2221-1

Hands-on Tutorial on Electronic Structure Computations

17 - 21 January 2011

Time-dependent density functional theory and how it is used

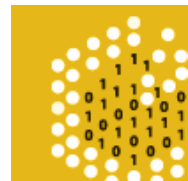Ralph Gebauer
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Time-dependent density functional theory and how it is used

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Thursday, January 20th, 2011

Overview

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
    - Cassida equation
    - TDDFPT-Lanczos scheme

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)

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

like DFT, TDDFT is **formally exact**

Recall: Basic ground-state DFT

For practical calculations: **Kohn-Sham framework**

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

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

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

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

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:

$$|\Psi(t_0)\rangle = |\Psi'(t_0)\rangle \equiv |\Psi_0\rangle$$
$$n(\boldsymbol{r}, t_0) = n'(\boldsymbol{r}, t_0) \equiv n^0(\boldsymbol{r})$$
$$\boldsymbol{j}(\boldsymbol{r}, t_0) = \boldsymbol{j}'(\boldsymbol{r}, t_0) \equiv \boldsymbol{j}^0(\boldsymbol{r})$$

Step 1: Different potentials v and v' yield different current densities j and j'

Step 2: Different current densities j and j' yield different densities n and n'

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

Using TDDFT in practice

Finding an equivalent of the Kohn-Sham formalism

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

With a time-dependent Hamiltonian:

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

Density and potentials are now defined like:

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

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

Which functional to use ?

The easiest and probably most widely used functional is the

Adiabatic Local Density Approximation (ALDA)

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

TDDFT in real time:

(1996:Bertsch; 2001: Octopus code)

- Consider a general time-dependent perturbation:

$$V_{pert}(\boldsymbol{r}, t)$$

- 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.

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.

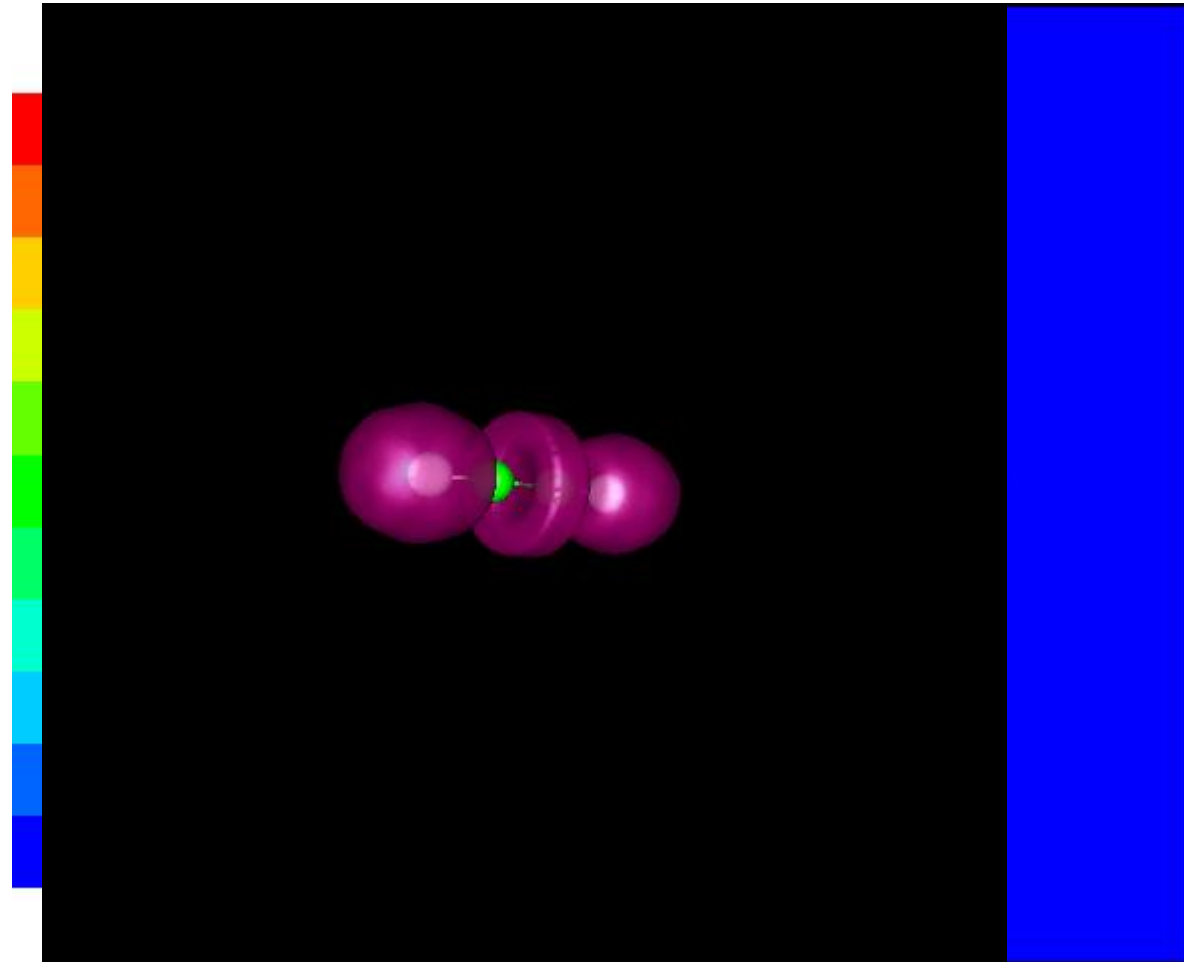- Visualizing chemical bonds: Electron localization function
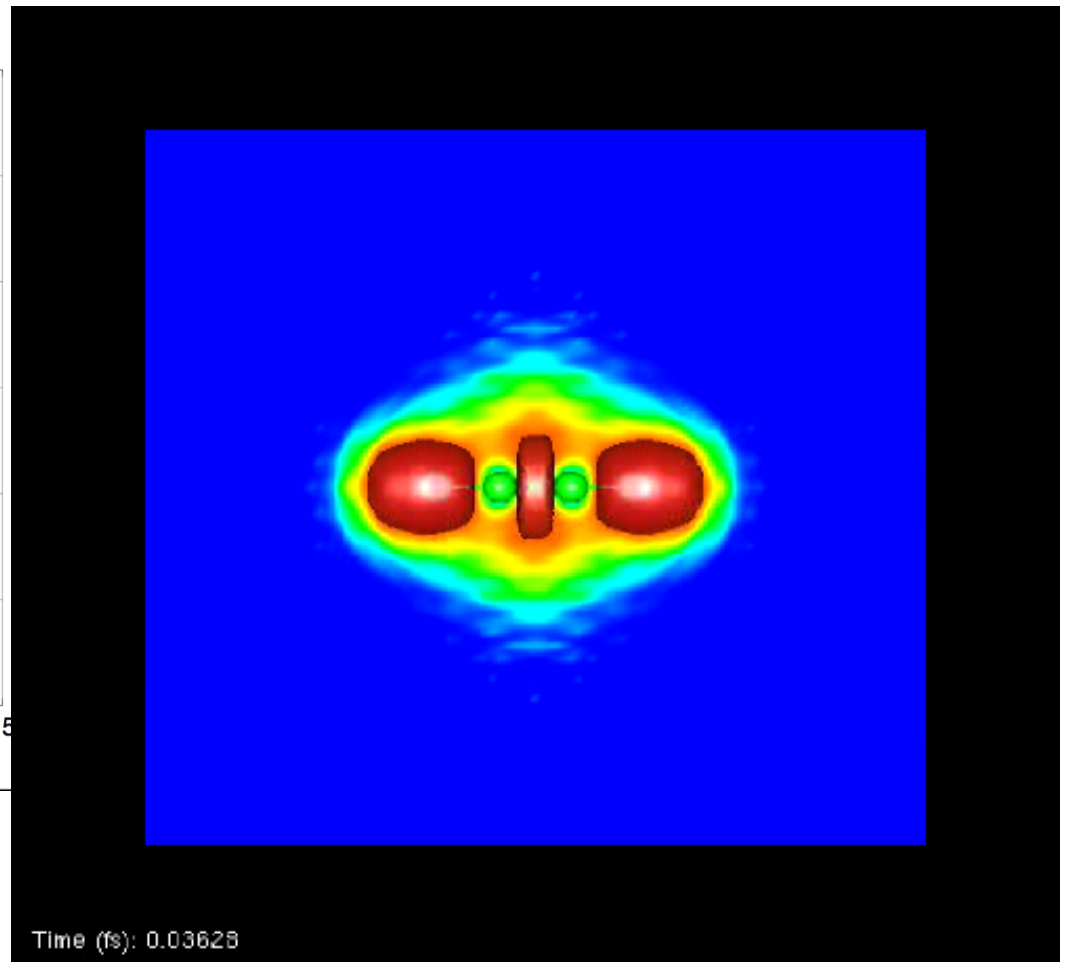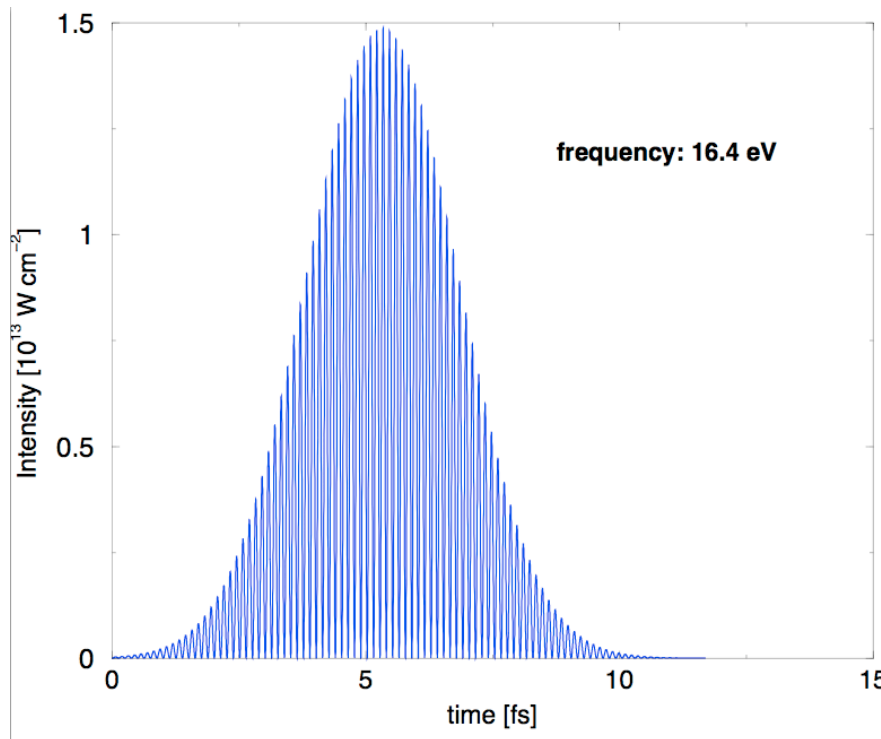
Nonlinear optical response

- Electron localization function:

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

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

Example: Ethyne C_2H_2

Example: Ethyne C₂H₂

frequency: 16.4 eV

Time (fs): 0.03625

How can we calculate optical spectra?

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

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

The induced dipole is given by the induced charge density:

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

Consider the perturbation due to an electric field:

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

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:

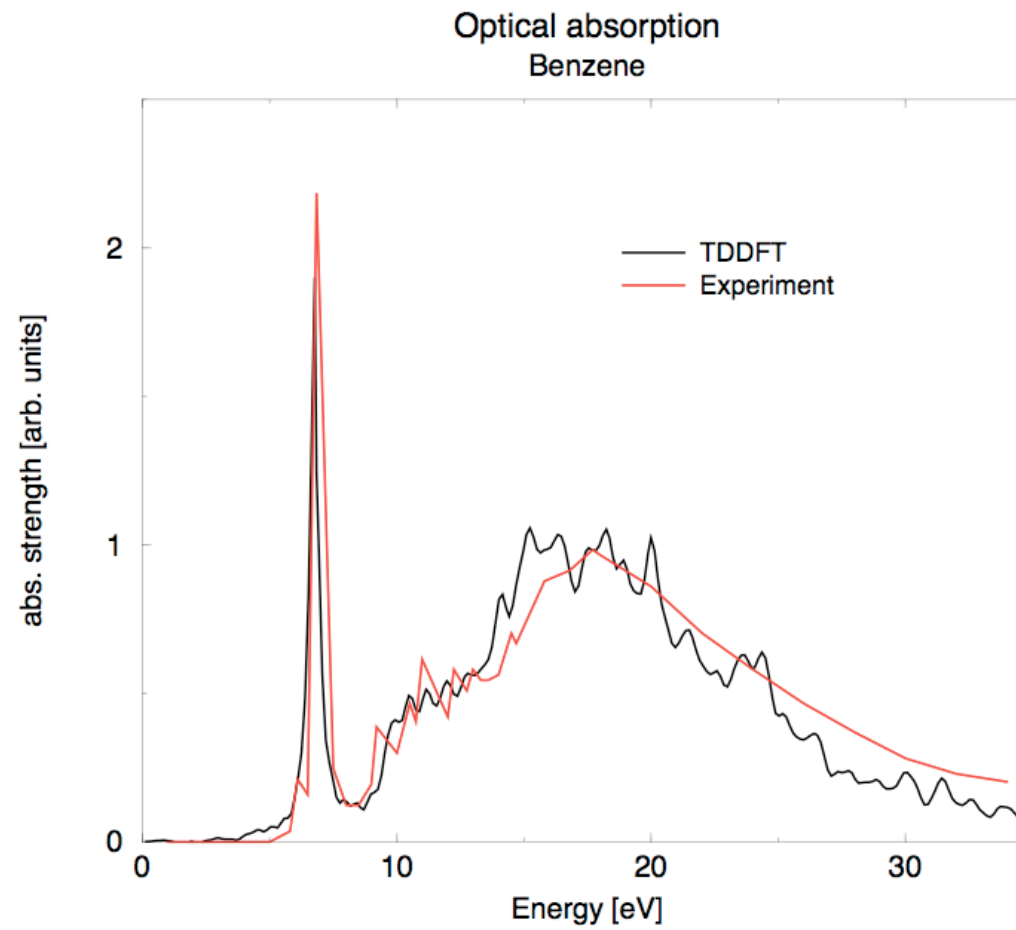$$S(\omega) = \frac{2m}{\pi e^2 \hbar} \omega \operatorname{Im} \alpha(\omega)$$

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

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

A typical dipole-function d(t) …
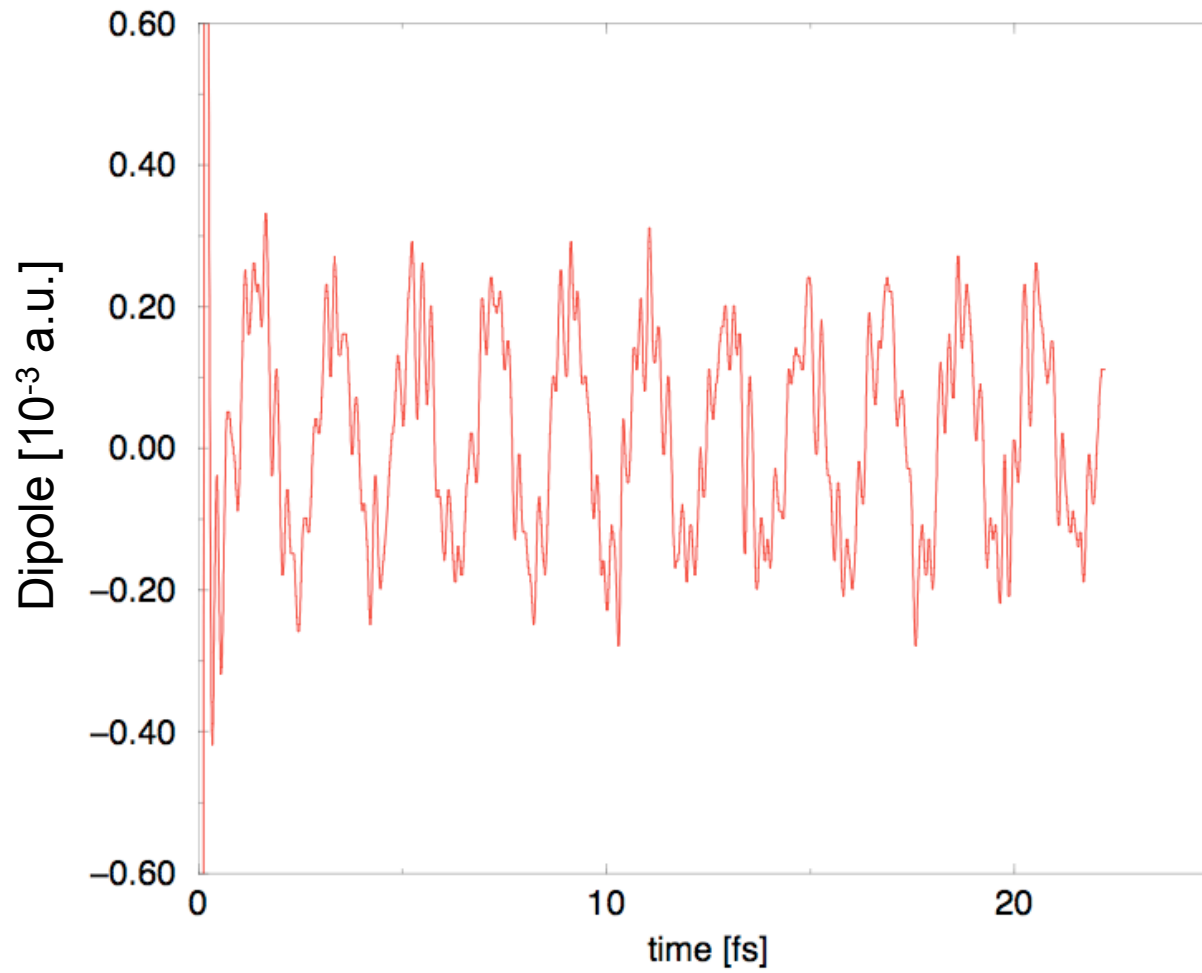
… and the resulting spectrum

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:

$$\omega\delta\psi_v^+(\boldsymbol{r}) = \left(H_{KS}^0 - \epsilon_v^0\right)\delta\psi_v^+ + \hat{P}_{\mathbf{c}}\left(\delta V_{SCF}^+(\boldsymbol{r}) + V_{pert}(\boldsymbol{r})\right)\psi_v^0(\boldsymbol{r})$$

$$-\omega\delta\psi_v^-(\boldsymbol{r}) = \left(H_{KS}^0 - \epsilon_v^0\right)\delta\psi_v^- + \hat{P}_{\mathbf{c}}\left(\delta V_{SCF}^-(\boldsymbol{r}) + V_{pert}(\boldsymbol{r})\right)\psi_v^0(\boldsymbol{r})$$

Now define the following linear combinations:

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

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

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

With the following definitions:

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

$$K \, |\boldsymbol{x}\rangle = \left\{ \left(H_{KS}^0 - \epsilon_i \right) x_i(\boldsymbol{r}) + \psi_i^0(\boldsymbol{r}) \sum_j \int d\boldsymbol{r}' \; f_{Hxc}(\boldsymbol{r}, \boldsymbol{r}') \psi_{i'}^0(\boldsymbol{r}') x_{i'}(\boldsymbol{r}') \right\}$$

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

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.)]

Advantages:

One obtains not only the frequency (and oscillator strength), but the fulll 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 fulll 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)

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 $\mathcal{E}_0 \delta(t)$.

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:

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

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

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

$$= 2 \left\langle a, 0 \,|\, x, y \right\rangle$$

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

Therefore:

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

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:

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

Build a Lanczos recursion chain:

$$\phi_{-1} = 0$$

$$\phi_0 = |v\rangle$$

$$b_{n+1}\phi_{n+1} = \left(H - a_n\right)\phi_n - b_n\phi_{n-1}$$

$$\langle\phi_{n+1}|\phi_{n+1}\rangle = 1$$

$$a_n = \langle\phi_n|H|\phi_n\rangle$$

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

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

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

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

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

Back to the calculation of spectra:

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

Therefore:

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

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!

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

$$= \cfrac{1}{\omega - a_1 + b_2 \cfrac{1}{\omega - a_2 + \cdots} c_2}$$

How does it work?
Benzene spectrum

Plum: 1000

Red: 2000

Green: 3000
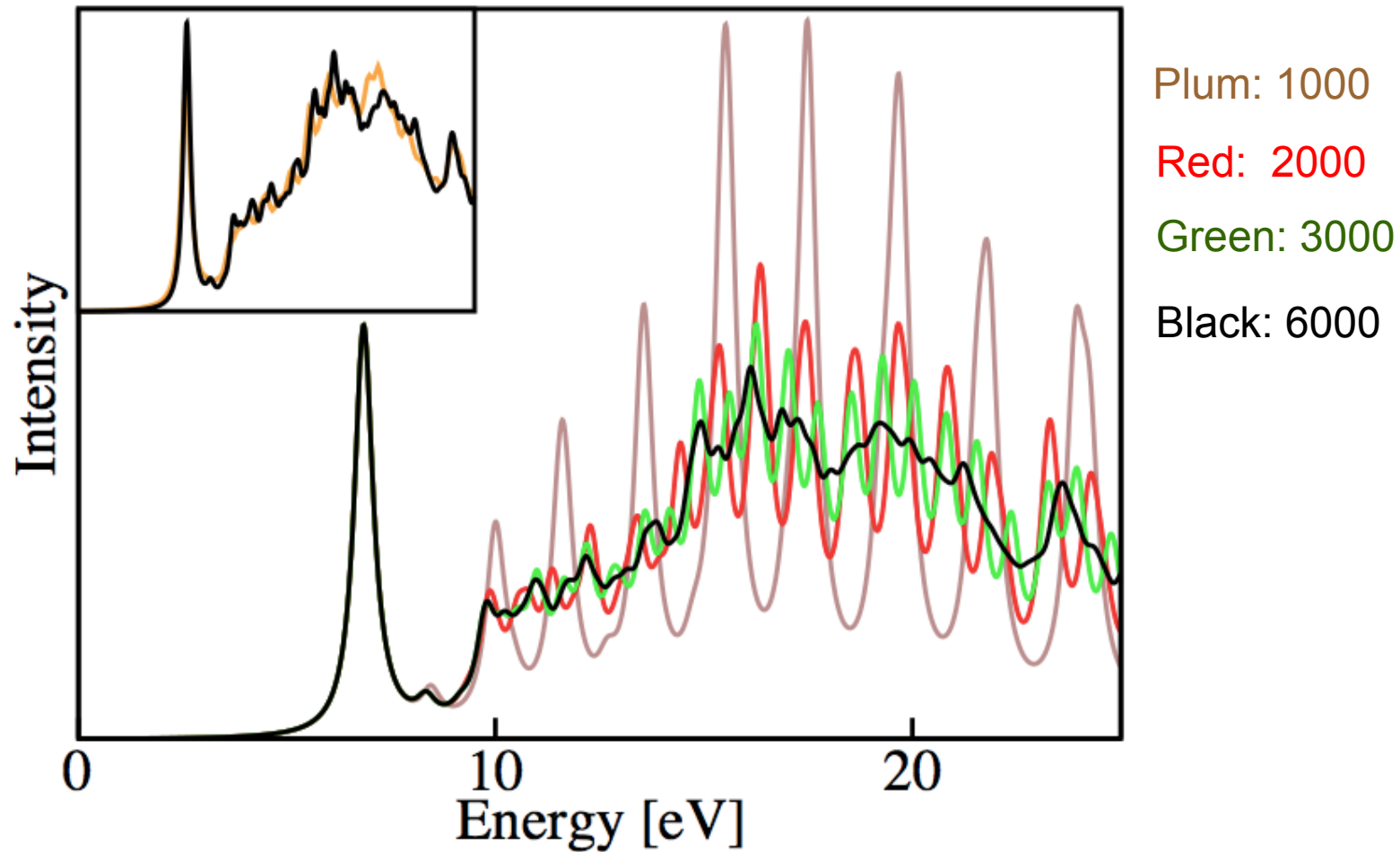
Black: 6000
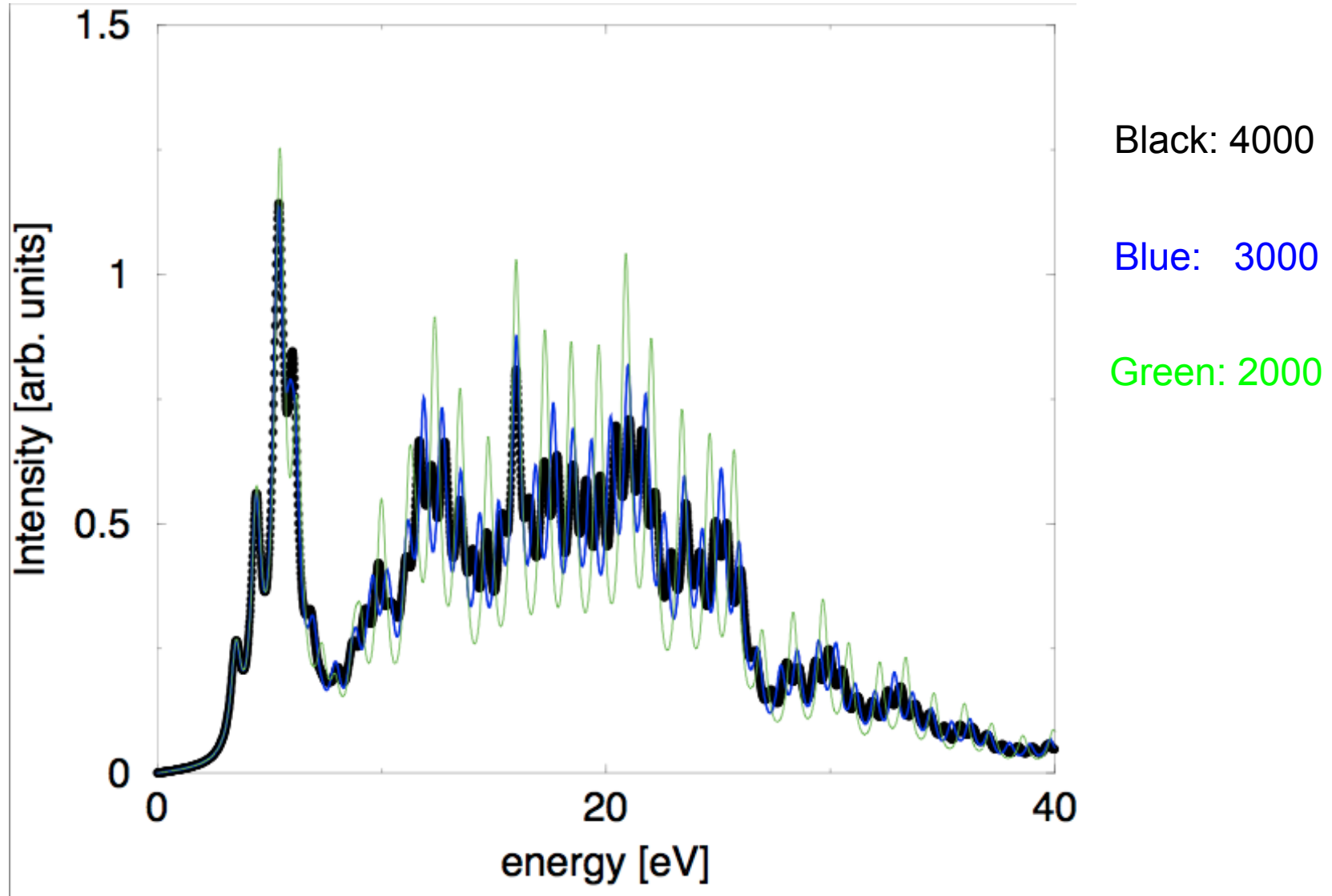
Spectrum of C_{60}: Ultrasoft pseudopotenitals
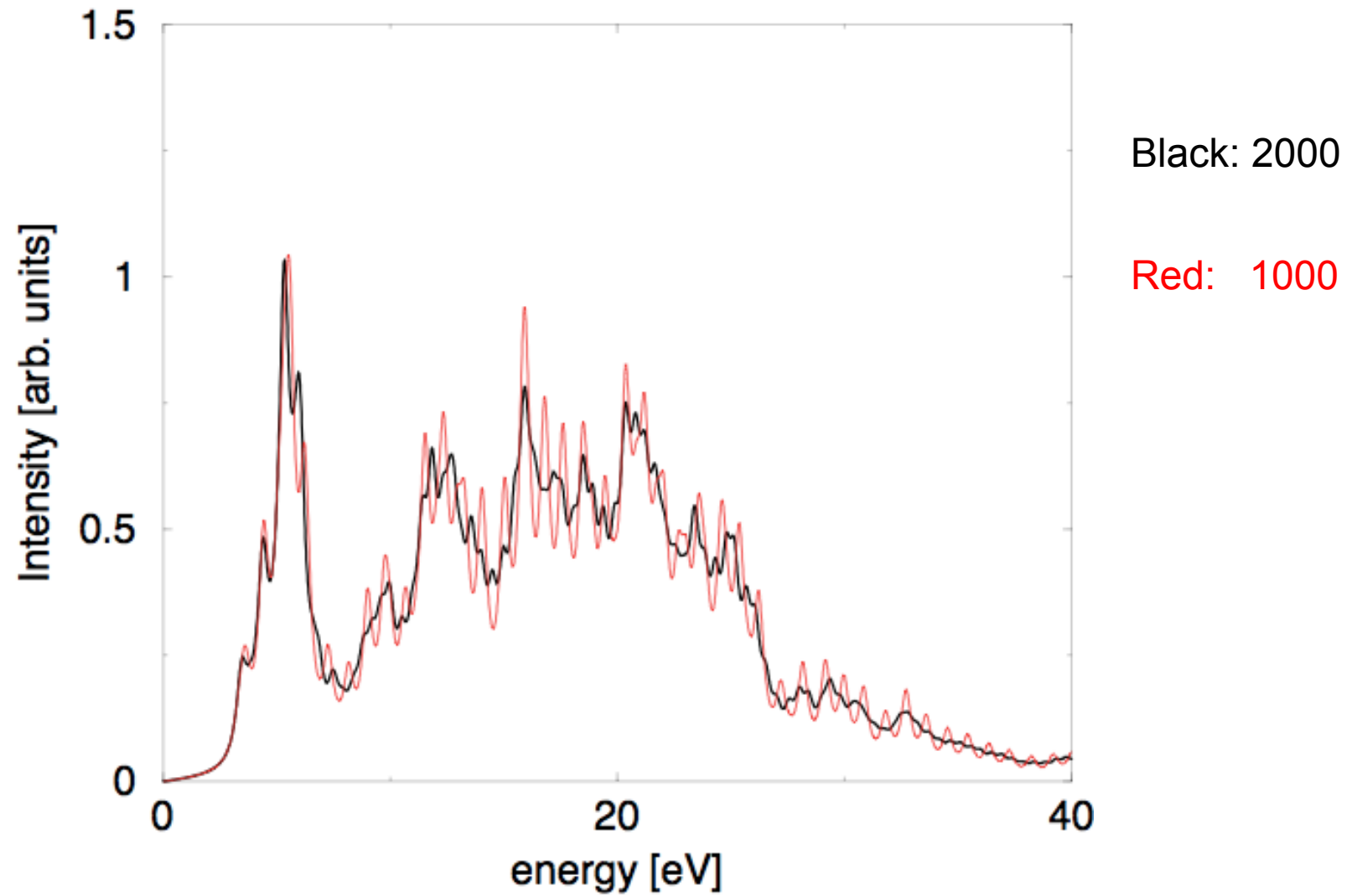
Speeding up convergence:
Looking at the Lanczos coefficients
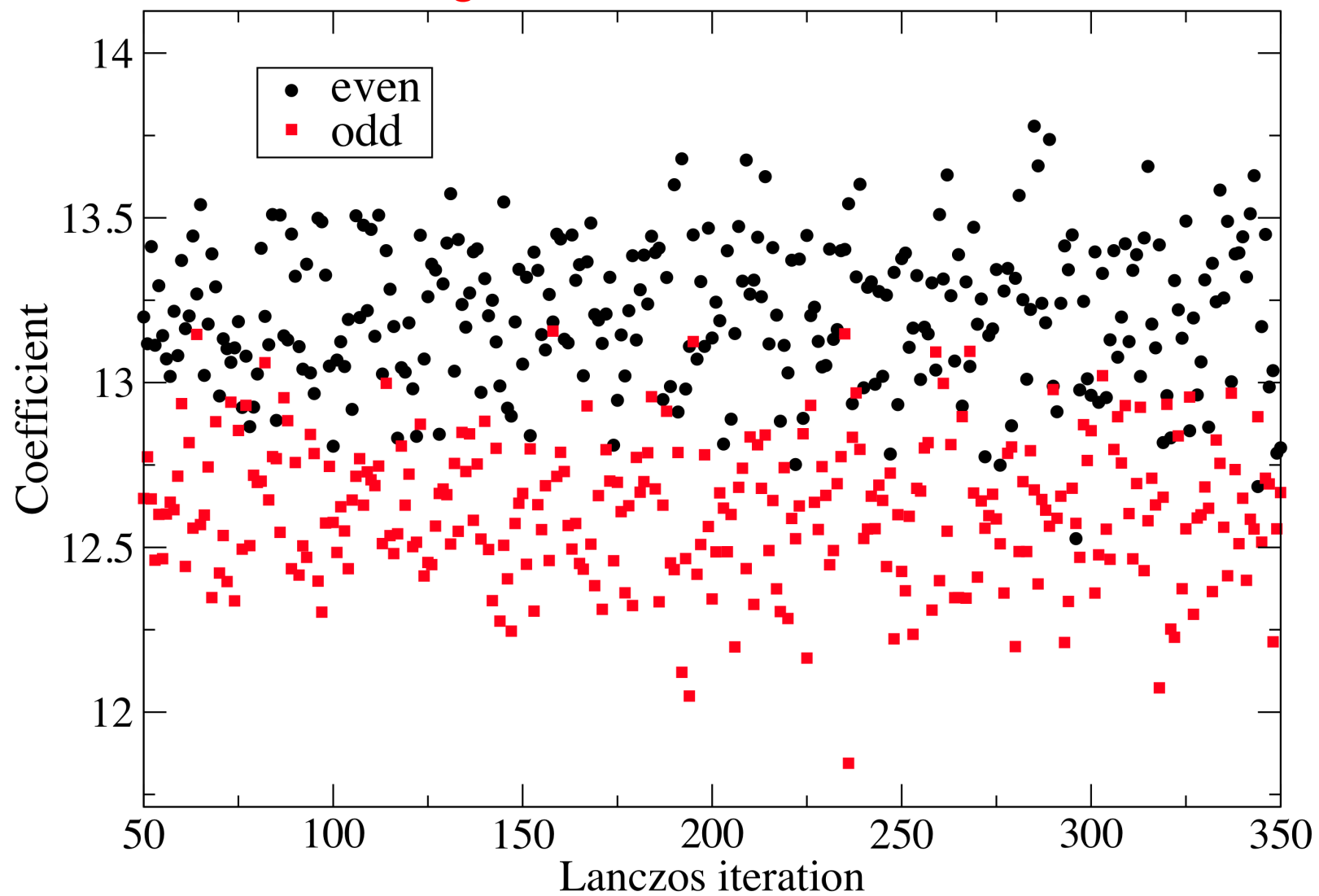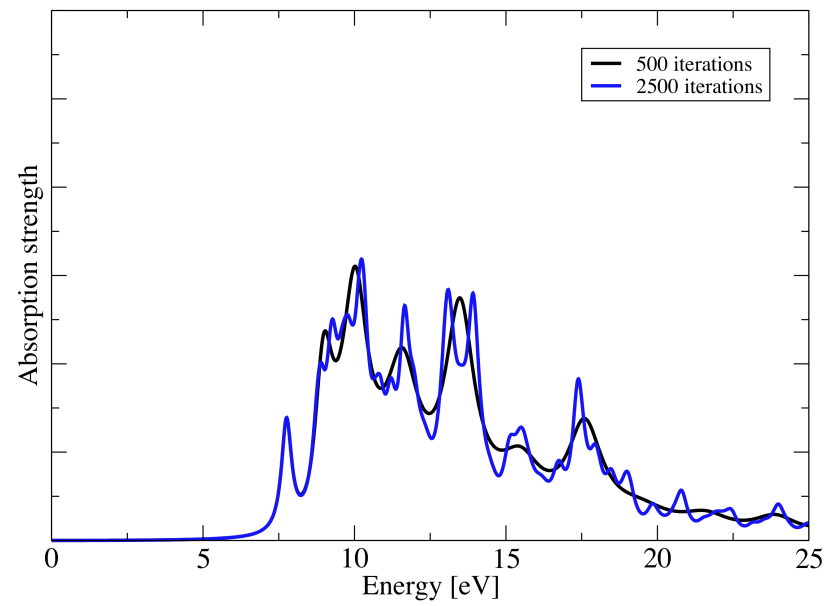
Effect of the terminator:
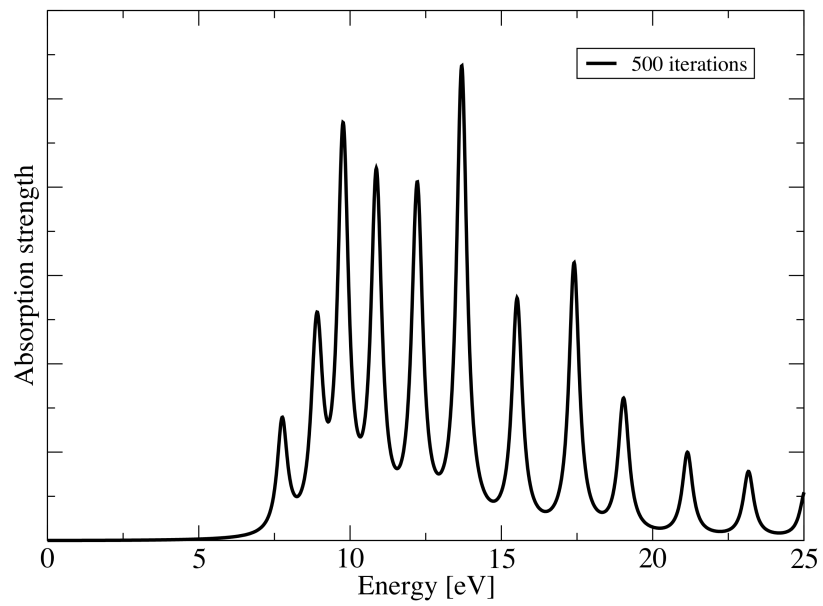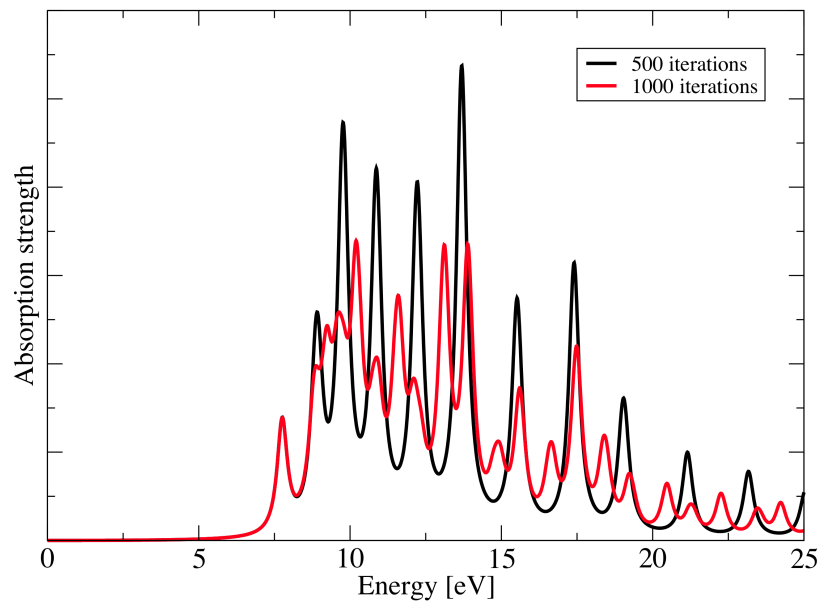
No terminator:

Effect of the terminator:

No terminator:

Effect of the terminator:
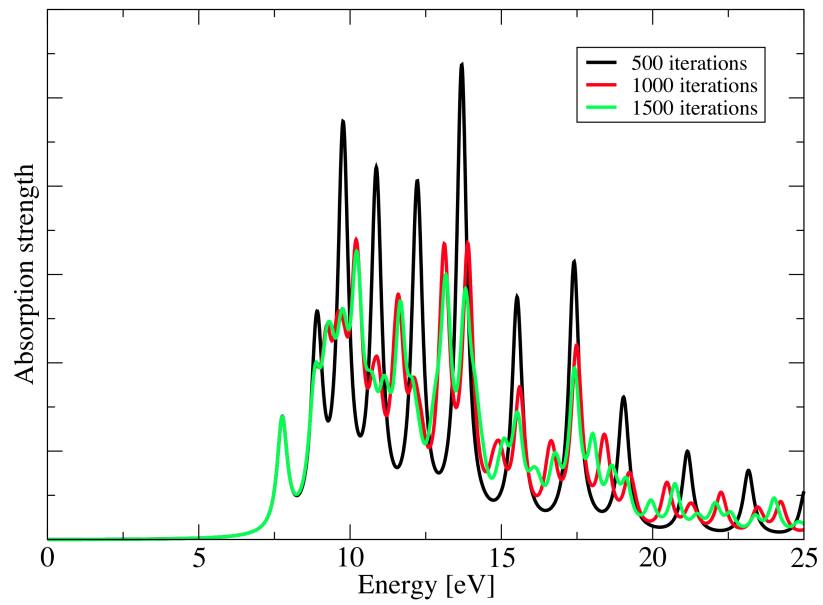
No terminator:

Effect of the terminator:
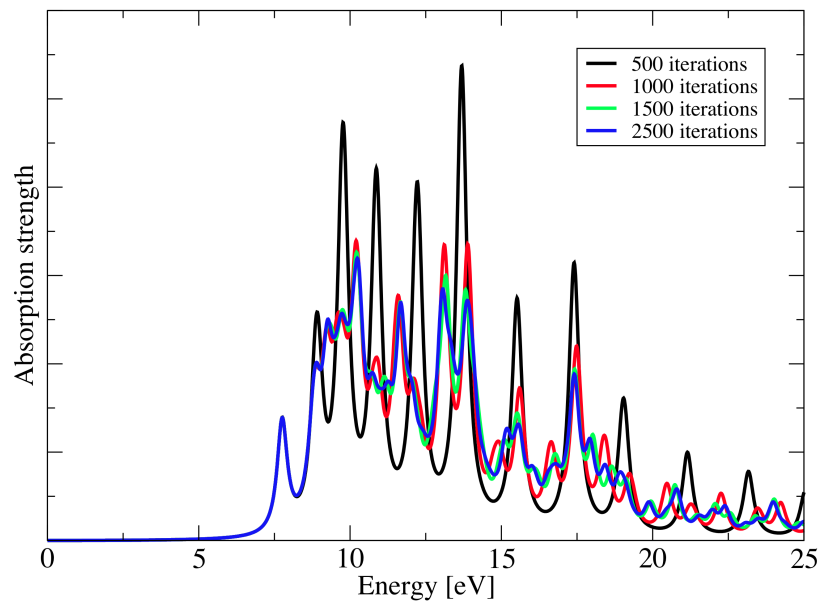
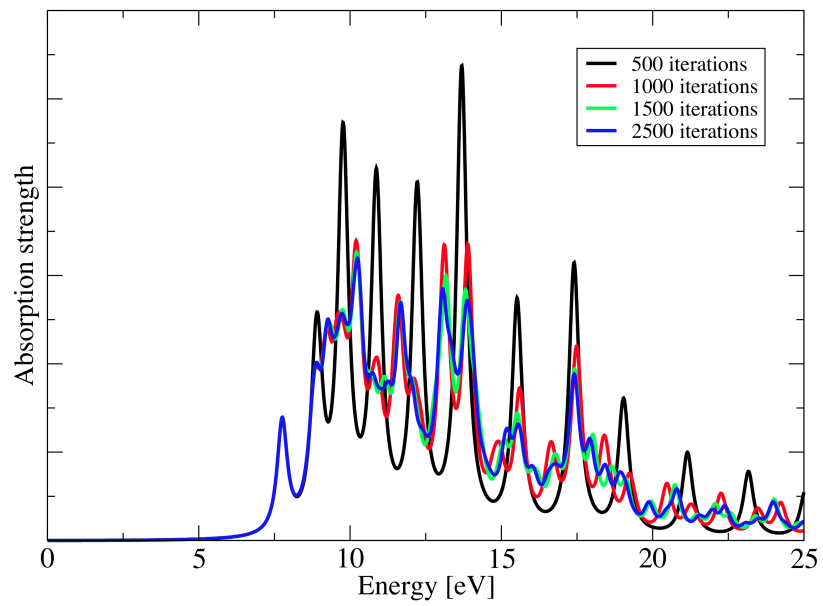No terminator:
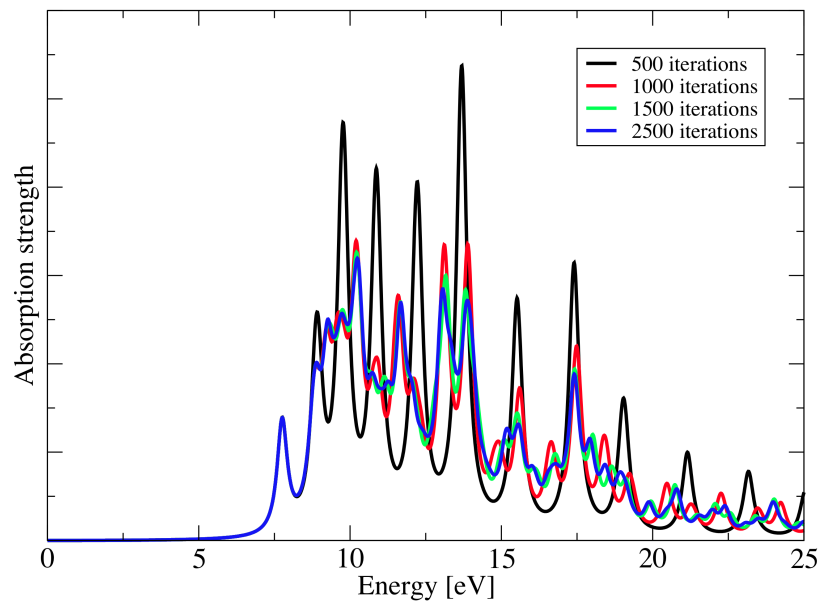
Effect of the terminator:

No terminator:

Terminator:

Effect of the terminator:

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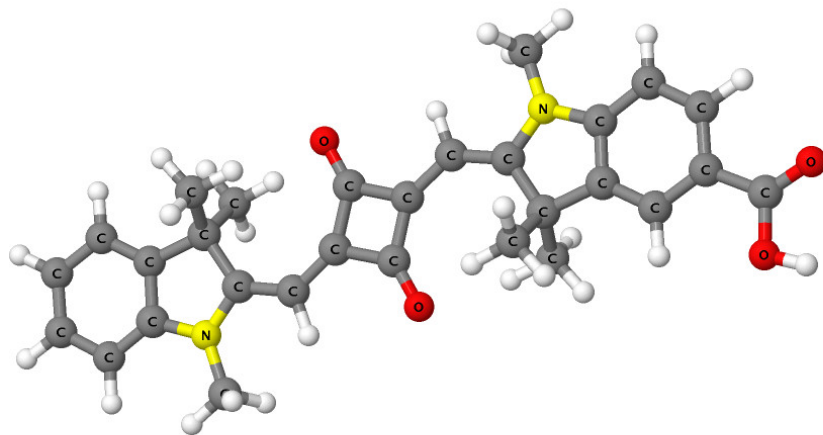
Terminator:
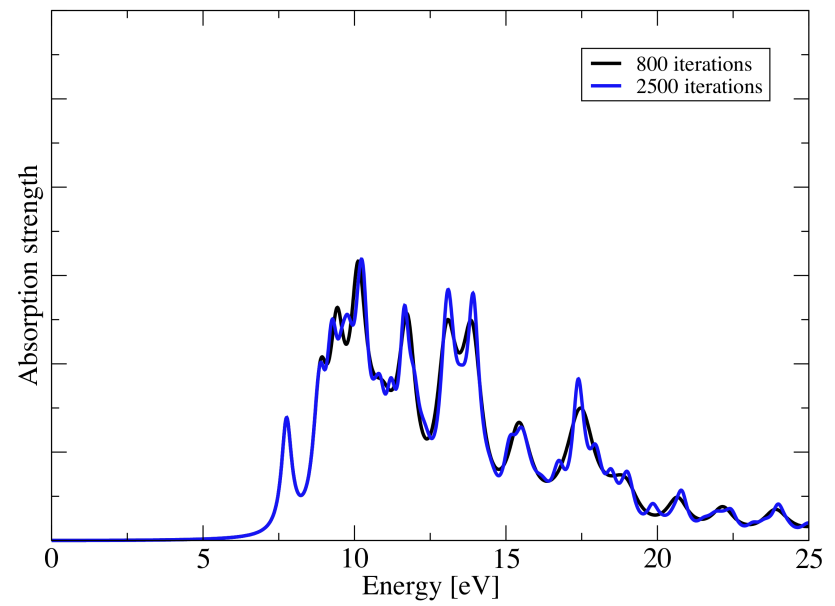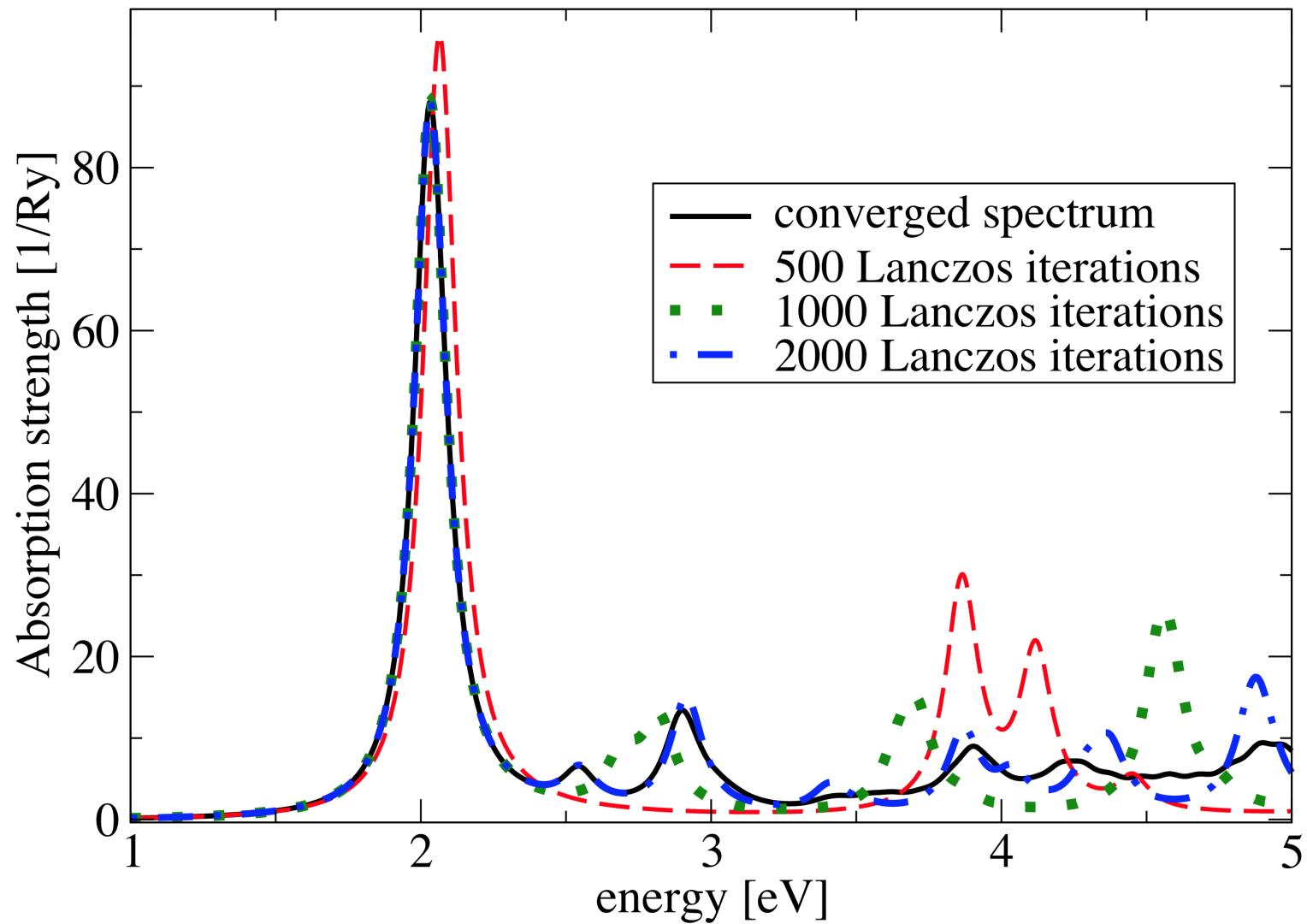
Example of a squaraine dye:

Can we analyze given features of the spectrum in terms of the electronic structure?
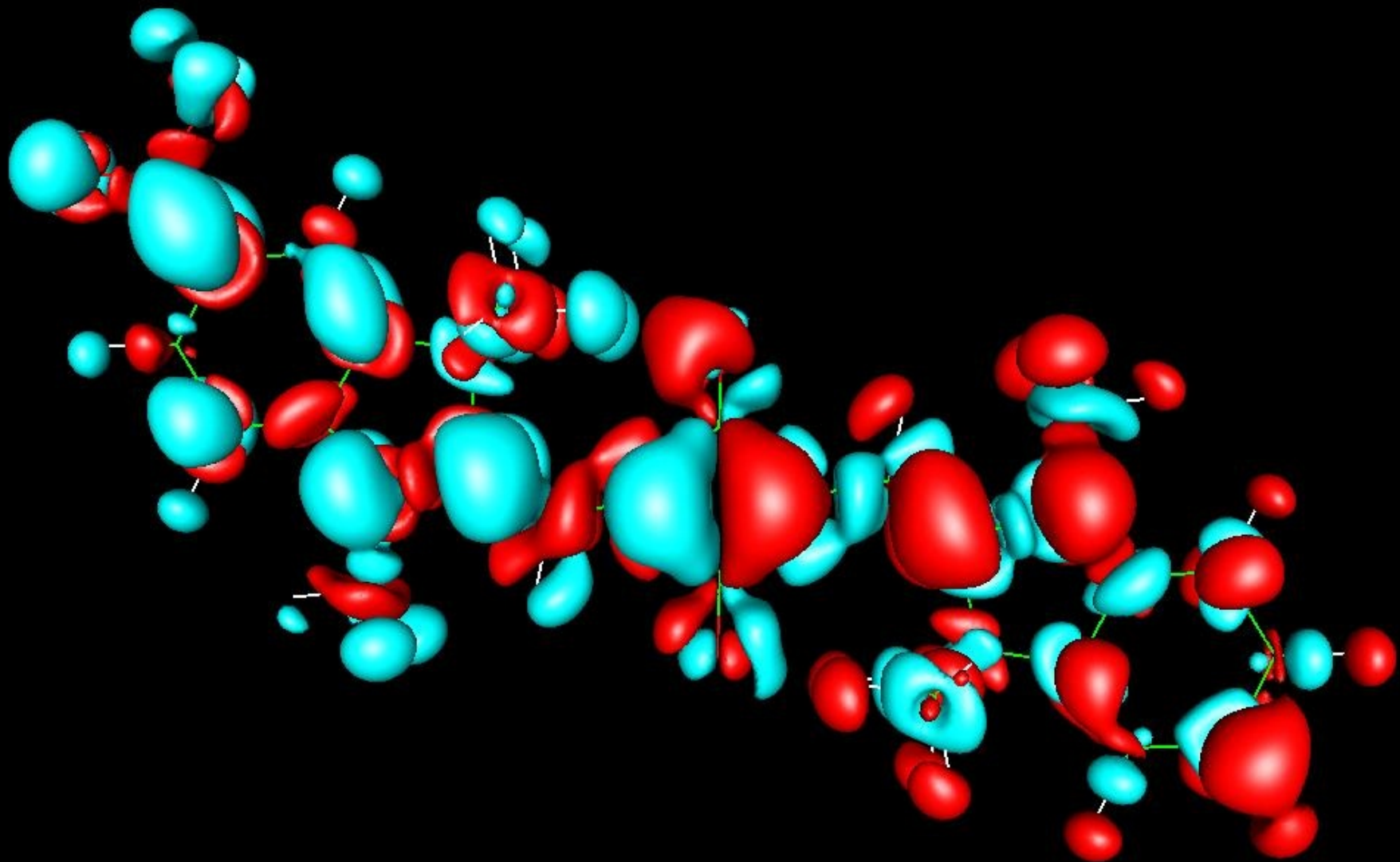
YES!

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

Convergence of the TDDFPT spectrum

Isolated squaraine molecule

Charge response at main absorption peak:

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

Thanks to:

- Stefano Baroni (SISSA & DEMOCRITOS, Trieste)

- Brent Walker (University College, London)

- Dario Rocca (UC Davis)

- Filippo De Angelis (Perugia)

- O. Baris Malcioglu (Liège)

To know more:

- Phys. Rev. Lett. **96**, 113001 (2006)
- J. Chem. Phys. **127**, 164106 (2007)
- J. Chem. Phys. **128**, 154105 (2008)
- Chem. Phys. Lett. **475**, 49 (2009)