

Joint ICTP-NSFC School and Advanced Workshop on Modern Electronic Structure Computations
Fudan University – Shanghai
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Time-dependent density functional theory and how it is used

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The Abdus Salam
**International Centre
for Theoretical Physics**



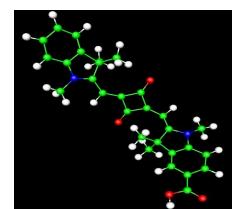
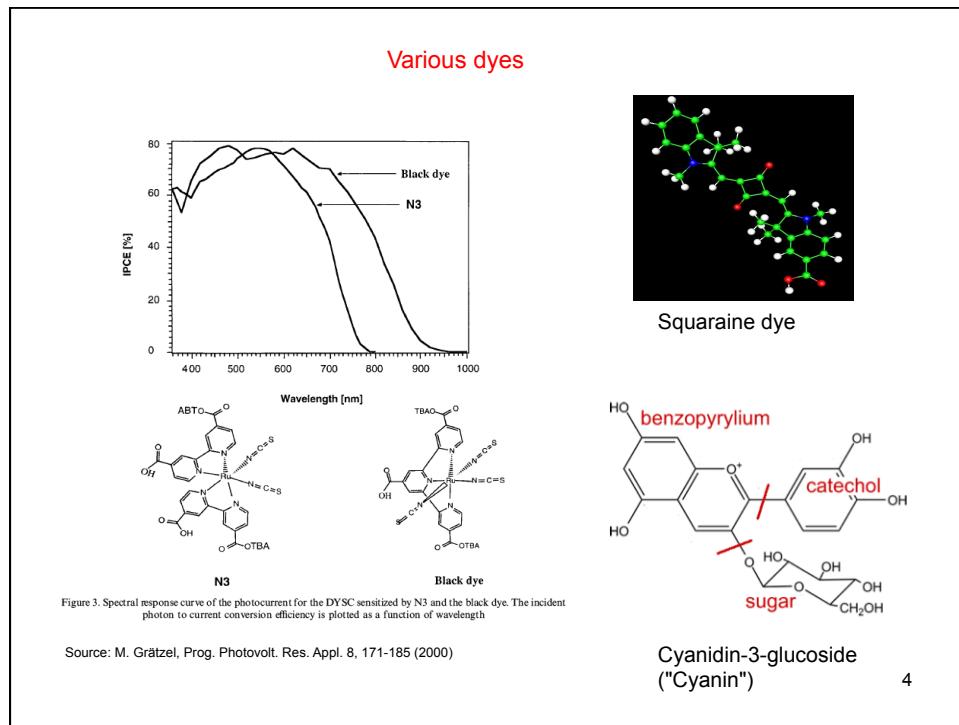
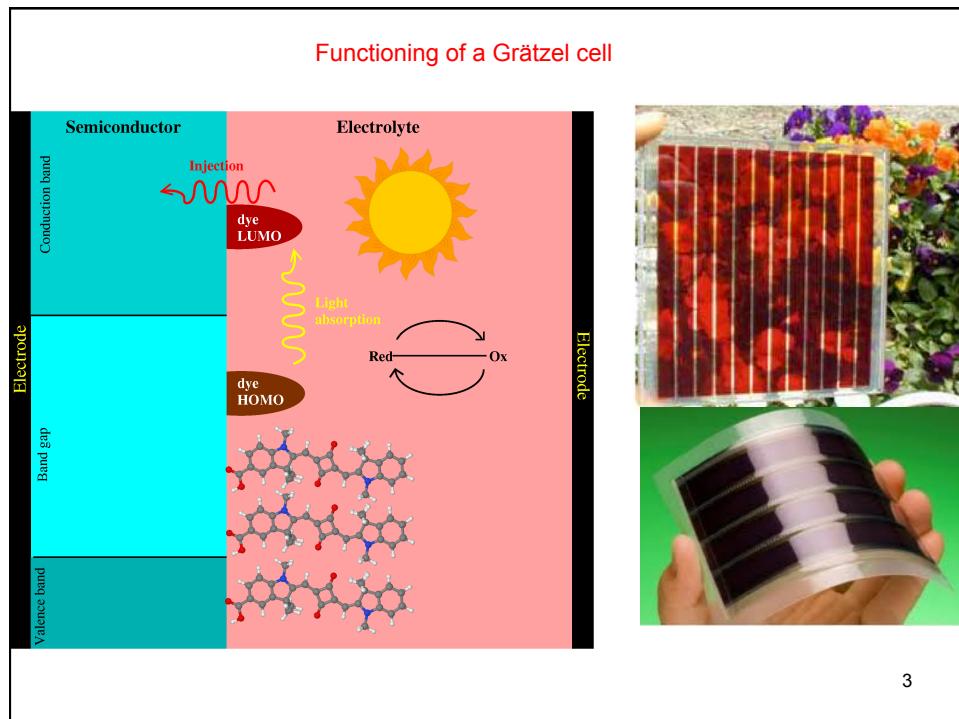
Friday, July 12th, 2013

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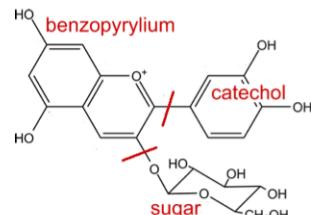
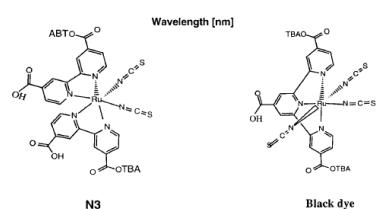
Overview

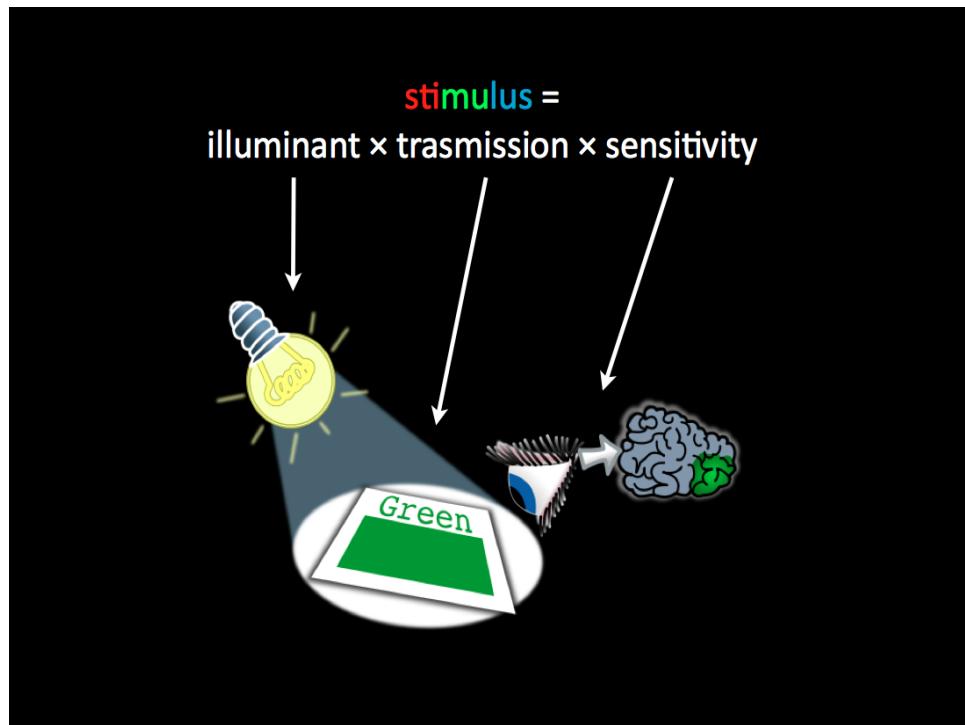
- Application of TDDFT to photovoltaics: large scale simulations
- The basics
- From the ground-state to excited states: The Runge-Gross theorem
- How TDDFT is used in practice
 - A first look at TDDFT in practice: Real-time propagations & photochemistry
 - TDDFT for optical spectra
 - real-time
 - Casida equation
 - TDDFPT-Lanczos scheme

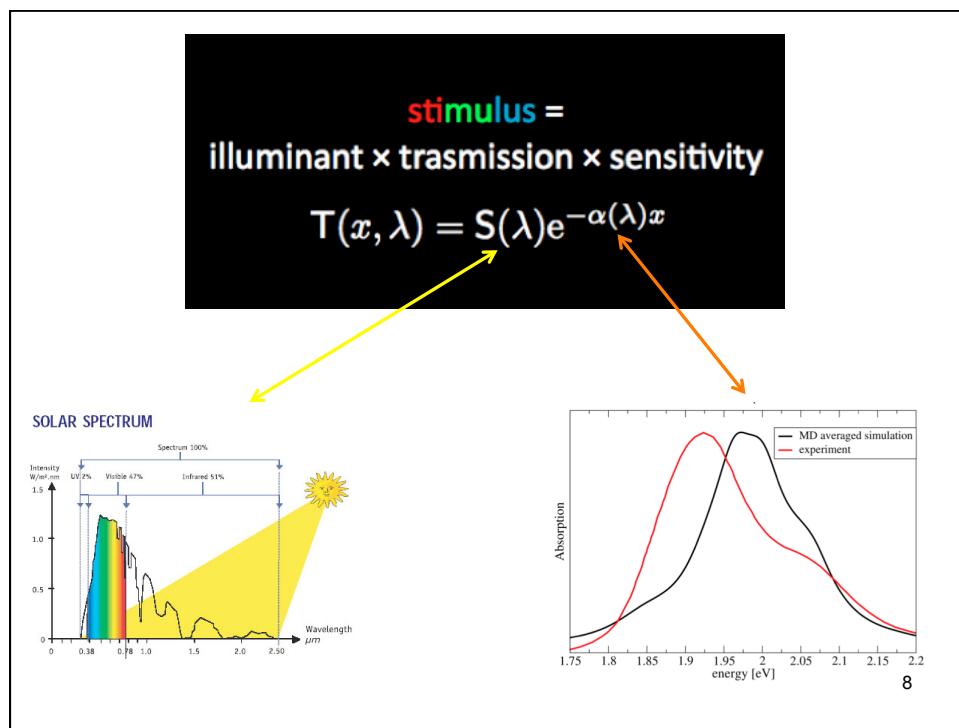
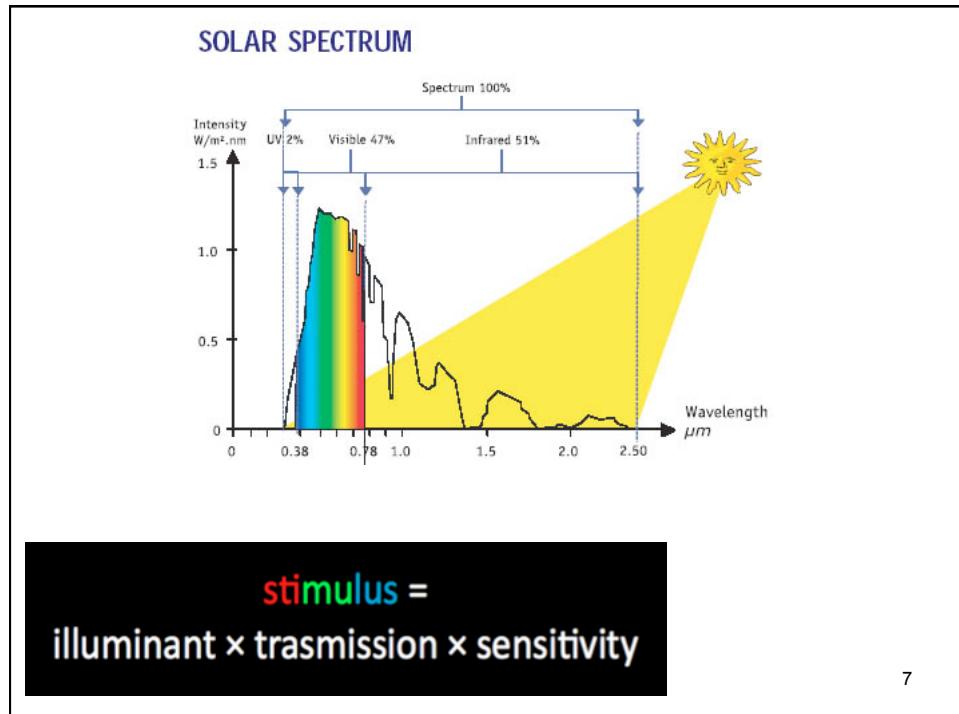
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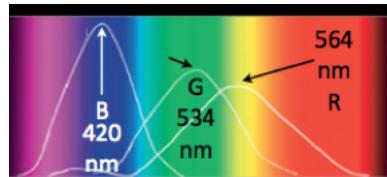
Squaraine dye







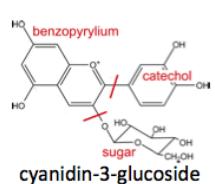
The colour we perceive



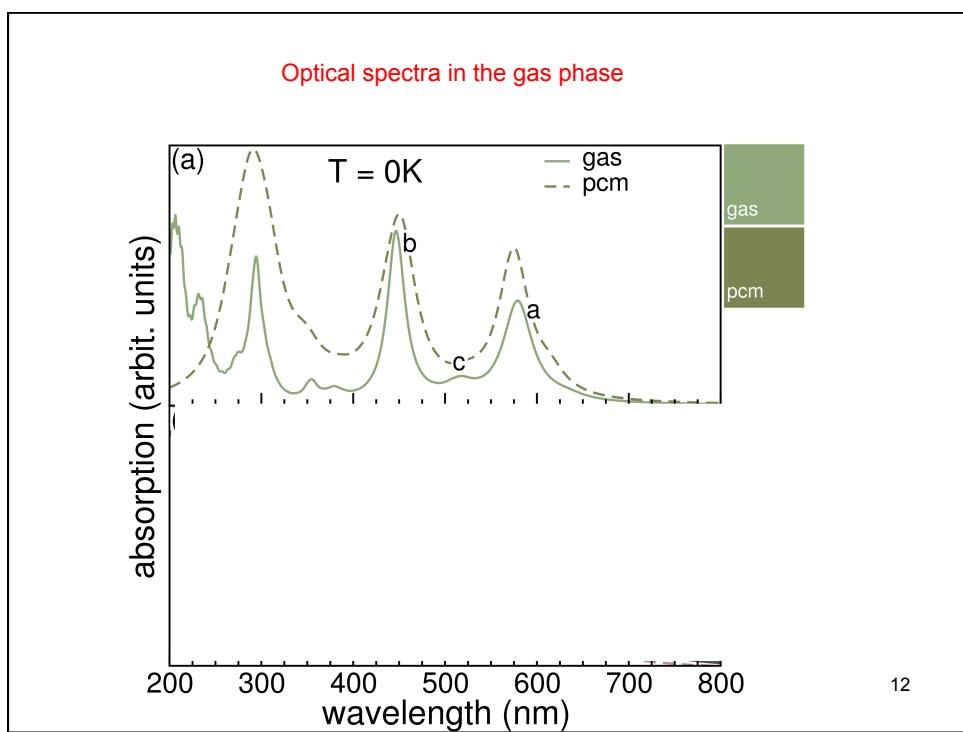
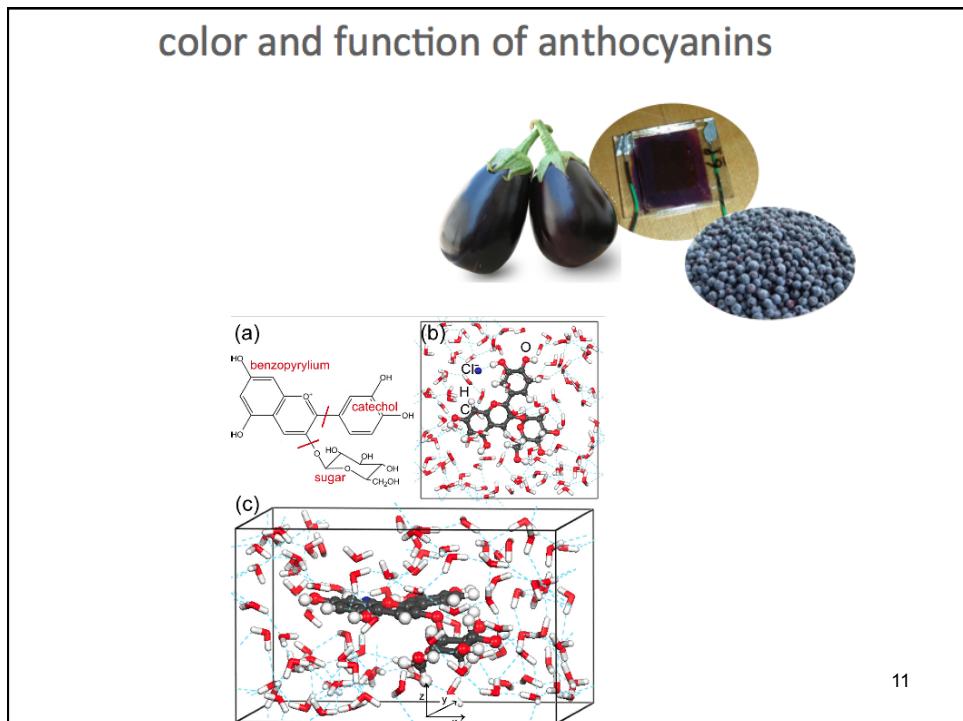
$$\text{RGB}(x) = \int S(\lambda) e^{-\alpha(\lambda)x} \mathbf{rgb}(\lambda) d\lambda$$

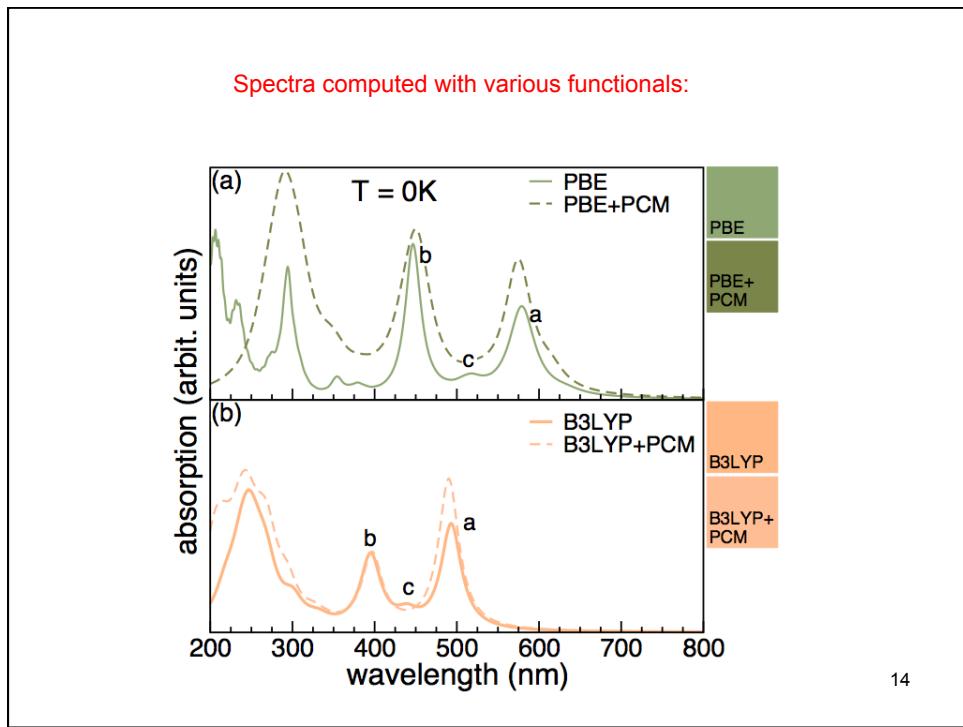
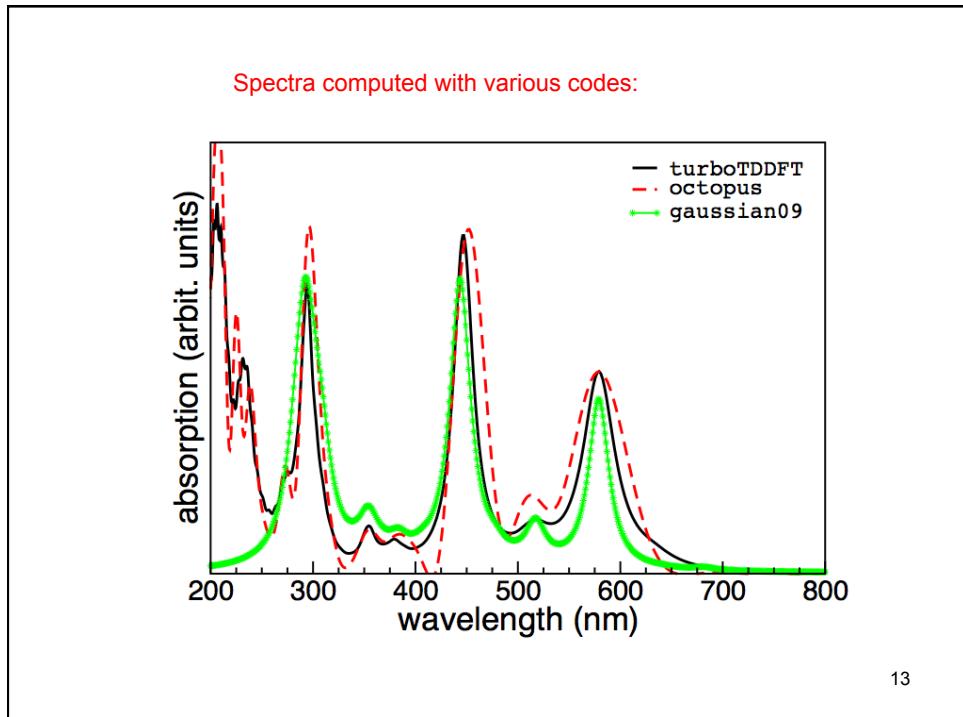
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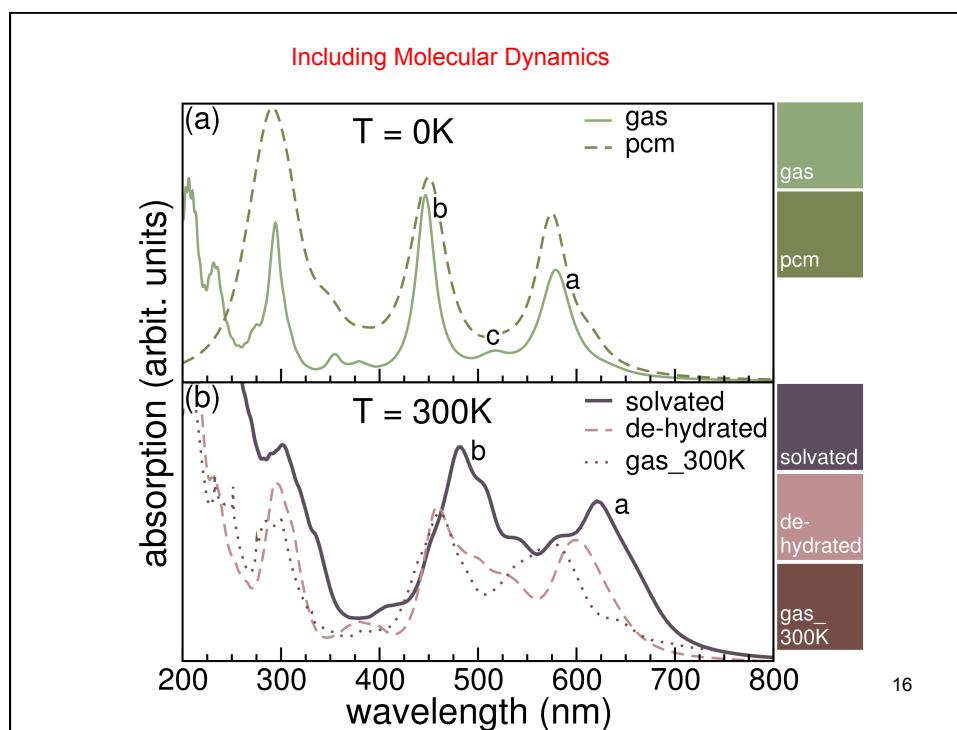
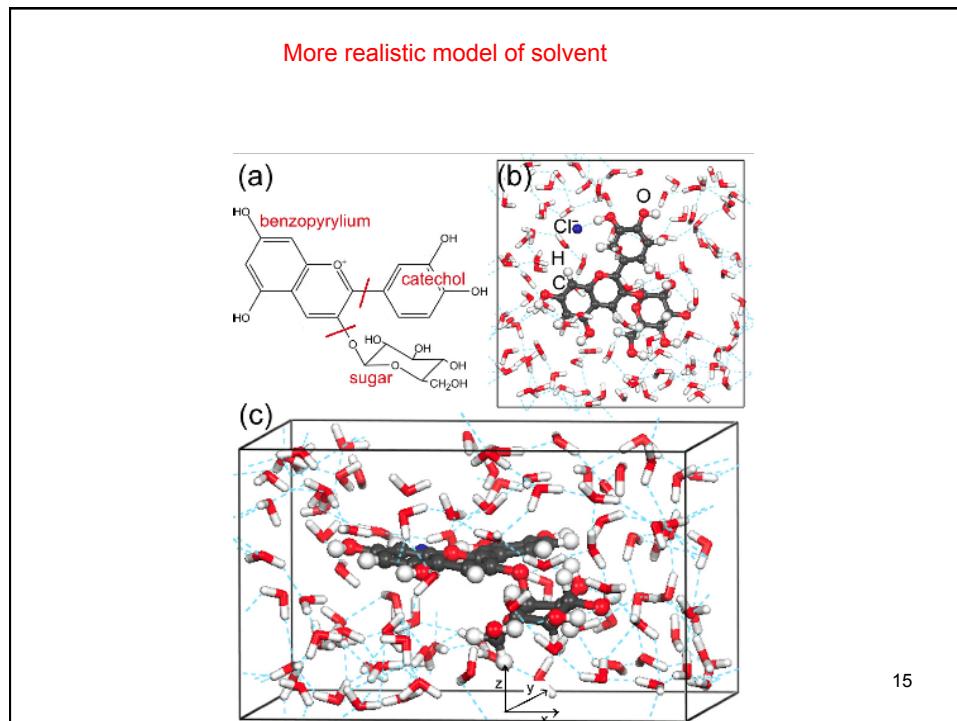
color and function of anthocyanins



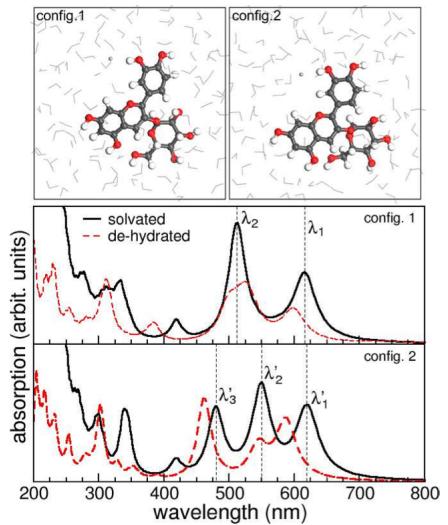
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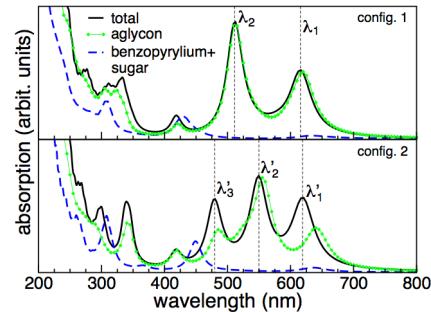
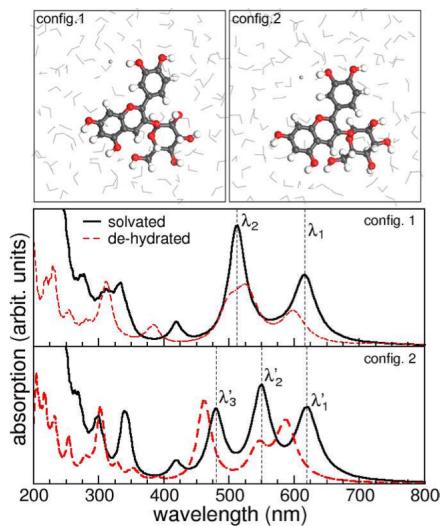


Analyzing configurational snapshots

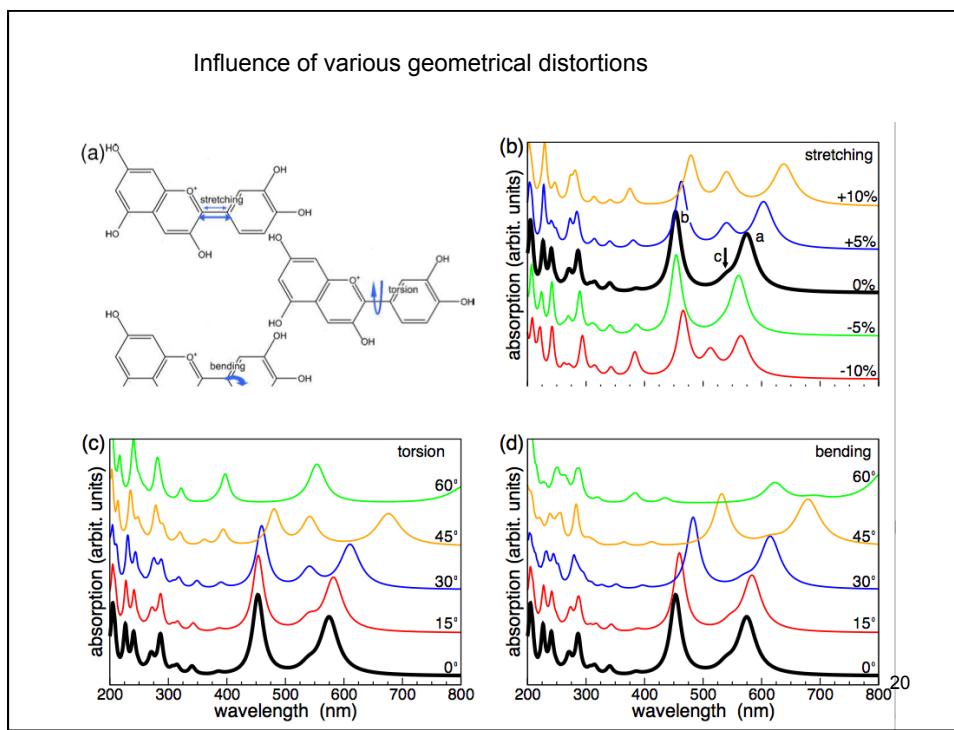
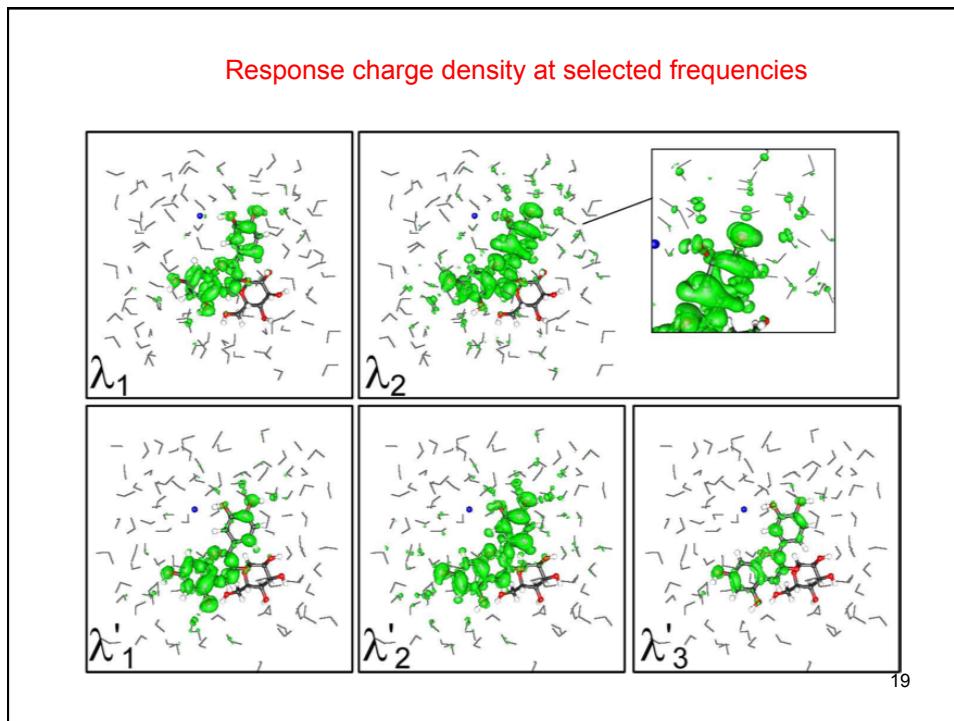


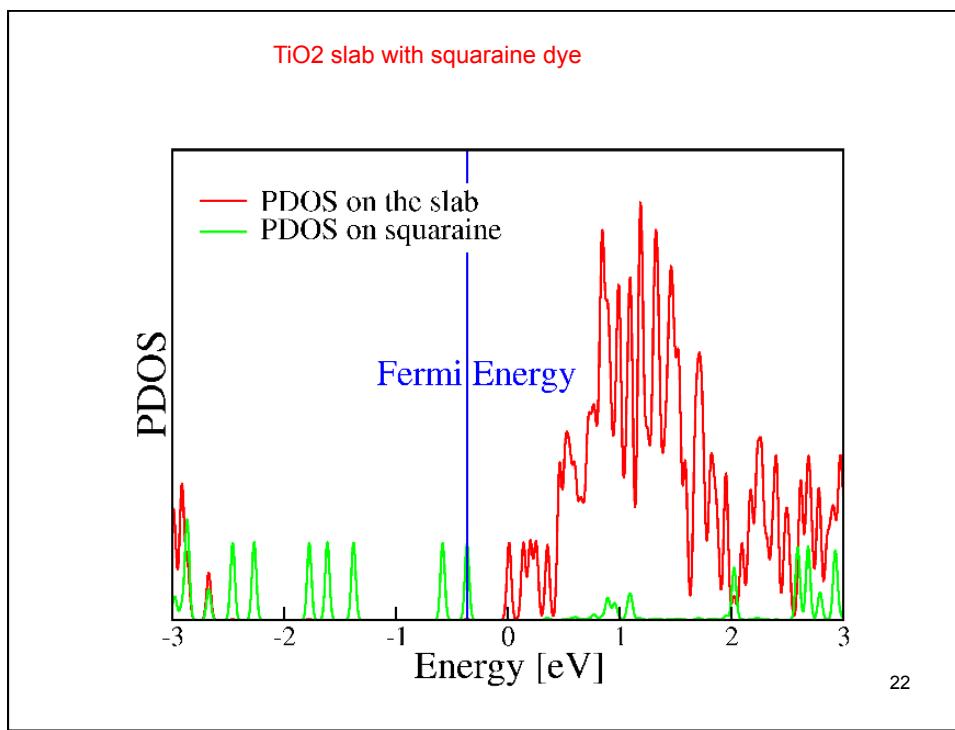
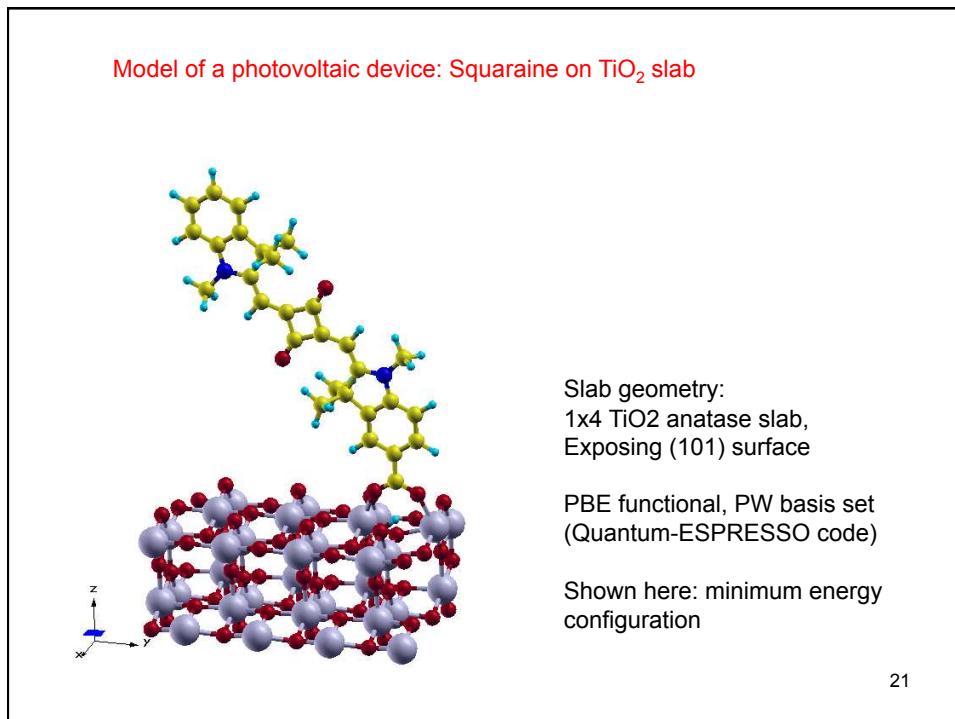
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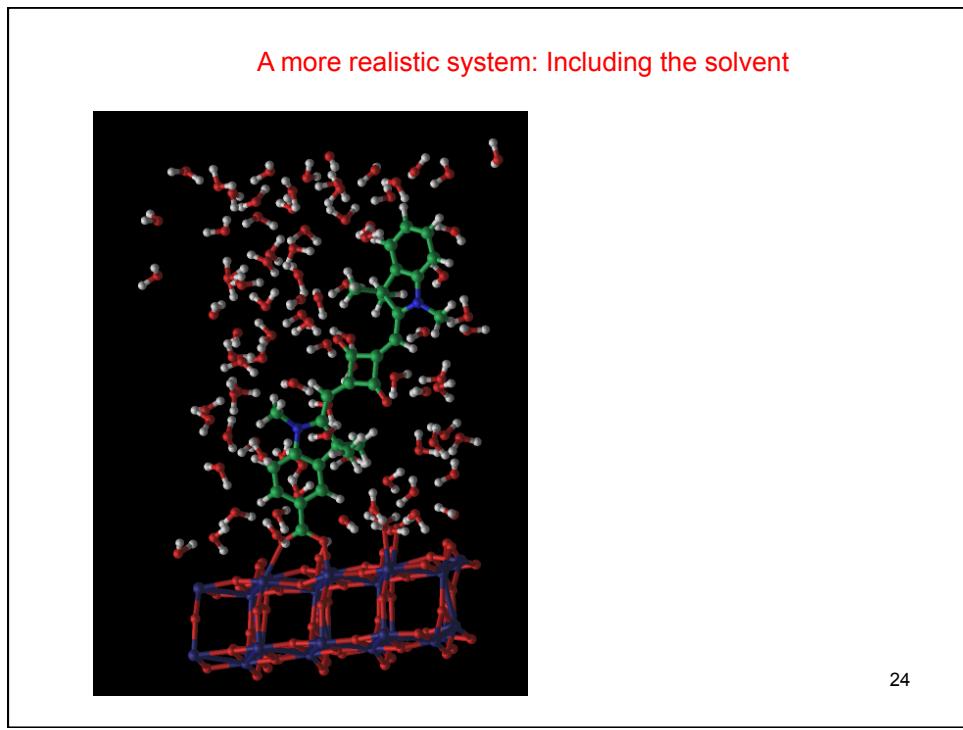
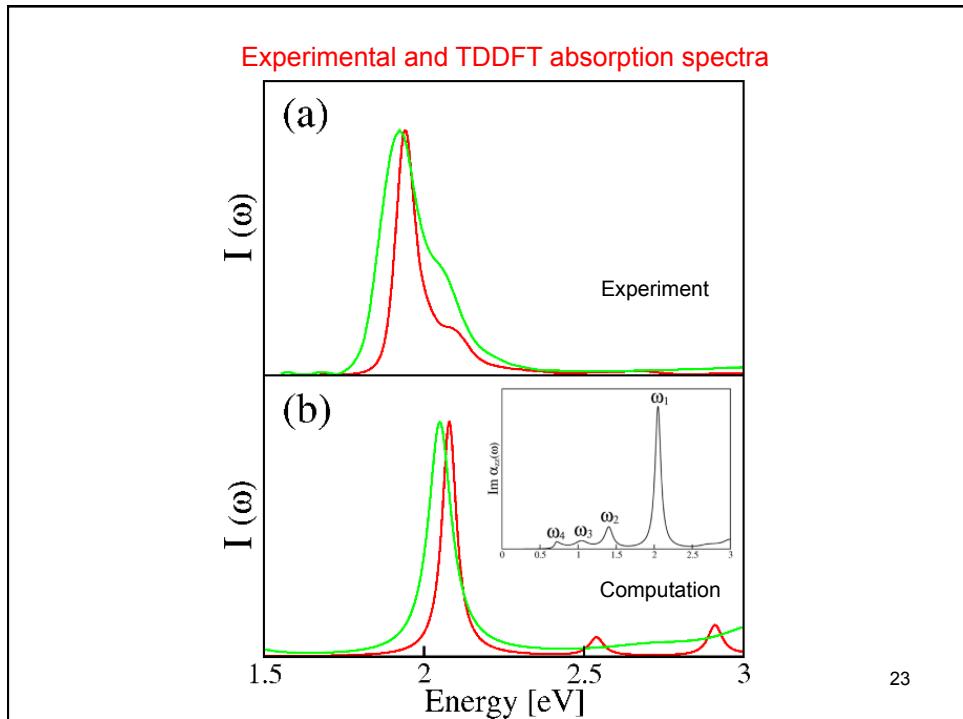
Analyzing configurational snapshots



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TDDFT calculation of optical spectra and related quantities

Various challenges:

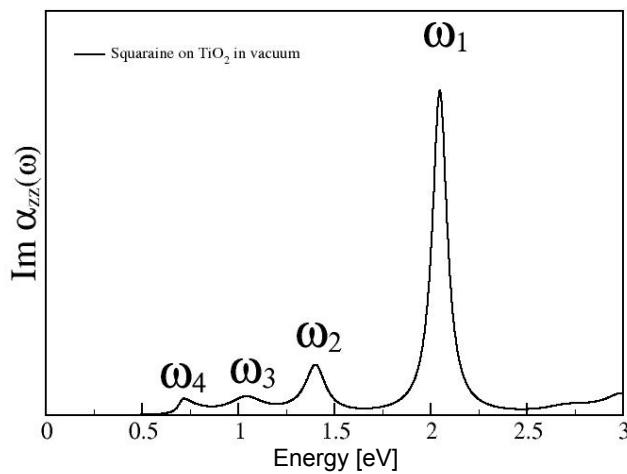
- System is large (429 atoms, 1.666 electrons, 181.581 PWs, resp. 717.690 PWs)
- Broad spectral region of interest
- Many excited states in spectral region

Computational tool:

- Recursive Lanczos algorithm for TDDFT

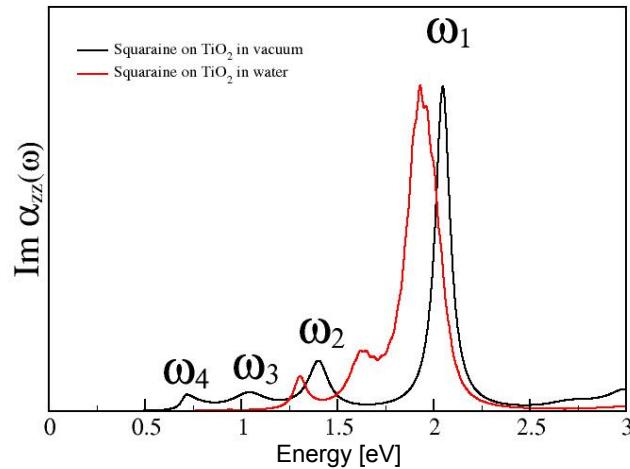
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TDDFT optical spectrum: dry system

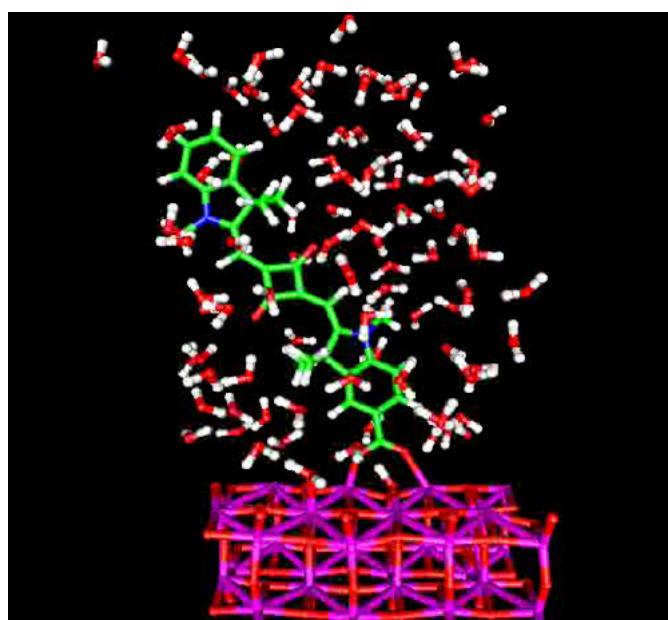


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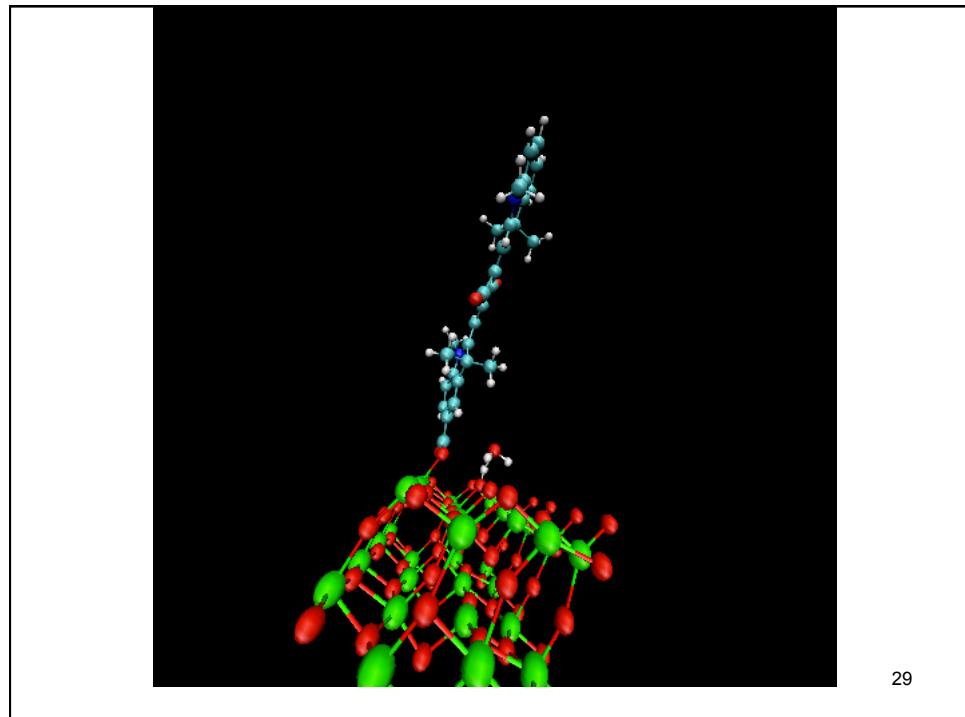
TDDFT optical spectrum including solvent



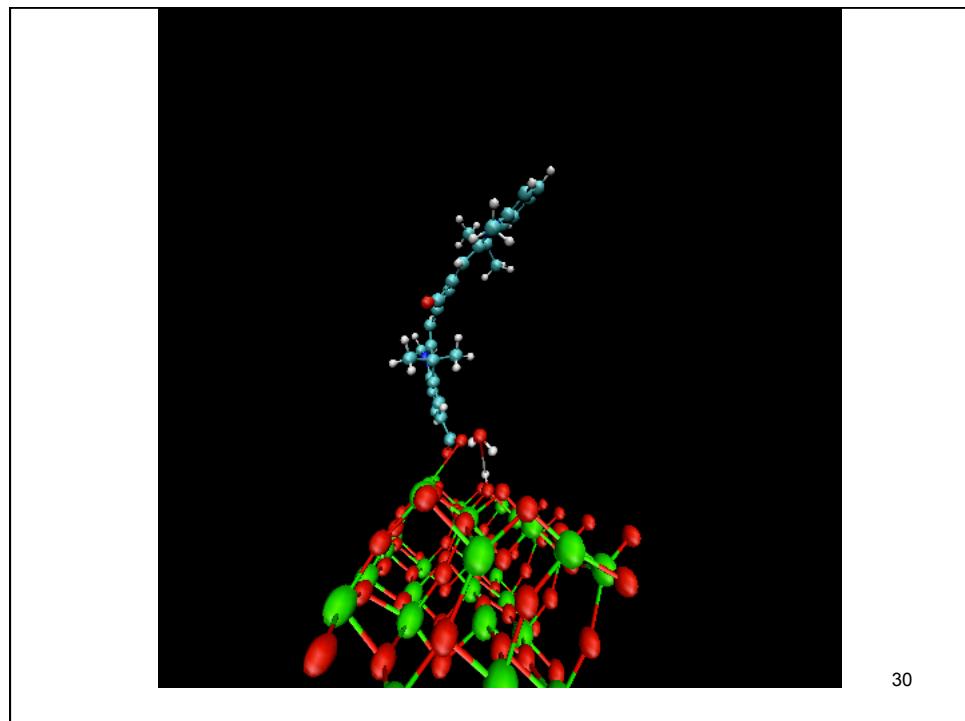
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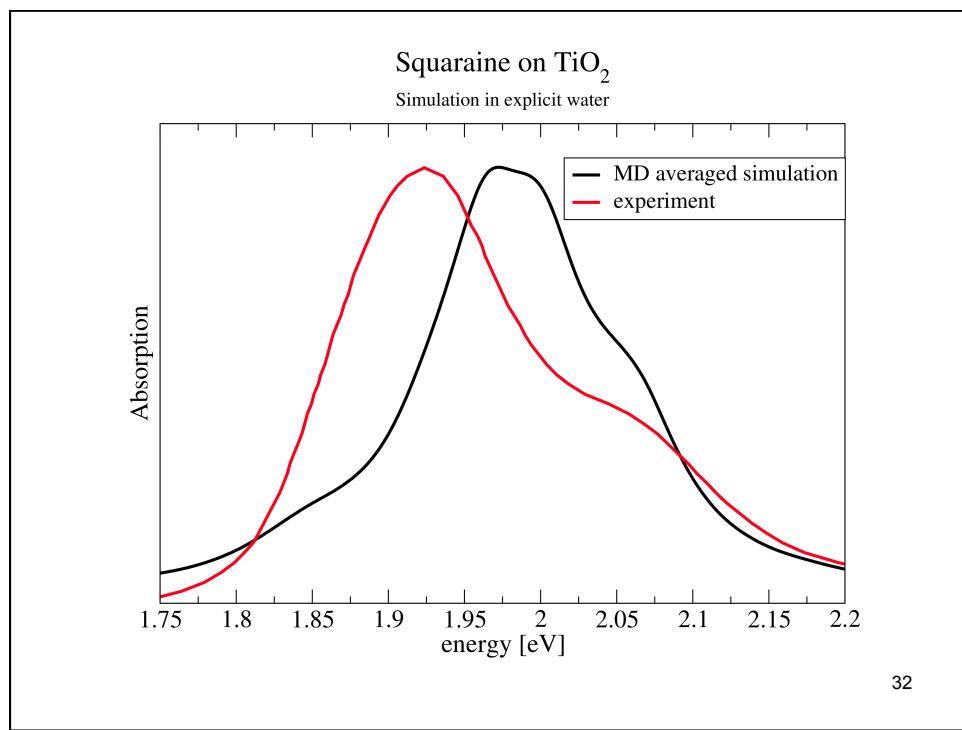
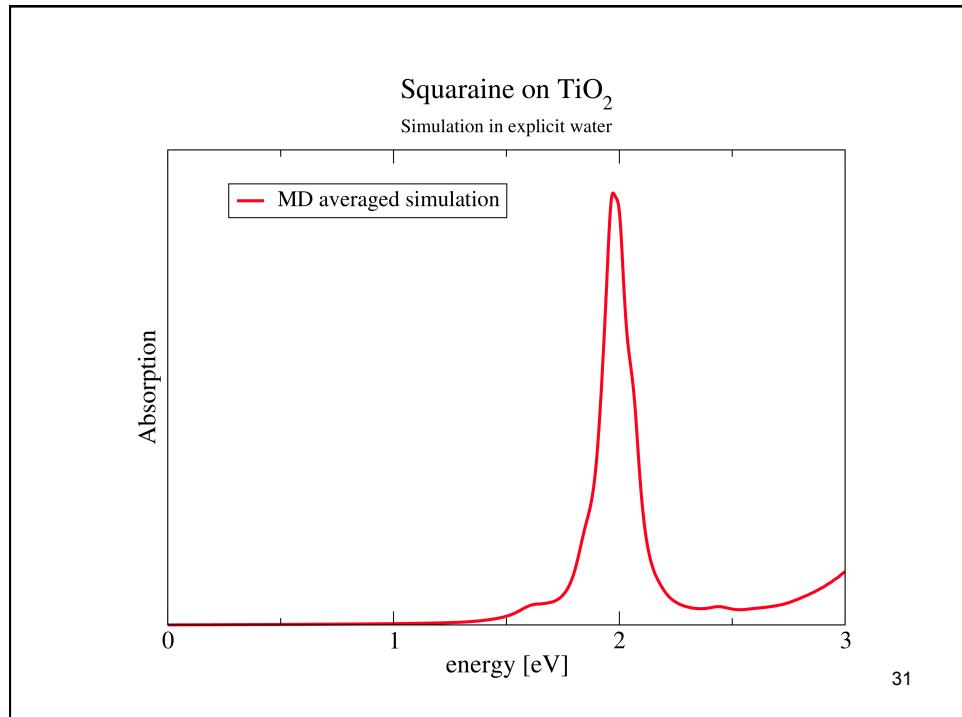
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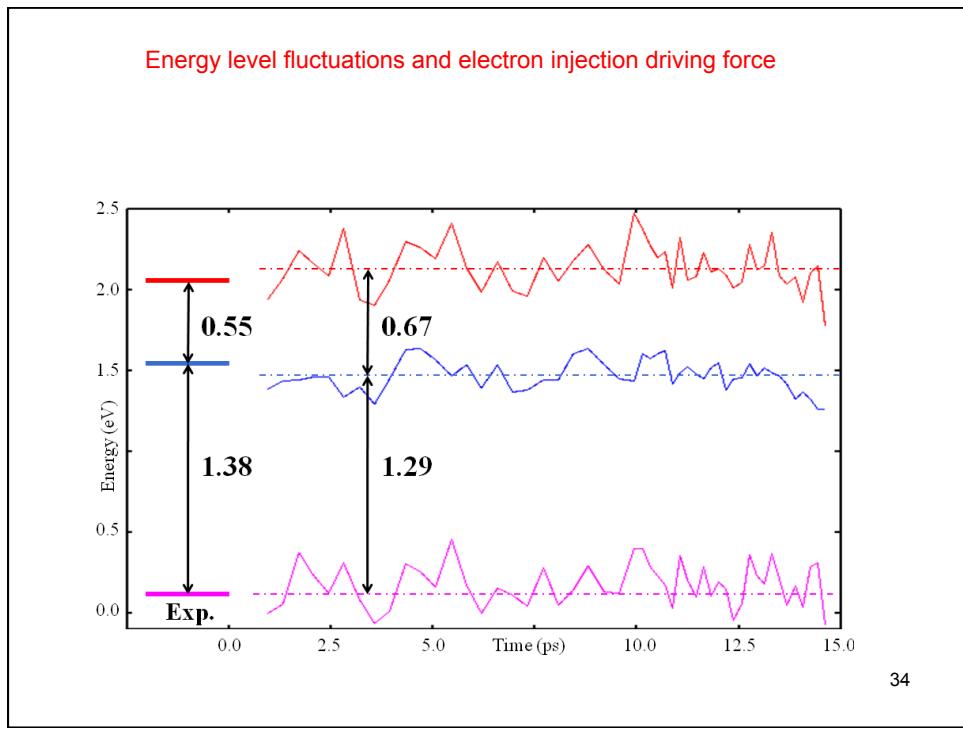
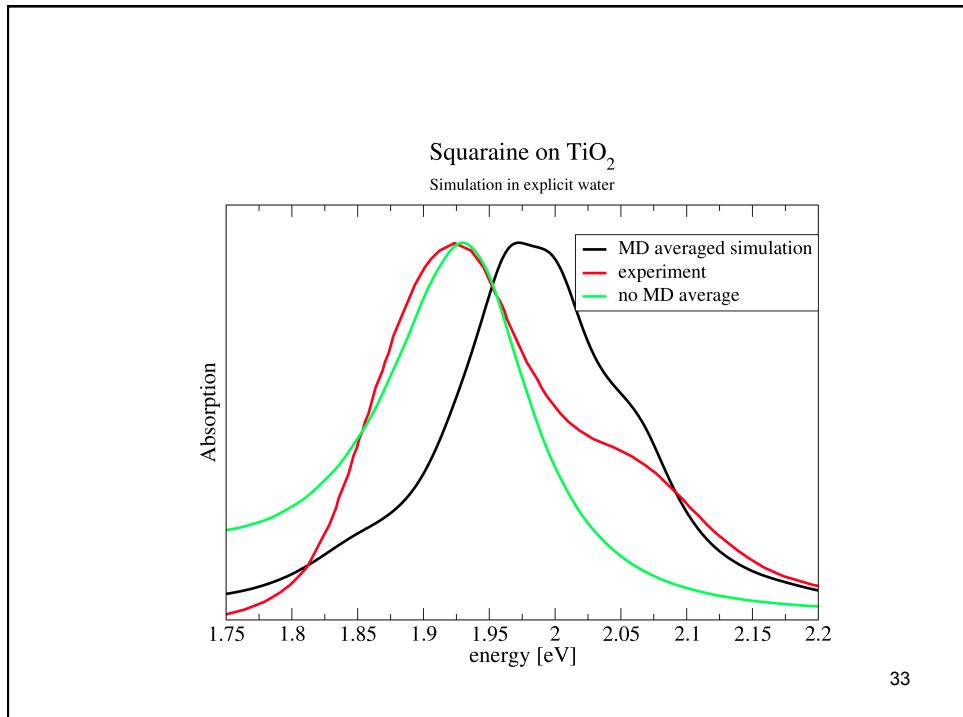


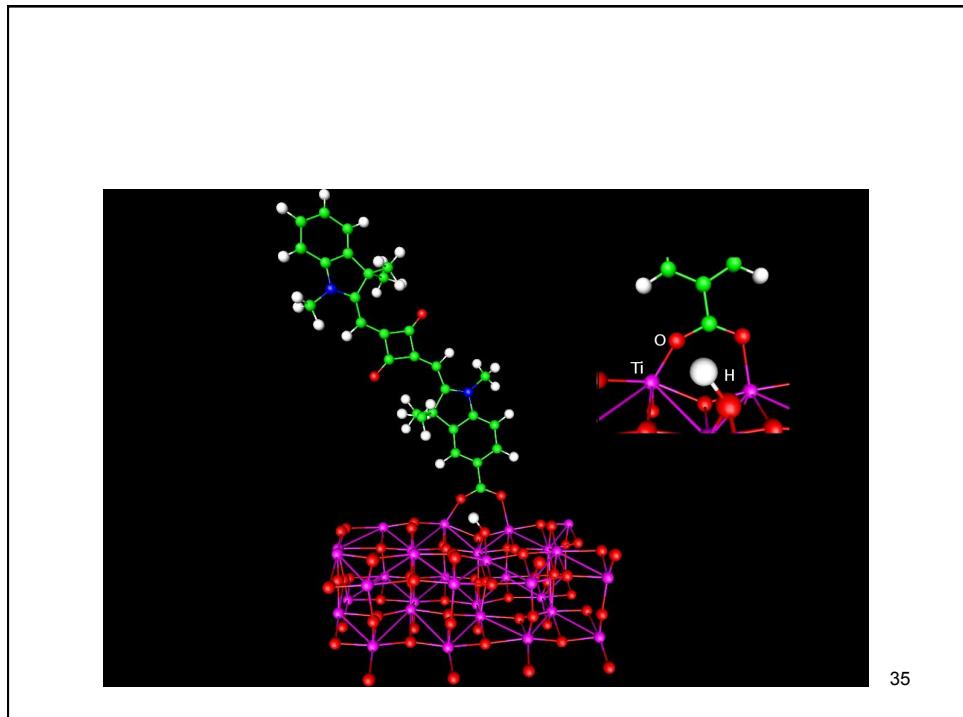
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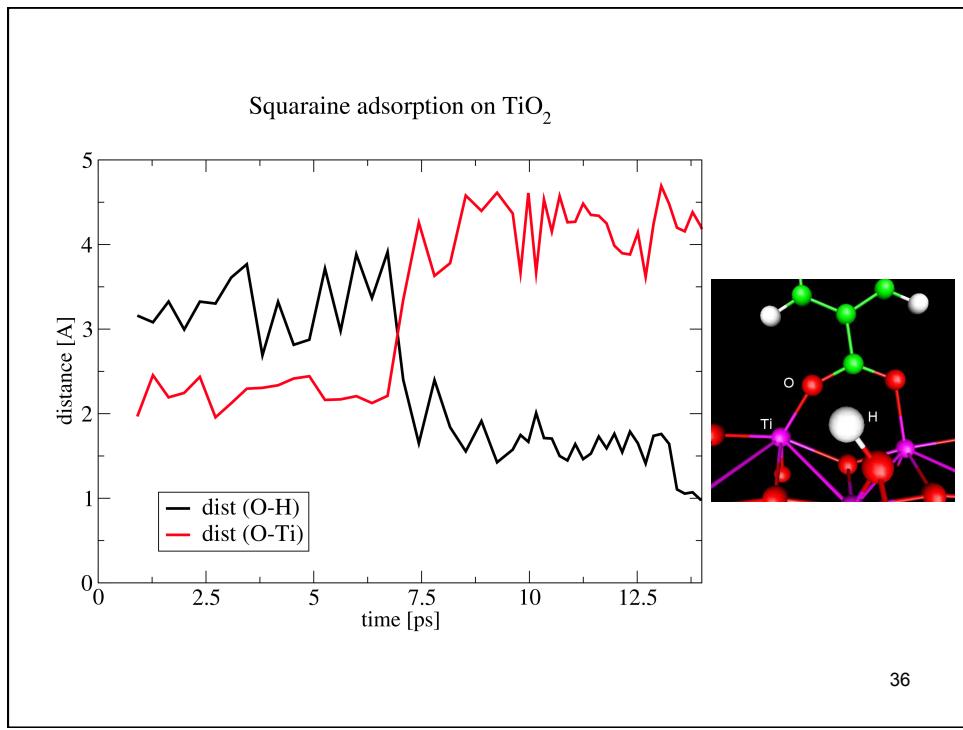
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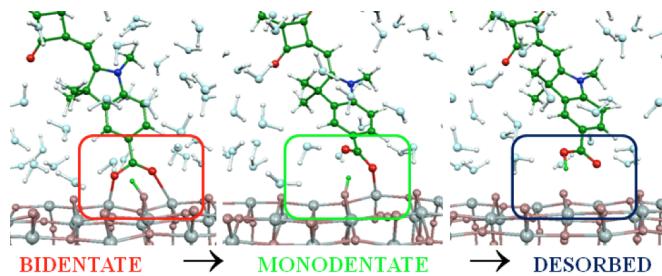


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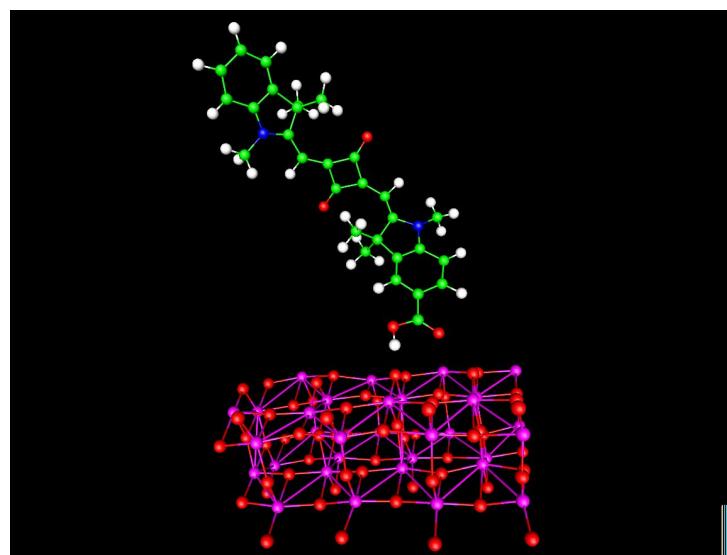


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Dye desorption steps:



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Framework: What is TDDFT all about?

1964: Hohenberg and Kohn: Density Functional Theory (DFT)

work in terms of electron density (instead of many-particle wavefunctions)

DFT is a **ground state** theory

1984: Runge and Gross: **Time-Dependent** Density Functional Theory (TDDFT)

Given $|\Psi(t=0)\rangle : V(\mathbf{r}, t) \Leftrightarrow n(\mathbf{r}, t)$

like DFT, TDDFT is **formally exact**

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Recall: Basic ground-state DFT

For practical calculations: Kohn-Sham framework

$$n_\sigma(\mathbf{r}) = \sum_i^{N_\sigma} |\phi_{i\sigma}(\mathbf{r})|^2$$

The density is written in terms of Kohn-Sham orbitals which satisfy

$$\left[-\frac{\nabla^2}{2} + v_\sigma^{KS}[n_\uparrow, n_\downarrow](\mathbf{r}) \right] \phi_{i\sigma}(\mathbf{r}) = \epsilon_{i\sigma} \phi_{i\sigma}(\mathbf{r})$$

$$\begin{aligned} F[n_\uparrow, n_\downarrow] &= T_s[n_\uparrow, n_\downarrow] + E_{Hartree} + E_{xc}[n_\uparrow, n_\downarrow] \\ E_{Hartree} &= \frac{1}{2} \int d^3r \int d^3r' \frac{n(\mathbf{r}) n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} \\ E_{xc}^{LDA} &= \int d^3r n(\mathbf{r}) \epsilon_{xc}^{unif}(n_\uparrow(\mathbf{r}), n_\downarrow(\mathbf{r})) \end{aligned}$$

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The Runge-Gross Theorem

Generalizing the HK theorem to time-dependent systems

There exists a one-to-one correspondence between the external $v(r,t)$ and the electron density $n(r,t)$, for systems evolving from a fixed many-body state.

Proof:

$$\begin{aligned} |\Psi(t_0)\rangle &= |\Psi'(t_0)\rangle \equiv |\Psi_0\rangle \\ n(\mathbf{r}, t_0) &= n'(\mathbf{r}, t_0) \equiv n^0(\mathbf{r}) \\ \mathbf{j}(\mathbf{r}, t_0) &= \mathbf{j}'(\mathbf{r}, t_0) \equiv \mathbf{j}^0(\mathbf{r}) \end{aligned}$$

Step 1: Different potentials v and v' yield different current densities \mathbf{j} and \mathbf{j}'

Step 2: Different current densities \mathbf{j} and \mathbf{j}' yield different densities n and n'

$$v(\mathbf{r}, t) \neq v'(\mathbf{r}, t) + c(t) \quad \Rightarrow \quad n(\mathbf{r}, t) \neq n'(\mathbf{r}, t)$$

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Using TDDFT in practice

Finding an equivalent of the Kohn-Sham formalism

$$i\frac{\partial}{\partial t}\varphi_{i\sigma}(\mathbf{r}, t) = \hat{H}_\sigma^{\text{KS}}(\mathbf{r}, t)\varphi_{i\sigma}(\mathbf{r}, t)$$

With a time-dependent Hamiltonian:

$$\hat{H}_\sigma^{\text{KS}}(\mathbf{r}, t) = -\frac{\nabla^2}{2} + v_\sigma^{\text{KS}}[n_\uparrow, n_\downarrow](\mathbf{r}, t)$$

Density and potentials are now defined like:

$$n_\sigma(\mathbf{r}, t) = \sum_i^{N_\sigma} |\varphi_{i\sigma}(\mathbf{r}, t)|^2$$

$$v_\sigma^{\text{KS}}[n_\uparrow, n_\downarrow](\mathbf{r}, t) = v_\sigma(\mathbf{r}, t) + \int d^3r' \frac{n(\mathbf{r}', t)}{|\mathbf{r} - \mathbf{r}'|} + v_\sigma^{\text{xc}}[n_\uparrow, n_\downarrow](\mathbf{r}, t)$$

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Which functional to use ?

The easiest and probably most widely used functional is the
Adiabatic Local Density Approximation (ALDA)

$$v_{\sigma}^{\text{xc ALDA}}(\mathbf{r}, t) = \frac{\partial}{\partial n_{\sigma}} [n \varepsilon_{\text{xc}}^{\text{unif}}(n_{\uparrow}, n_{\downarrow})] \Big|_{n_{\alpha}=n_{\alpha}(\mathbf{r}, t)}$$

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TDDFT in real time:

(1996:Bertsch; 2001: Octopus code)

- Consider a general time-dependent perturbation:
 $V_{\text{pert}}(\mathbf{r}, t)$
- Obtain orbitals, charge density, and potentials by solving the Schrödinger equation explicitly in real time:

$$\psi_j(t + \Delta) = \exp \left(-iH(t + \frac{\Delta}{2})\Delta \right) \psi_j(t)$$

(Nonlinear TD Schrödinger equation)

- Can be used for *linear response* calculations, or for general TD *non-linear* problems.

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A first application: Photochemistry

- Recent experimental progress made it possible to produce ultra-short intense laser pulses (few fs)
- This allows one to probe bond breaking/formation, charge transfer, etc. on the relevant time scales
- Nonlinear real-time TDDFT calculations can be a valuable tool to understand the physics of this kind of probe.
- Visualizing chemical bonds: Electron localization function

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Nonlinear optical response

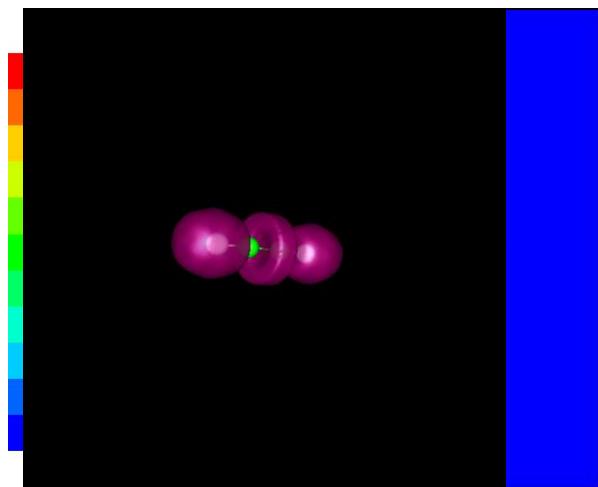
- Electron localization function:

$$ELF(\mathbf{r}, t) = \frac{1}{1 + [D_\sigma(\mathbf{r}, t)/D_\sigma^0(\mathbf{r}, t)]^2}$$

$$D_\sigma(\mathbf{r}, t) = \tau_\sigma(\mathbf{r}, t) - \frac{1}{4} \frac{[\nabla n_\sigma(\mathbf{r}, t)]^2}{n_\sigma(\mathbf{r}, t)} - \frac{j_\sigma^2(\mathbf{r}, t)}{n_\sigma(\mathbf{r}, t)}$$

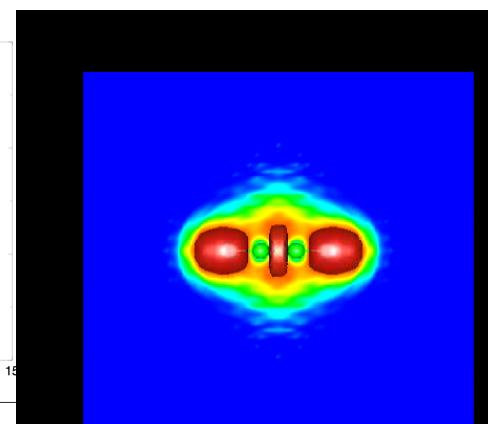
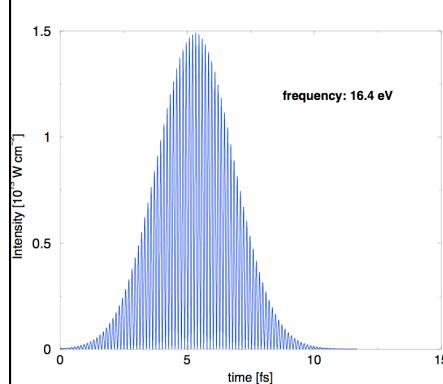
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Example: Ethyne C₂H₂



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Example: Ethyne C₂H₂



How can we calculate optical spectra?

Consider a perturbation δV applied to the ground-state system:

$$\delta n(r, t) = \int d^3 r' dt' \chi(r, r'; t - t') \delta V(r', t')$$

The induced dipole is given by the induced charge density:

$$d(t) = \int d^3 r \delta n(r, t) \hat{r}$$

Consider the perturbation due to an electric field:

$$\delta V(r, t) = -e E_{ext}(t) \cdot \hat{r}$$

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How can we calculate optical spectra?

The dipole susceptibility is then given by:

$$d(t) = \int dt' \alpha(t - t') E_{ext}(t')$$

The experimentally measured strength function S is related to the Fourier transform of α :

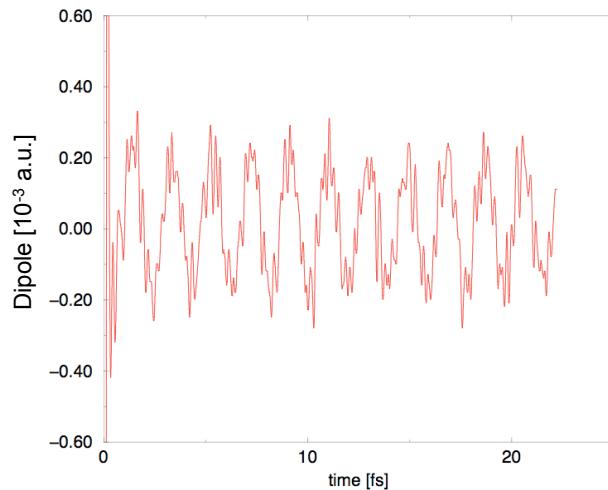
$$S(\omega) = \frac{2m}{\pi e^2 \hbar} \omega \operatorname{Im} \alpha(\omega)$$

In practice: We take an E-field pulse $E_{ext} = E_0 \delta(t)$, calculate $d(t)$, and obtain the spectrum $S(\omega)$ by calculating

$$d(\omega) = \int_0^\infty dt e^{i\omega t - \delta t} d(t)$$

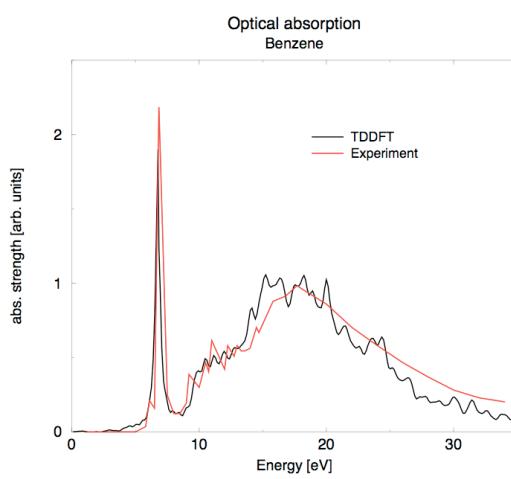
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A typical dipole-function $d(t)$...



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... and the resulting spectrum



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Linear response formalism in TDDFT:

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

$$V_{pert}(\mathbf{r}, t) = V_0(\mathbf{r}) (\exp(i\omega t) + \exp(-i\omega t))$$
- Linear response: assume the time-dependent response:

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

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

$$\delta V(\mathbf{r}, t) = V_{pert}(\mathbf{r}, t) + \delta V_{SCF}^+(\mathbf{r}) e^{i\omega t} + \delta V_{SCF}^-(\mathbf{r}) e^{-i\omega t}$$
- Put these expressions into the TD Schrödinger equation

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Linear response formalism in TDDFT:

$$\begin{aligned}\omega \delta\psi_v^+(\mathbf{r}) &= (H_{KS}^0 - \epsilon_v^0) \delta\psi_v^+ + \hat{P}_{\mathbf{e}} (\delta V_{SCF}^+(\mathbf{r}) + V_{pert}(\mathbf{r})) \psi_v^0(\mathbf{r}) \\ -\omega \delta\psi_v^-(\mathbf{r}) &= (H_{KS}^0 - \epsilon_v^0) \delta\psi_v^- + \hat{P}_{\mathbf{e}} (\delta V_{SCF}^-(\mathbf{r}) + V_{pert}(\mathbf{r})) \psi_v^0(\mathbf{r})\end{aligned}$$

Now define the following linear combinations:

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

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

With the following definitions:

$$\begin{aligned} D |\mathbf{x}\rangle &= \left\{ (H_{KS}^0 - \epsilon_i) \mathbf{x}_i(\mathbf{r}) \right\} \\ K |\mathbf{x}\rangle &= \left\{ (H_{KS}^0 - \epsilon_i) \mathbf{x}_i(\mathbf{r}) + \psi_i^0(\mathbf{r}) \sum_j \int d\mathbf{r}' f_{Hxc}(\mathbf{r}, \mathbf{r}') \psi_{i'}^0(\mathbf{r}') \mathbf{x}_{i'}(\mathbf{r}') \right\} \end{aligned}$$

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

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Linear response TD-DFT essentially means solving a **non-hermitean** eigenvalue equation of dimension $2 N_v \times N_c$.

Standard way to proceed (Casida's equations):

- Solve the time-independent problem to **completely diagonalize** the ground-state Hamiltonian.

[Some computer time can be saved by limiting the diagonalization to the lower part of the spectrum]

- Obtain as many eigenstates/frequencies of the TD-DFT problem as needed (or as possible).

[Some computer time can be saved by transforming the non-hermitean problem to a hermitean one (e.g. Tamm-Dancoff approx.)]

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Advantages:

One obtains not only the frequency (and oscillator strength), but the full eigenvector of each elementary excitation.

[Info can be used for spectroscopic assignments, to calculate forces, etc]

Disadvantages:

One obtains not only the frequency (and oscillator strength), but the full eigenvector of each elementary excitation.

[Info is often not needed, all the information is immediately destroyed after computation]

Computationally extremely demanding (large matrices to be diagonalized)

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Time-dependent density functional perturbation theory (TDDFPT)

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 $\alpha(t)$ and thus $\alpha(\omega)$.

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

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Consider an observable A:

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

Its Fourier transform is:

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

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

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

Therefore:

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

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

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

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

Build a Lanczos recursion chain:

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

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

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

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

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

$$(\omega - H)^{-1} = \frac{1}{\omega - a_0 + \frac{b_1^2}{\omega - a_1 + \frac{b_2^2}{\omega - a_2 + \dots}}}$$

63

Back to the calculation of spectra:

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

Therefore:

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

Use a recursion to represent \mathcal{L} as a tridiagonal matrix:

$$\mathcal{L} = \begin{pmatrix} a_1 & b_1 & 0 & & & \\ c_1 & a_2 & b_2 & & & \\ 0 & c_2 & a_3 & b_3 & & \\ & & & \ddots & \ddots & b_{N-1} \\ & & & & c_{N-1} & a_N \end{pmatrix} \quad 64$$

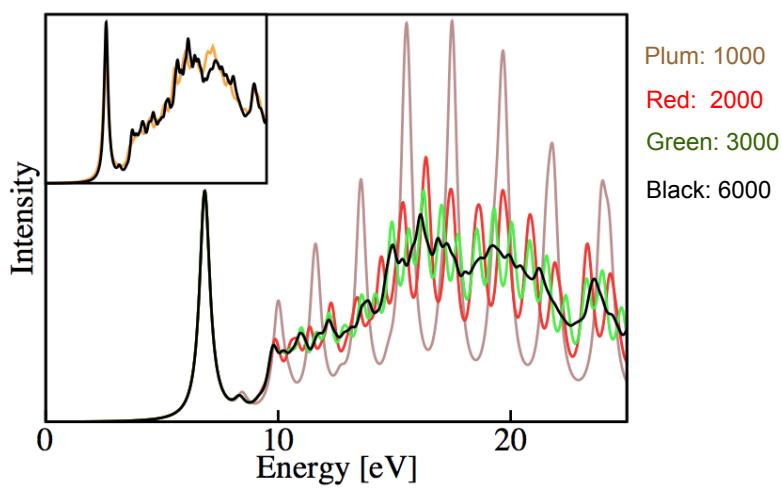
And the response can be written as a continued fraction!

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

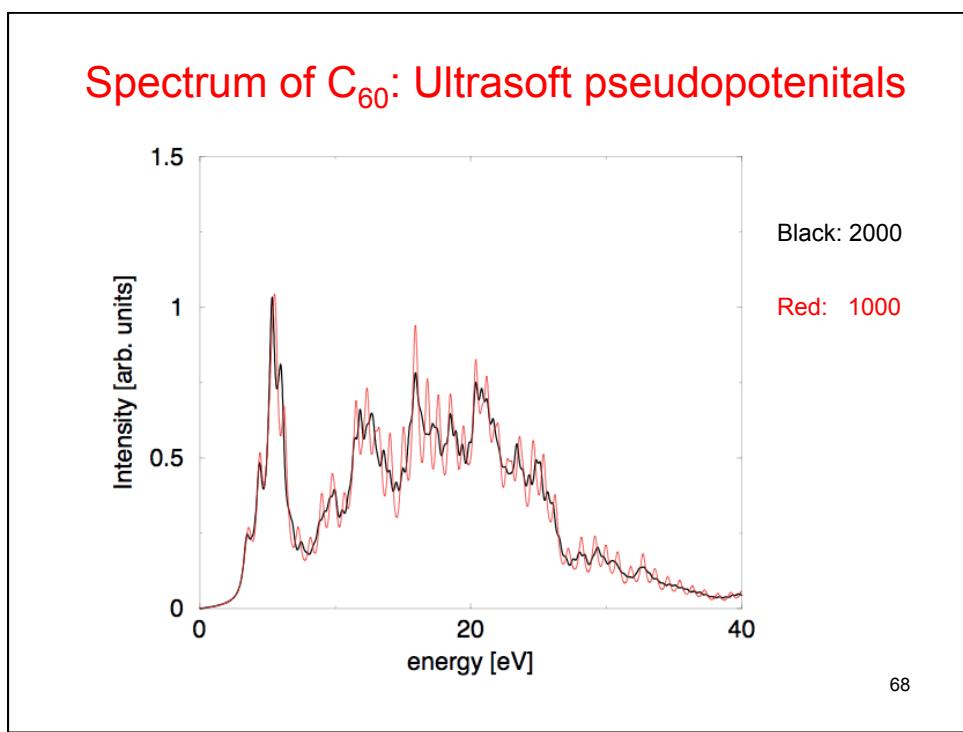
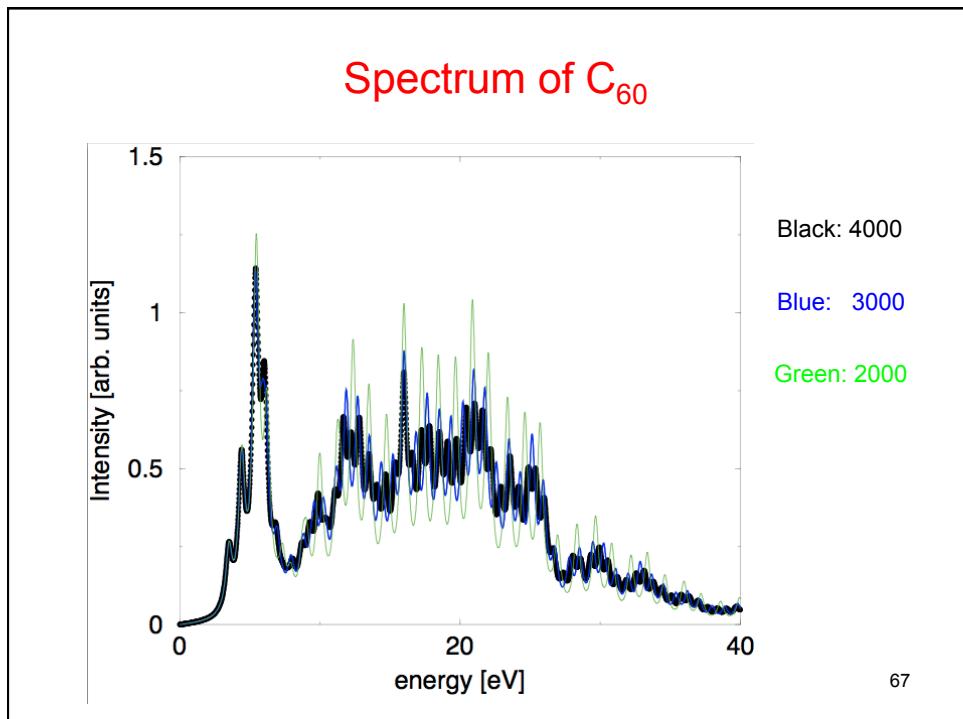
$$= \frac{1}{\omega - a_1 + b_2 \frac{1}{\omega - a_2 + \dots} c_2}$$

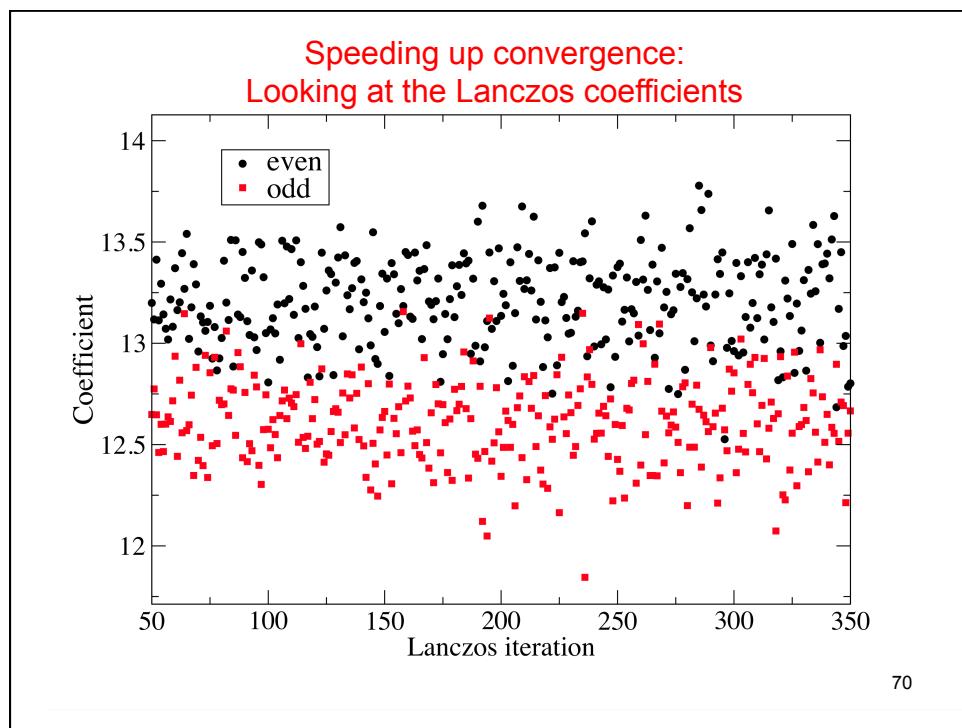
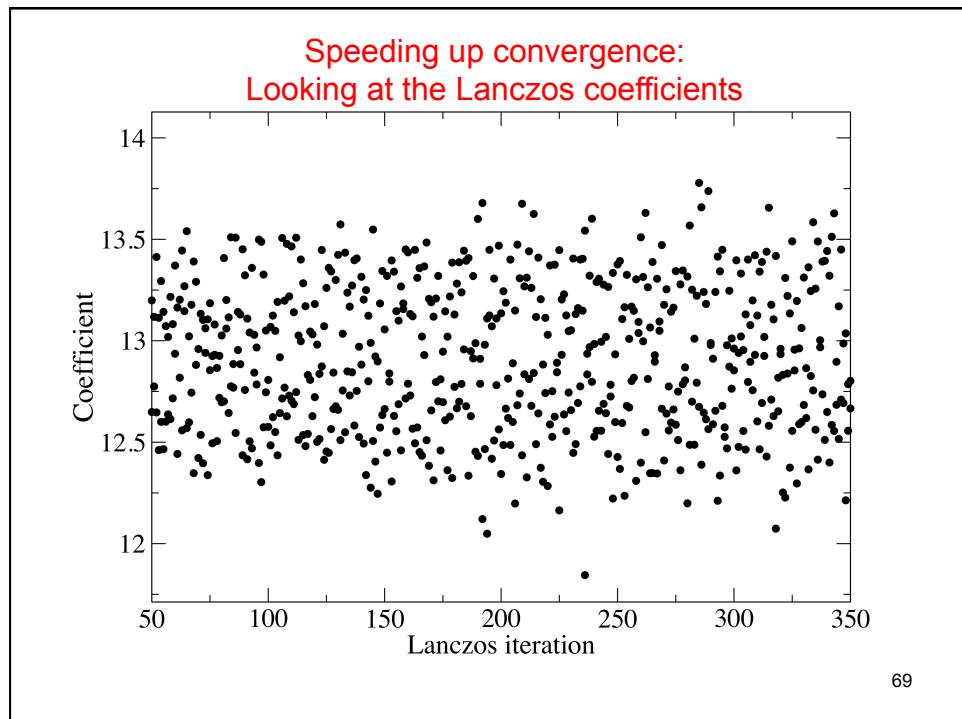
65

How does it work?
Benzene spectrum



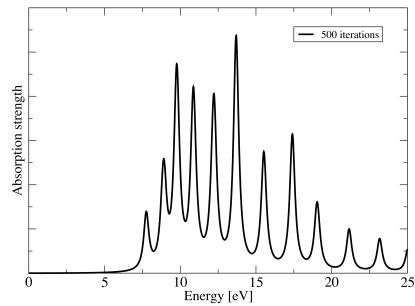
66





Effect of the terminator:

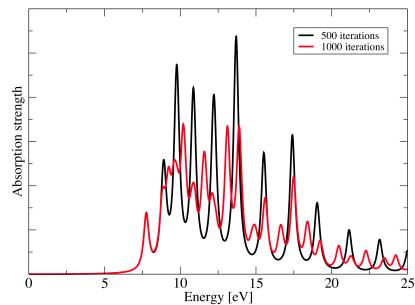
No terminator:



71

Effect of the terminator:

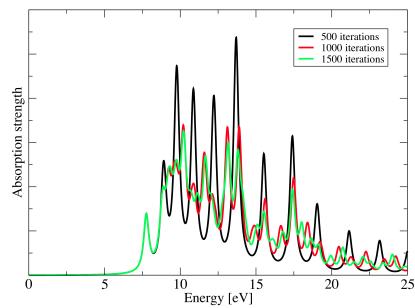
No terminator:



72

Effect of the terminator:

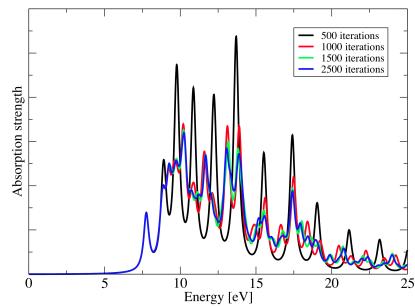
No terminator:



73

Effect of the terminator:

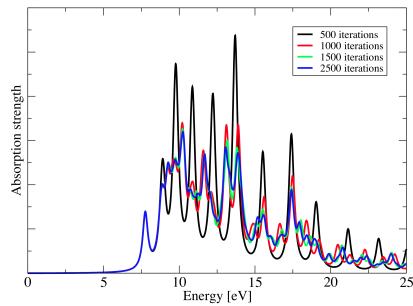
No terminator:



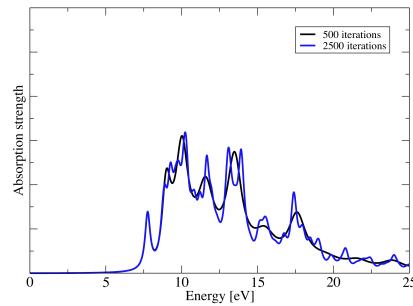
74

Effect of the terminator:

No terminator:



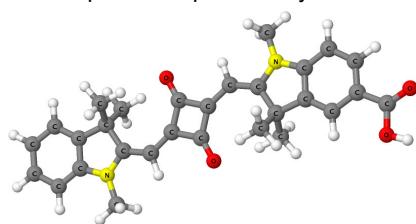
Terminator:



75

Analyzing the spectrum

Example of a squaraine dye:



Can we analyze given features of the ^{l_{mol}} spectrum in terms of the electronic structure?

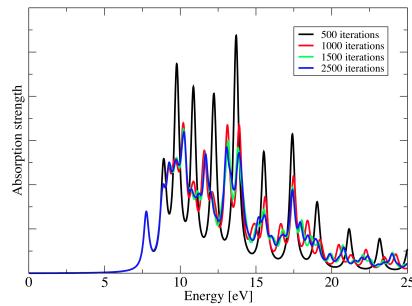
YES!

It is possible to compute the response charge density for any given frequency using a second recursion chain.

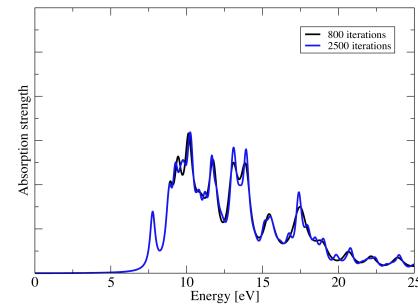
76

Effect of the terminator:

No terminator:



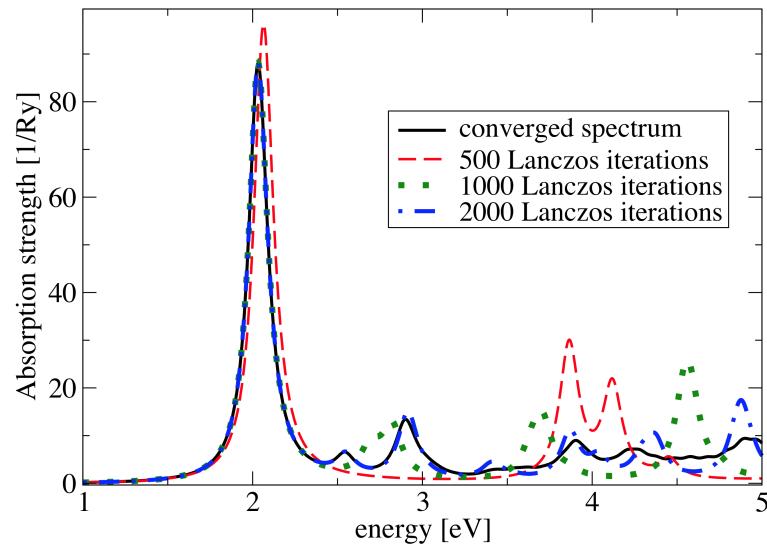
Terminator:



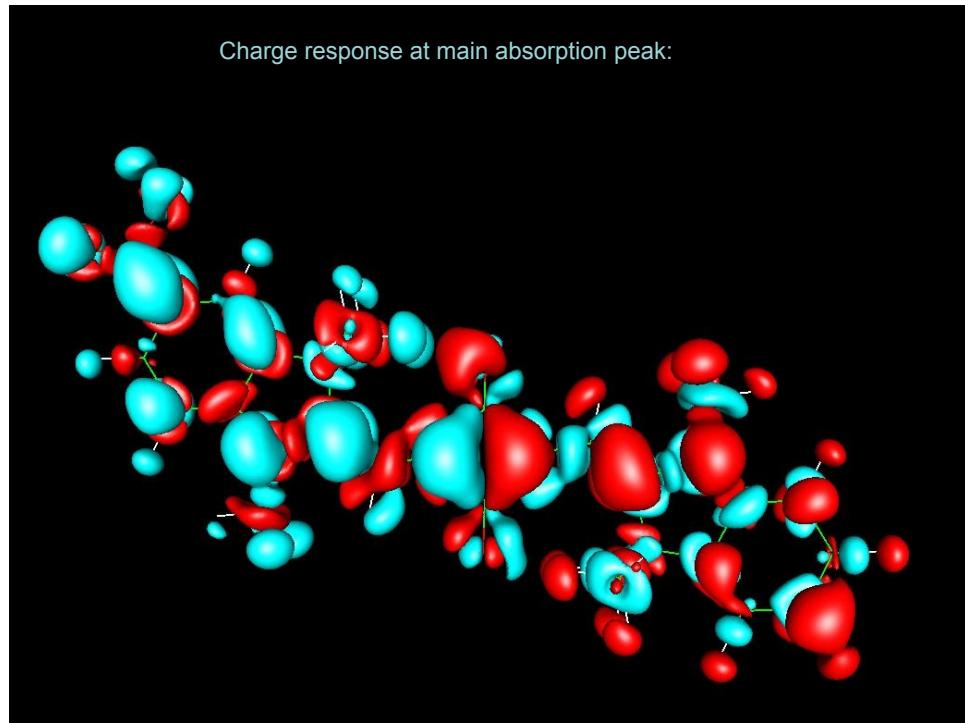
77

Convergence of the TDDFPT spectrum

Isolated squaraine molecule



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Conclusions

- TDDFT as a formally exact extension of ground-state DFT for electronic excitations
- Allows to follow the electronic dynamics in real time
- Using TDDFT in linear response allows one to calculate spectra

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- Arrigo Calzolari (Modena)
- Quantum ESPRESSO and its community

To know more:

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Applications to DSSCs:

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