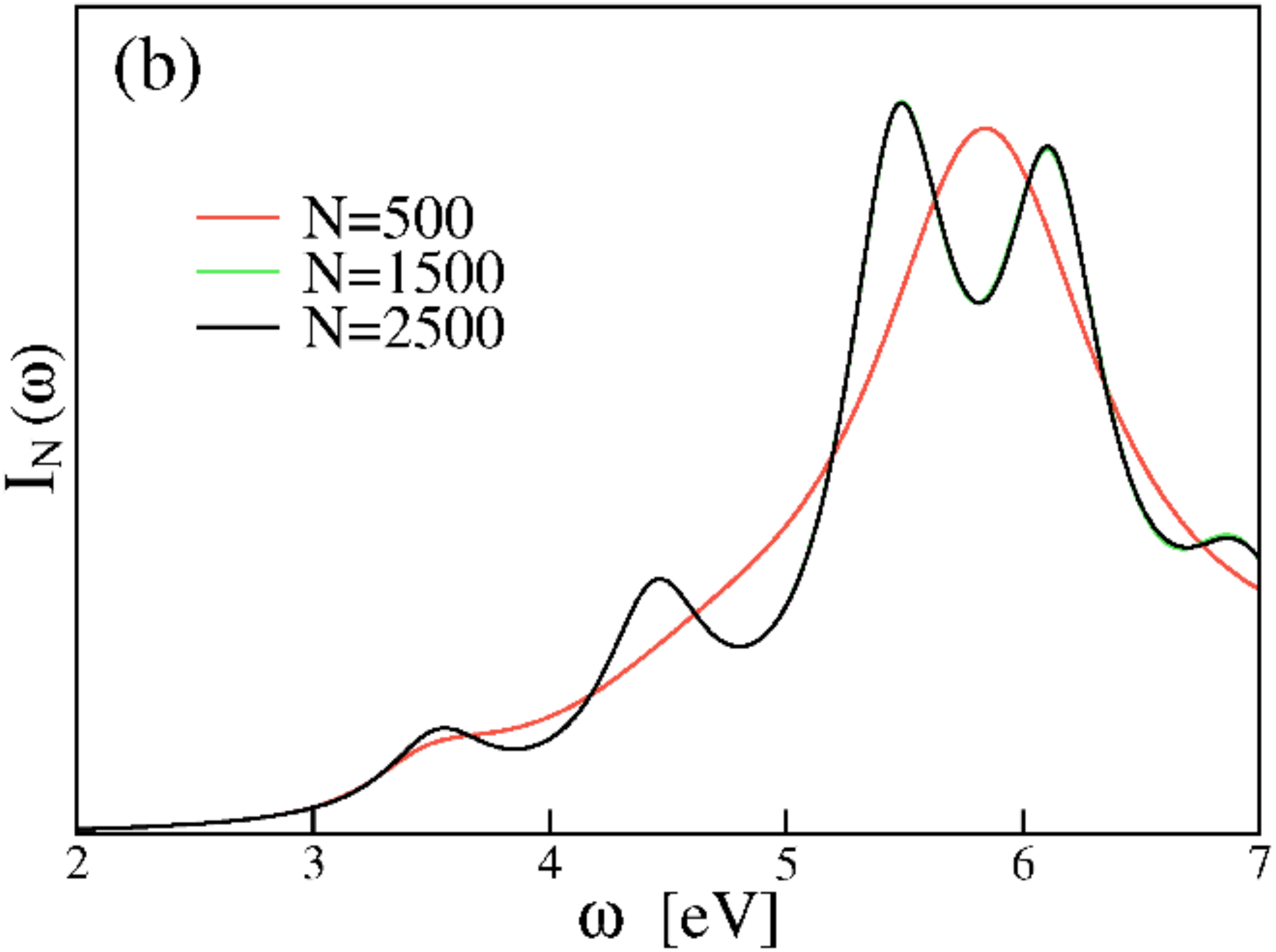
Extrapolating the coefficients: VERY fast convergence



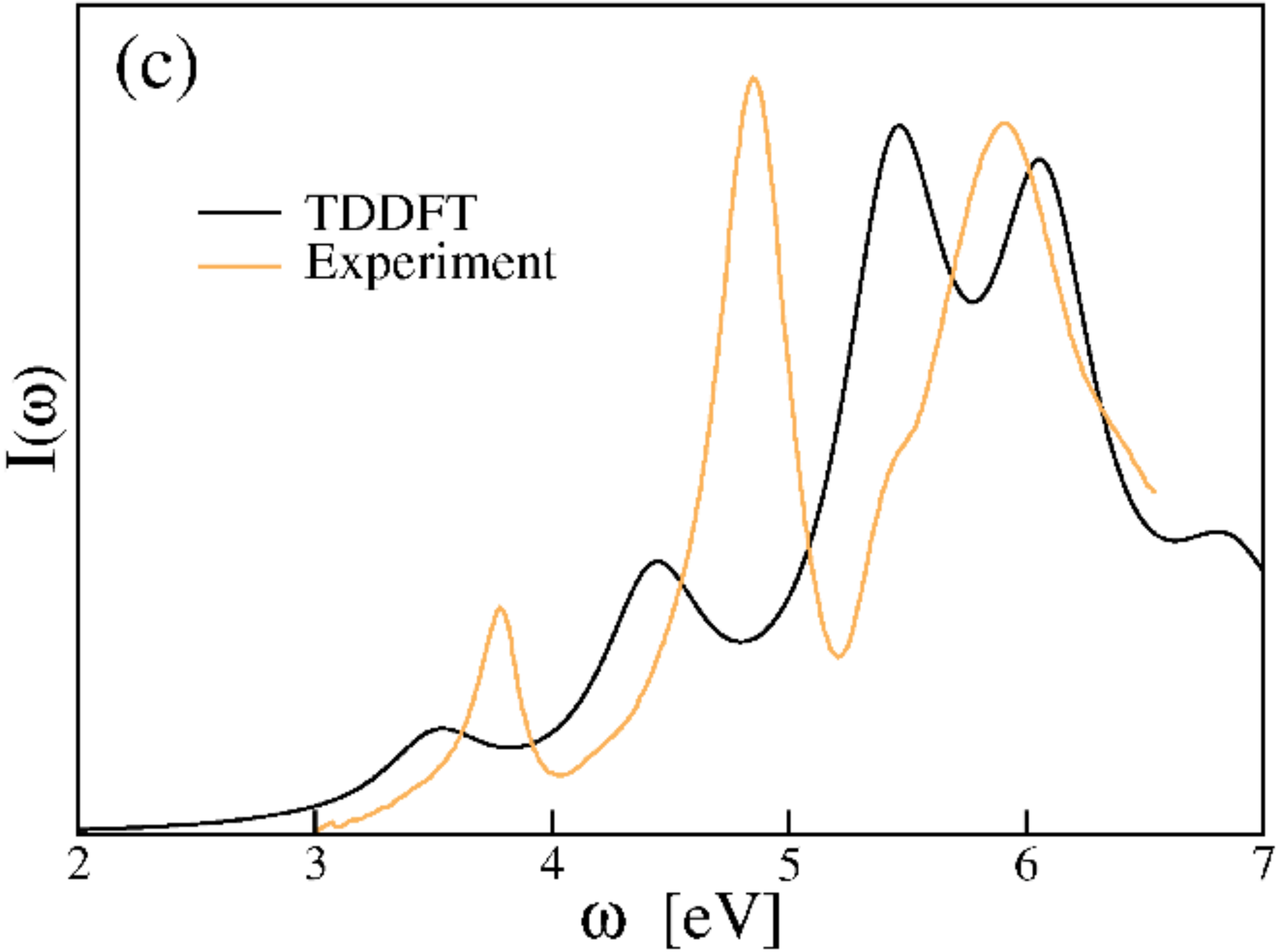
Spectrum of fullerene C_{60}



Low frequency spectrum in C_{60}



C_{60}: Comparison with experiment



Conclusions

DFT and TDDFT are useful tools to understand the functioning of new photovoltaic materials

TDDFT allows one to better understand the key optical transitions involved

Bringing together ab initio MD and TDDFT allows for a realistic simulation of such systems

Caveat: Important failures of standard methods in these systems