**2145-31**

**Spring College on Computational Nanoscience**

*17 - 28 May 2010*

**A Computationally Efficient Approach to the Computation of TDDFT Spectra in Complex Systems**
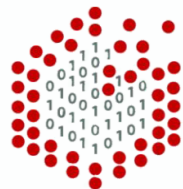
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# A computationally efficient approach to the calculation of TDDFT spectra in complex systems

## Ralph Gebauer



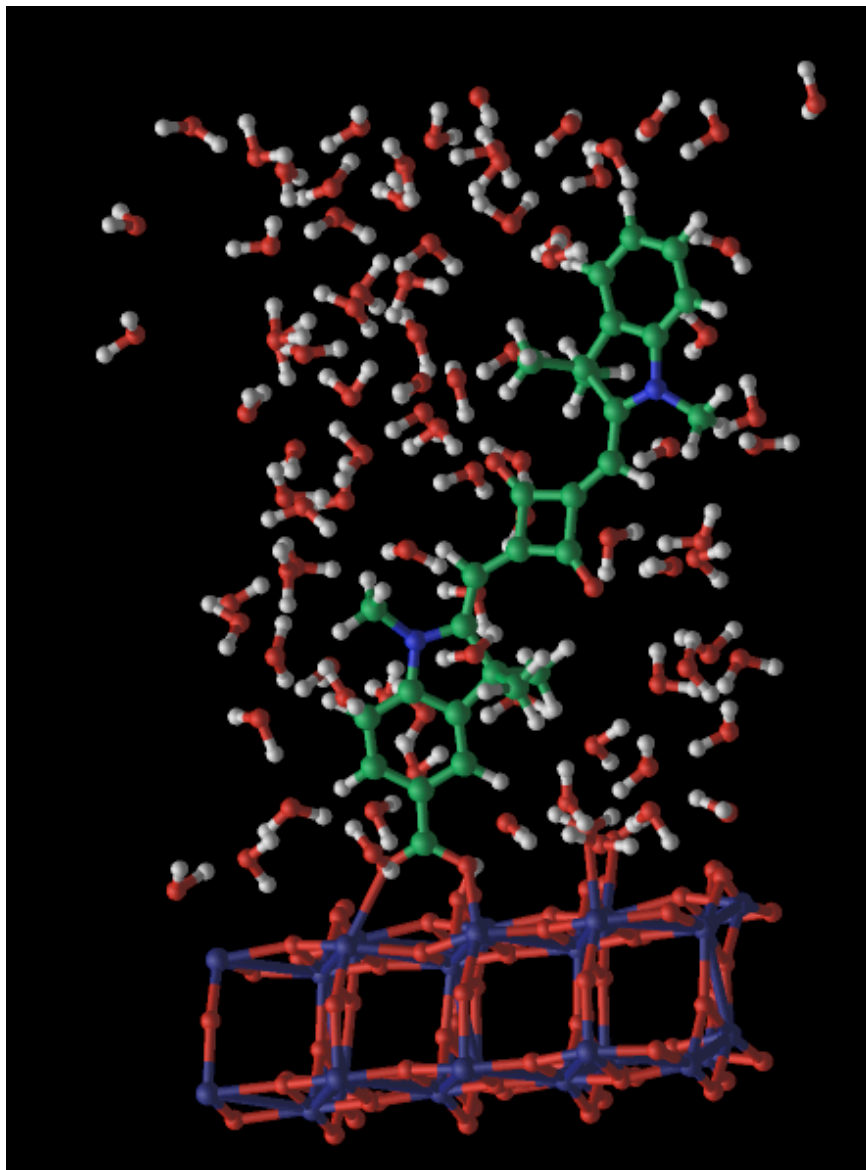Monday, May 24th, 2010

# <u>Overview</u>

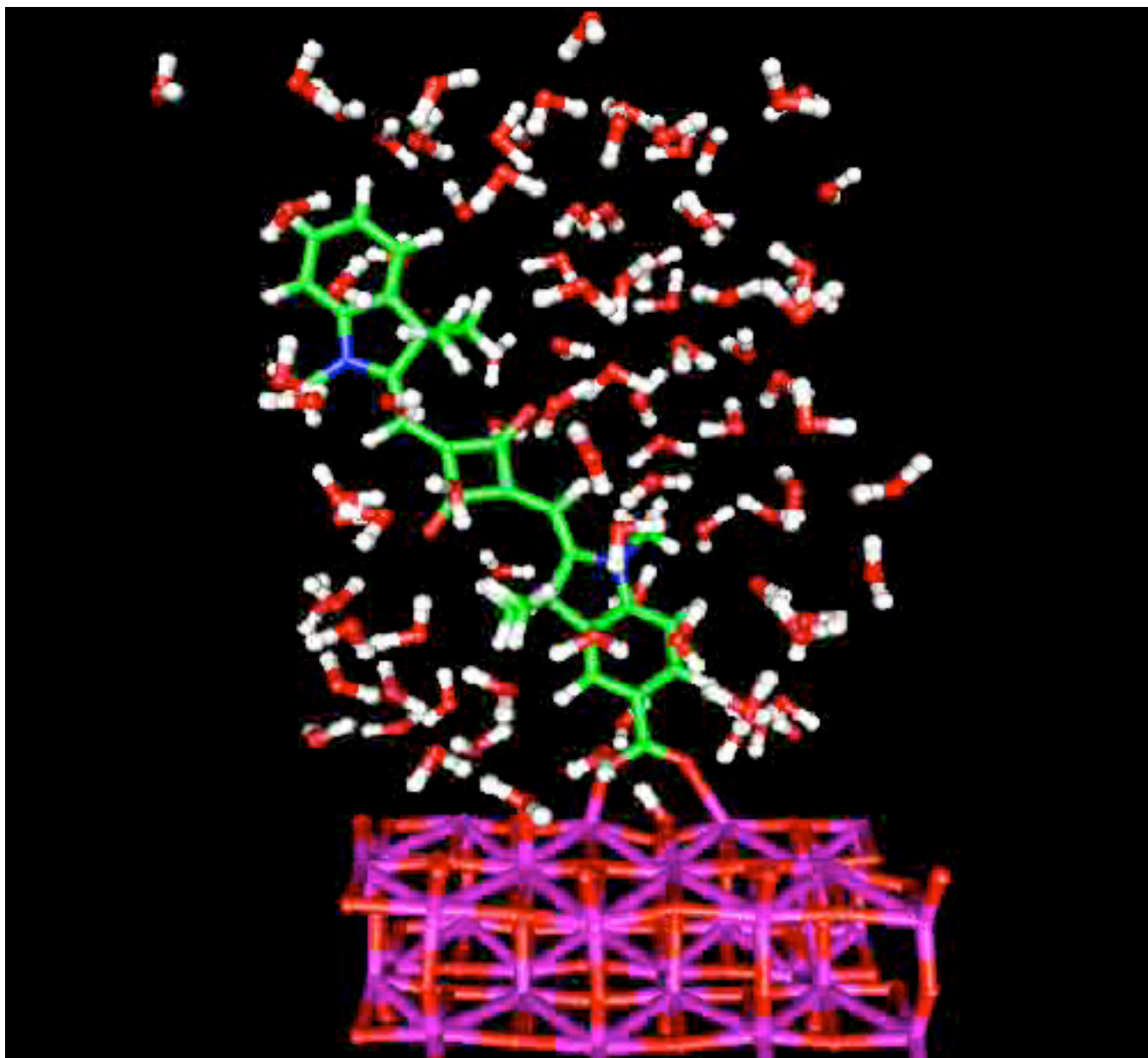Large scale application of TDDFT

- Combined MD and TDDFT study of a photovoltaic cell

Linear Response TDDFT in the frequency domain

- The basic equations

- How they are commonly solved (advantages/disadvantages)

- Using Lanczos recursions

- Some examples

# 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

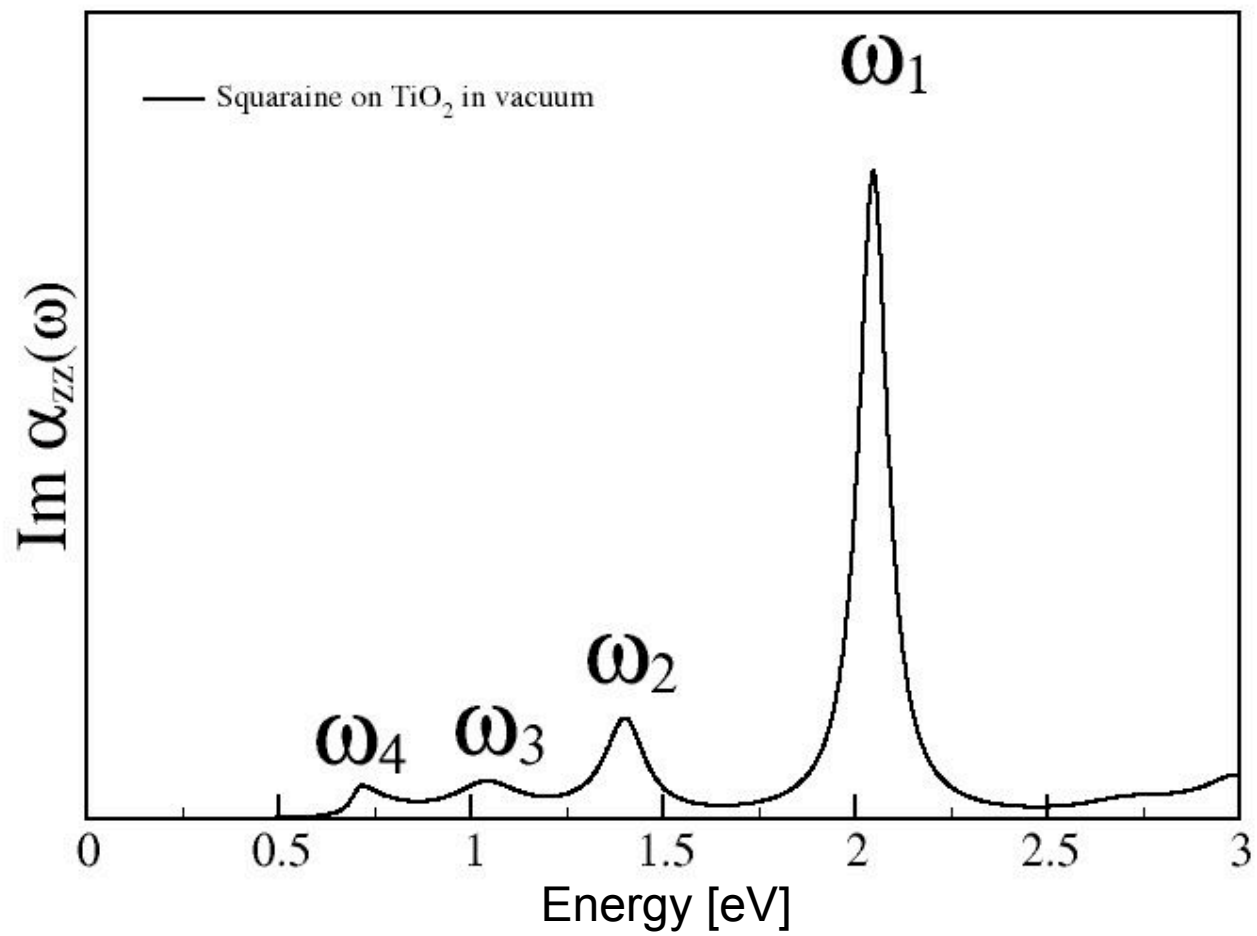TDDFT calculation of optical spectra and related quantities

Various challenges:

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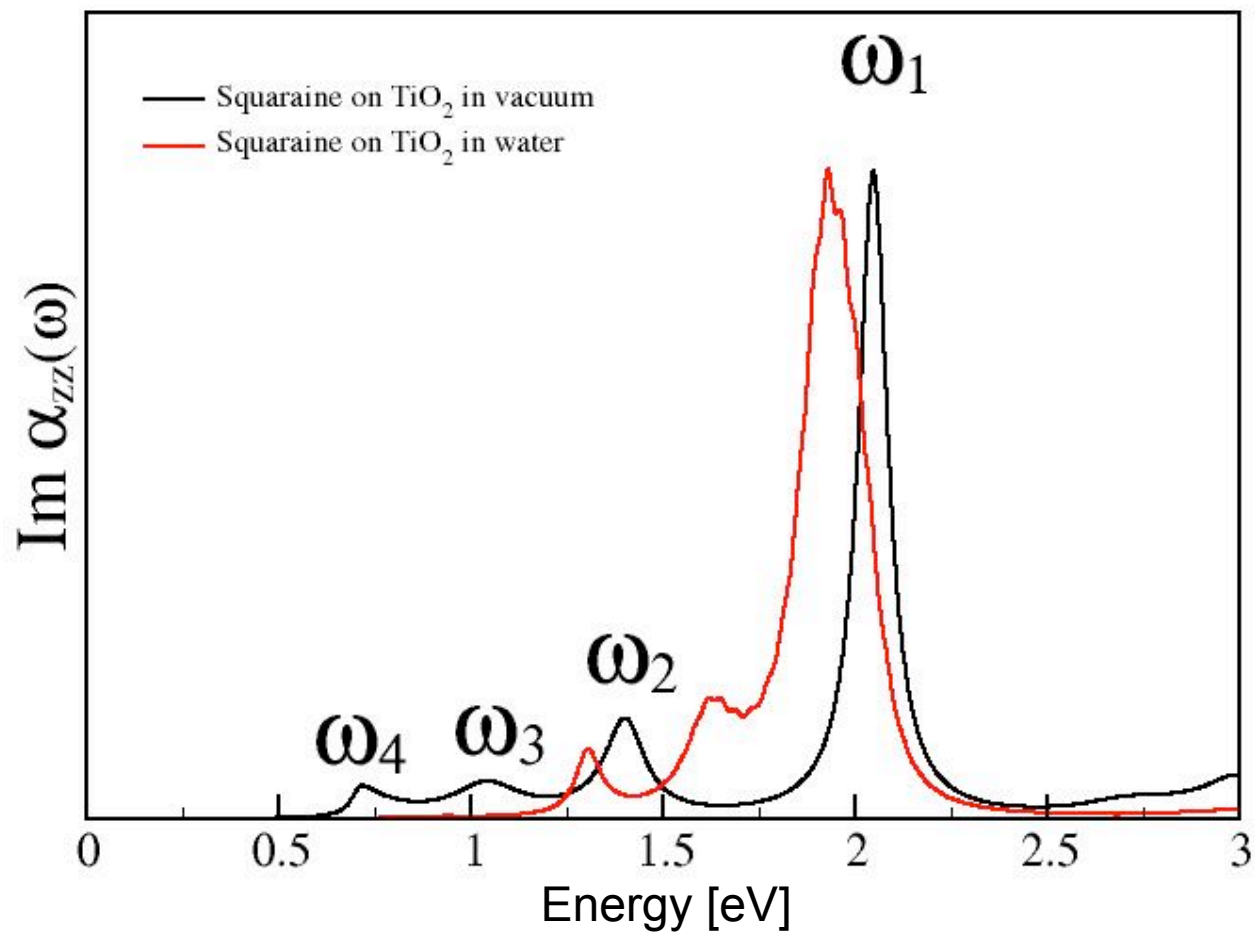- Many excited states in spectral region

Computational tool:

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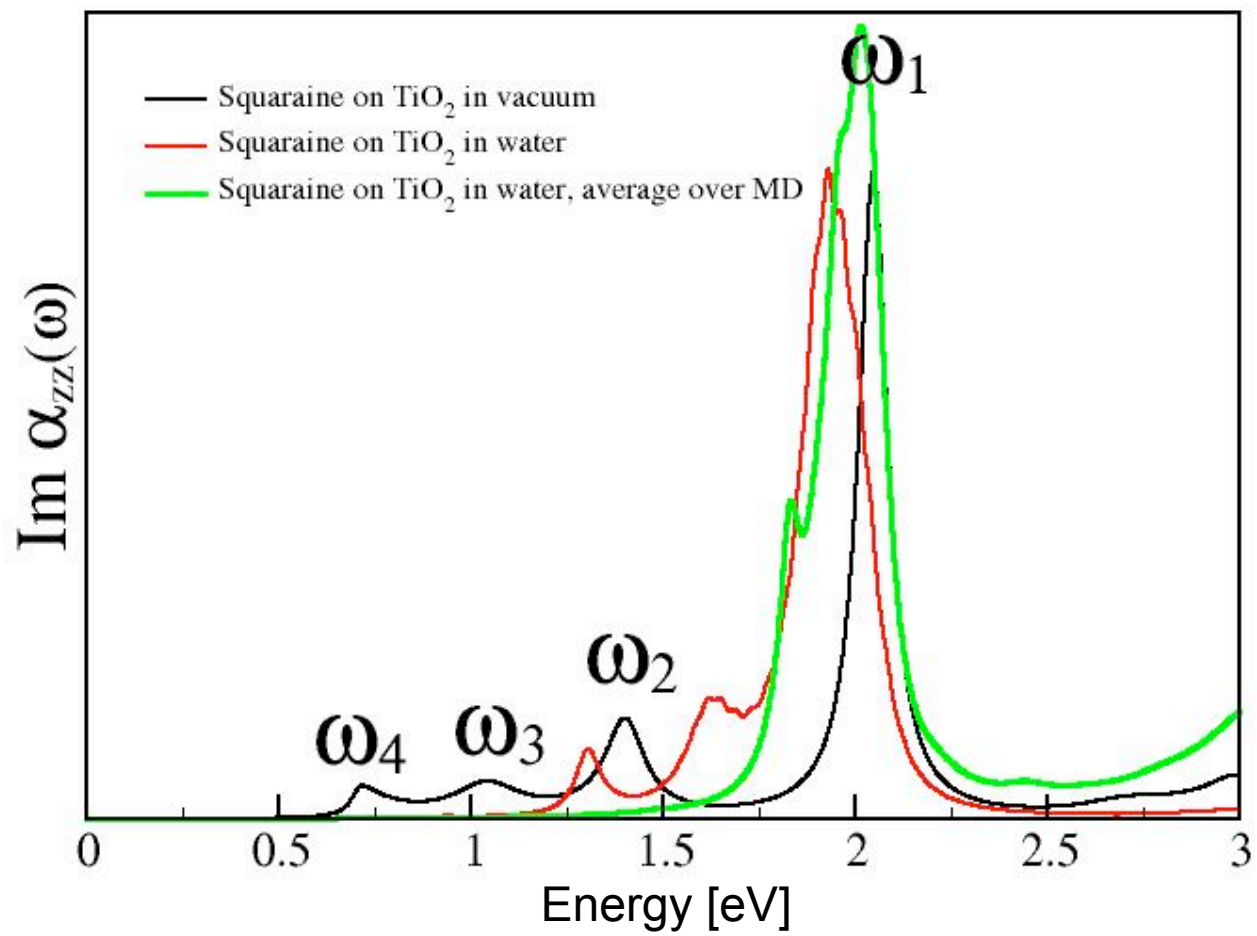- Here: Adiabatic GGA functional
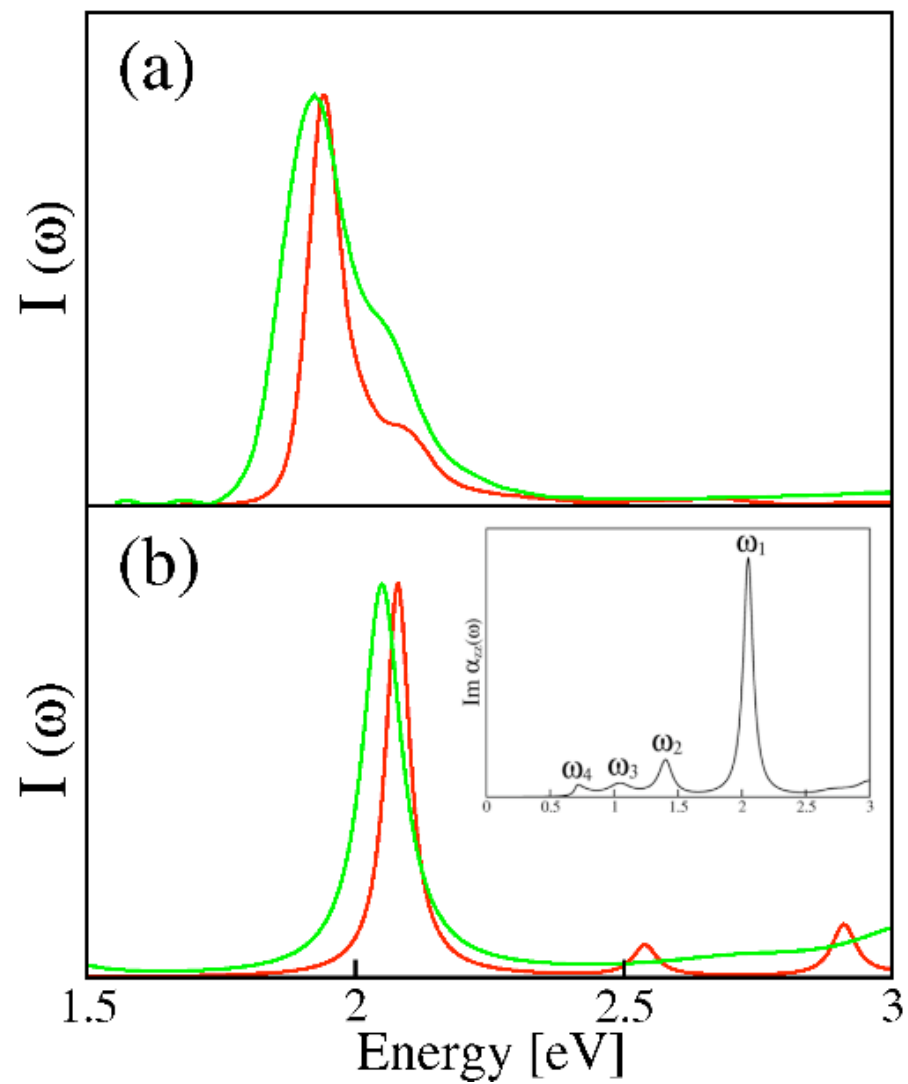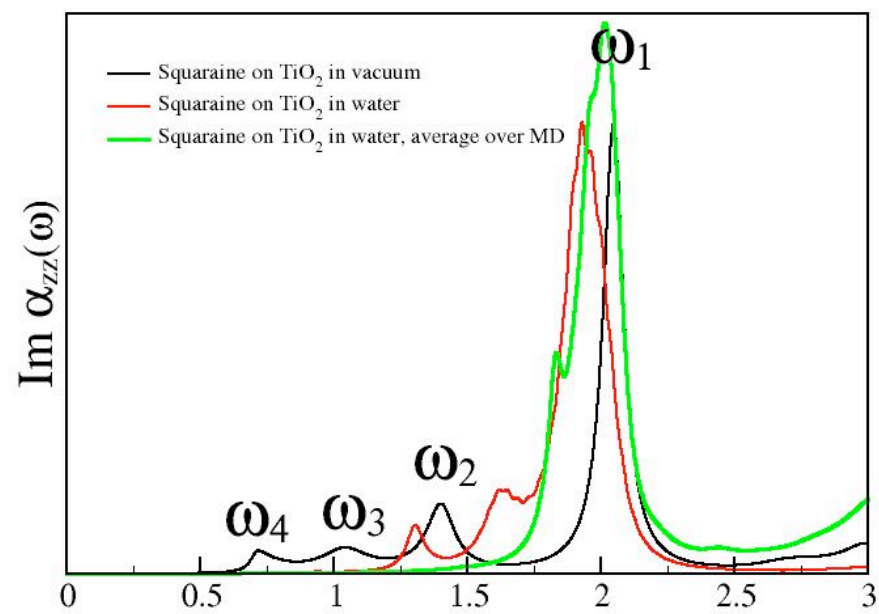
Back to the optical spectra

# 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:

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

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

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

With the following definitions:

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

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

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

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

## Standard way to proceed:

• 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)

# 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 $\alpha(t)$ 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:

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

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

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

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

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

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

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

Therefore:

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

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:

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

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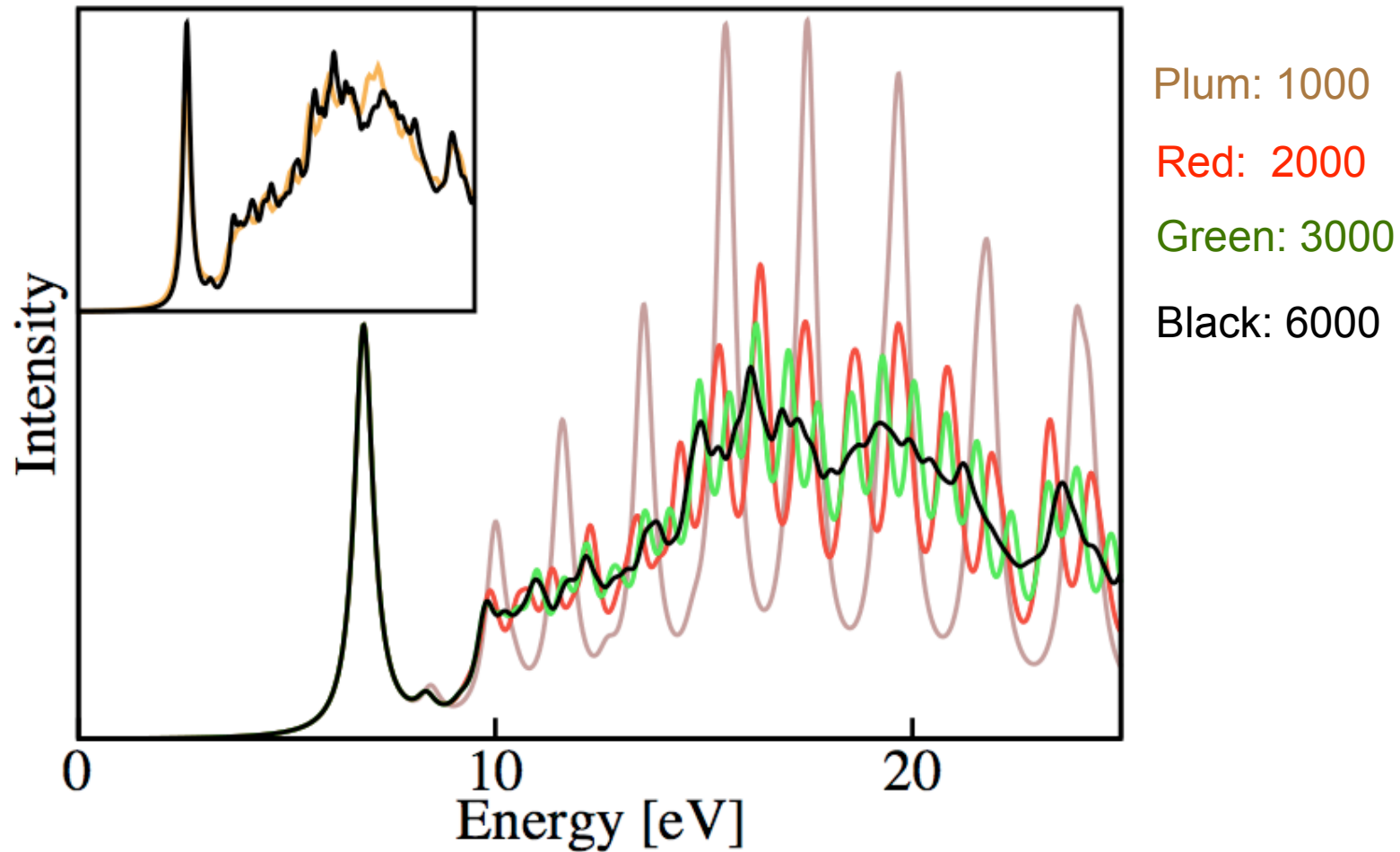
$$H = \begin{pmatrix} a_0 & b_1 & 0 & \cdots & 0 \\ b_1 & a_1 & b_2 & 0 & \vdots \\ 0 & b_2 & a_2 & \ddots & 0 \\ \vdots & 0 & \ddots & \ddots & b_n \\ 0 & \cdots & 0 & b_n & a_n \end{pmatrix}$$

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

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

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

# Back to the calculation of spectra:

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

Therefore:

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

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!

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

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

# How does it work?
## Benzene spectrum



Plum: 1000

Red: 2000

Green: 3000

Black: 6000

# Spectrum of C$_{60}$



Black: 4000

Blue:  3000
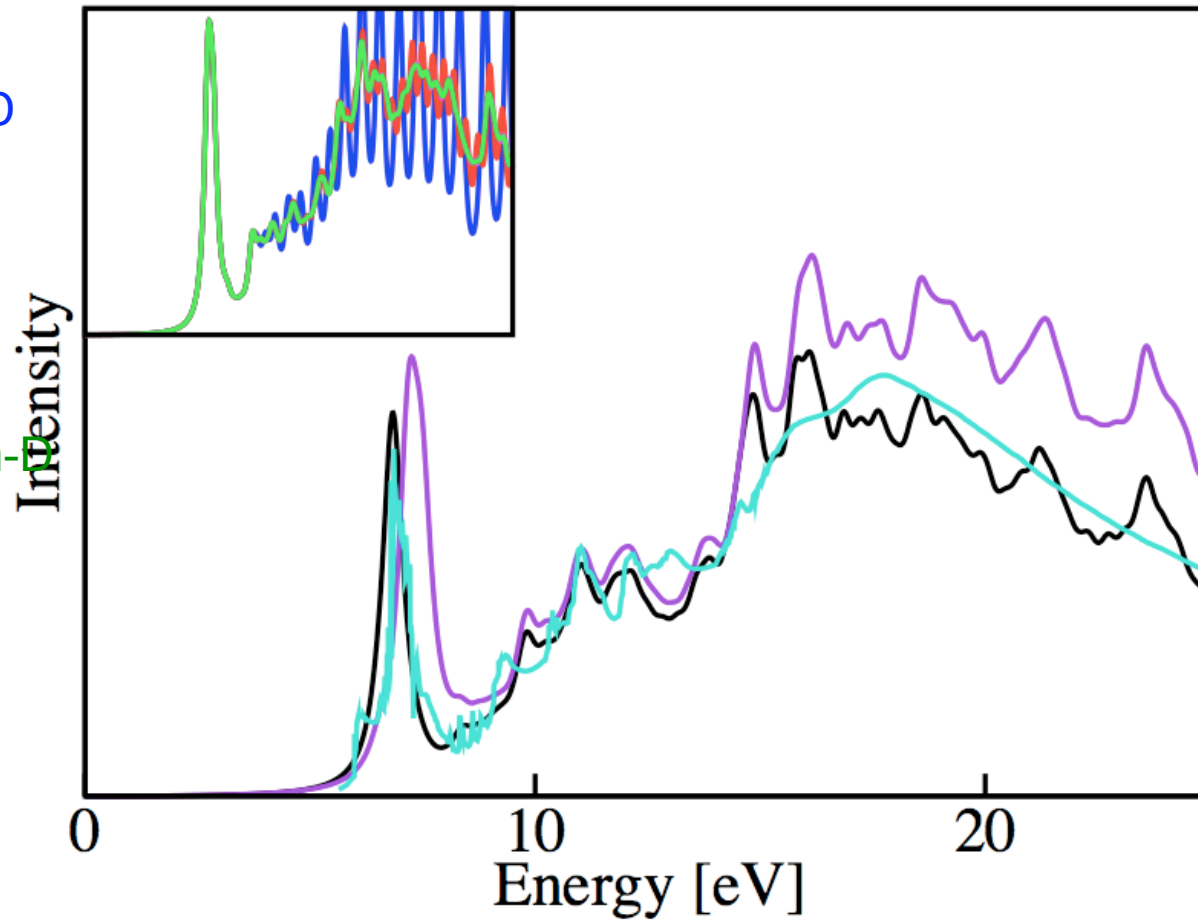
Green: 2000
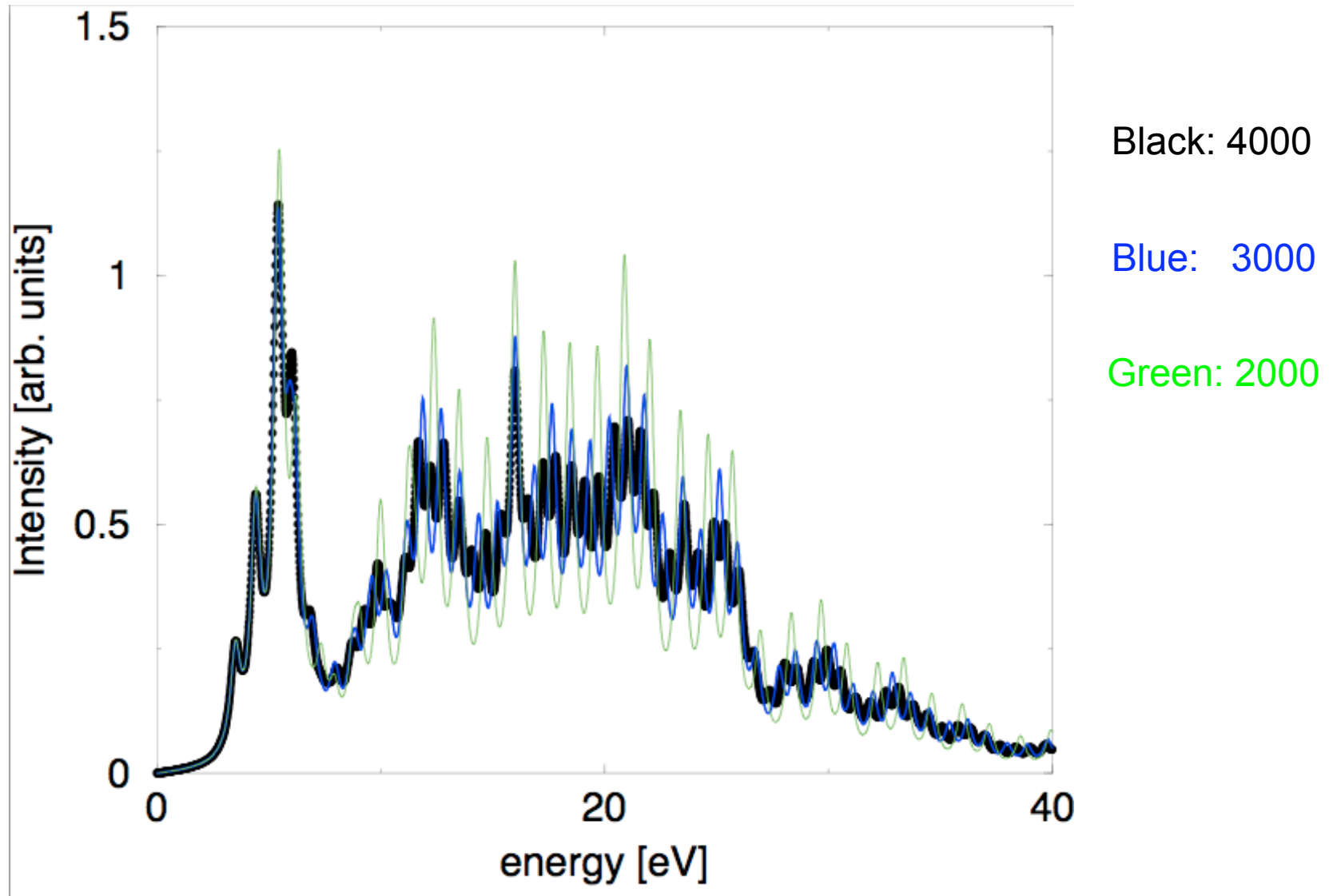
# Spectrum of $C_{60}$: Ultrasoft pseudopotenitals
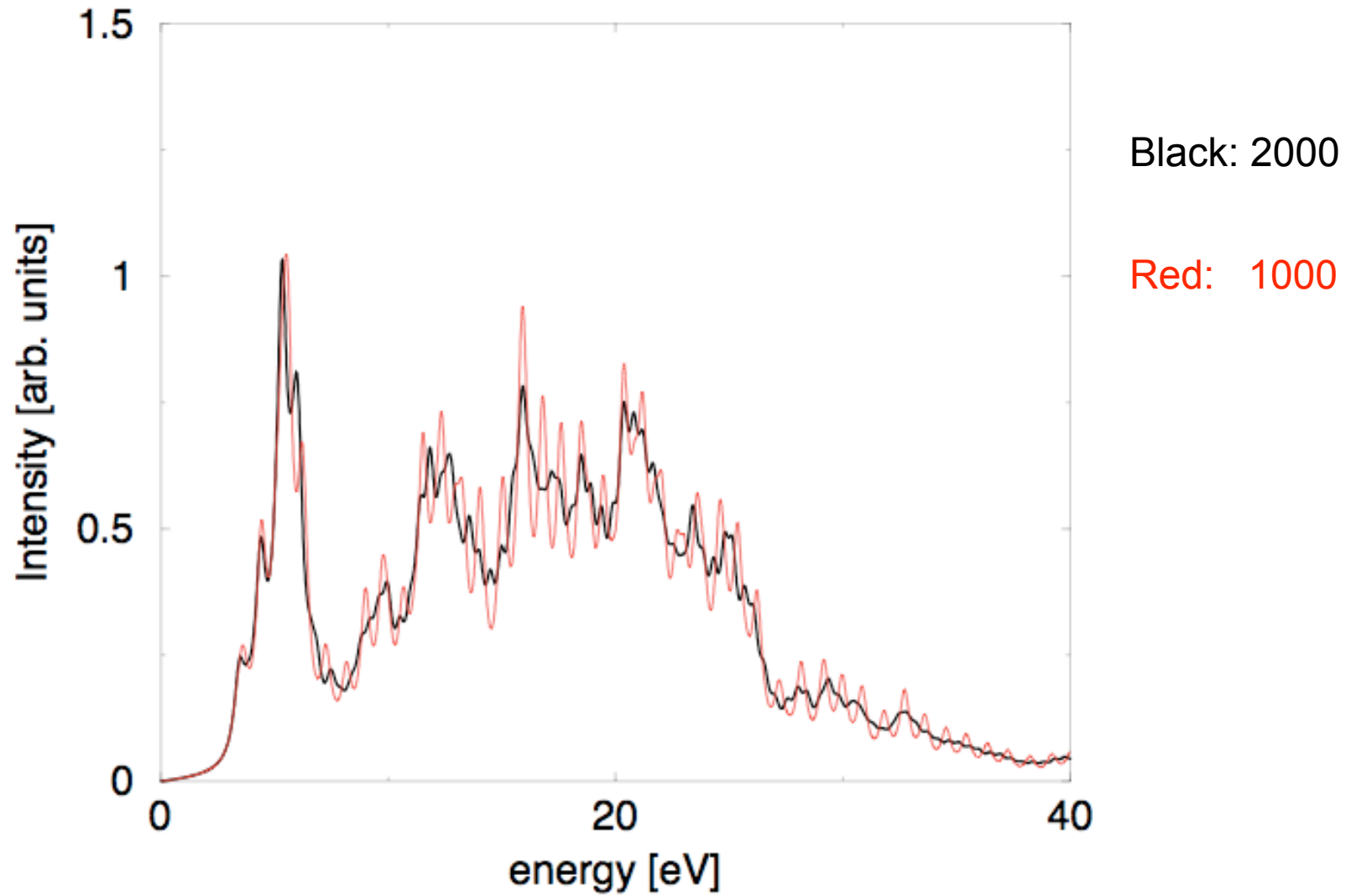
# Speeding up the convergence
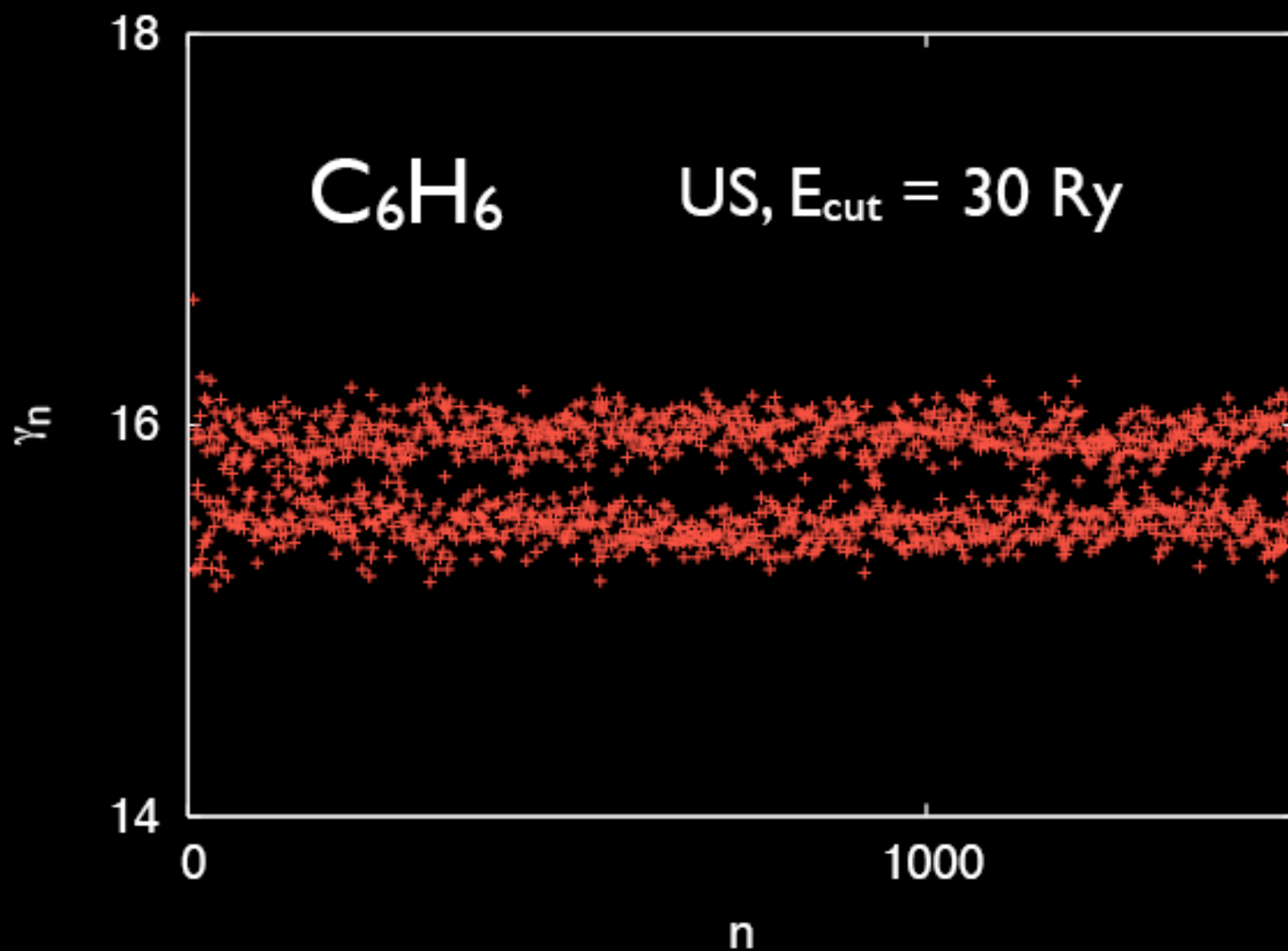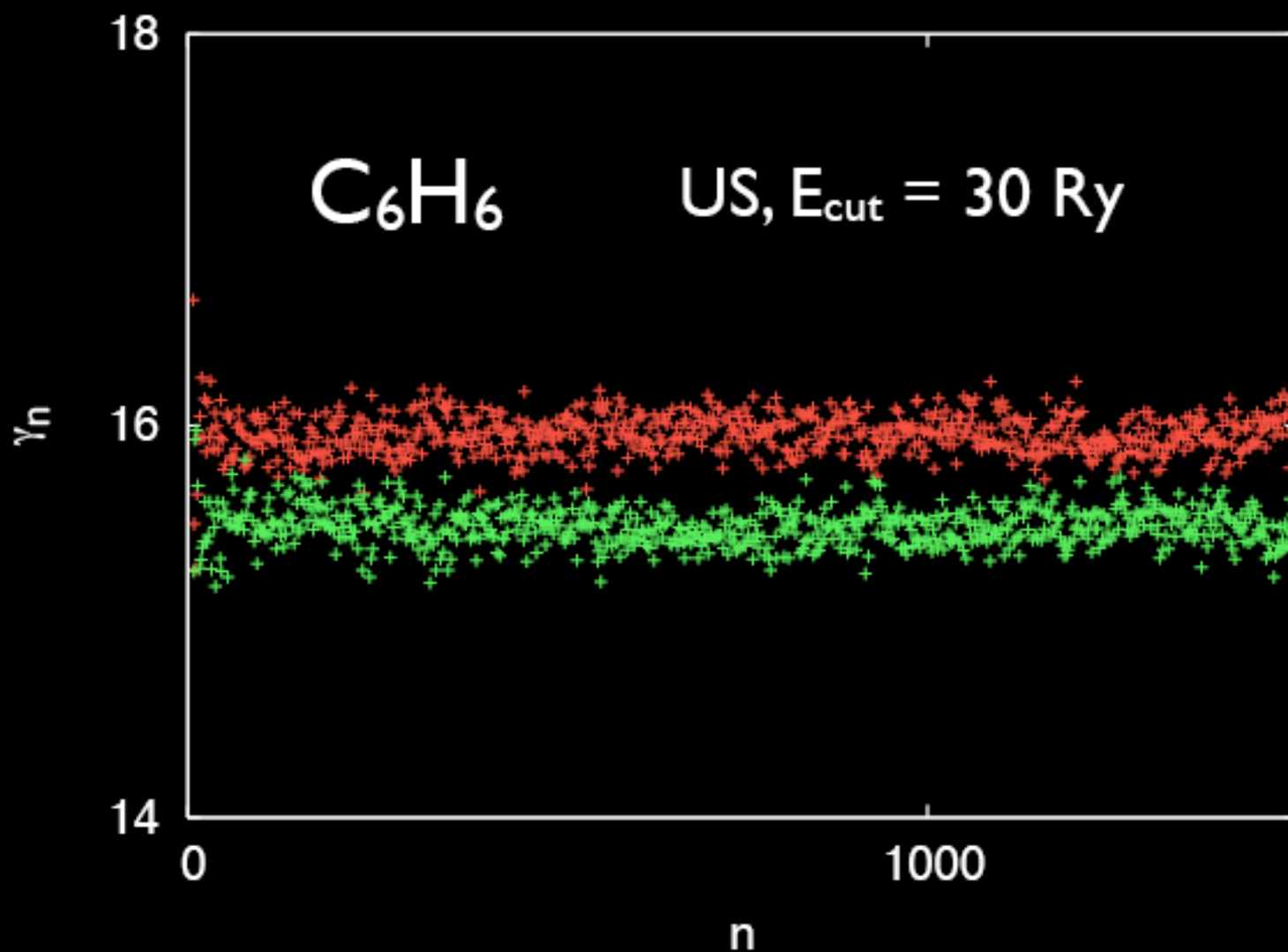
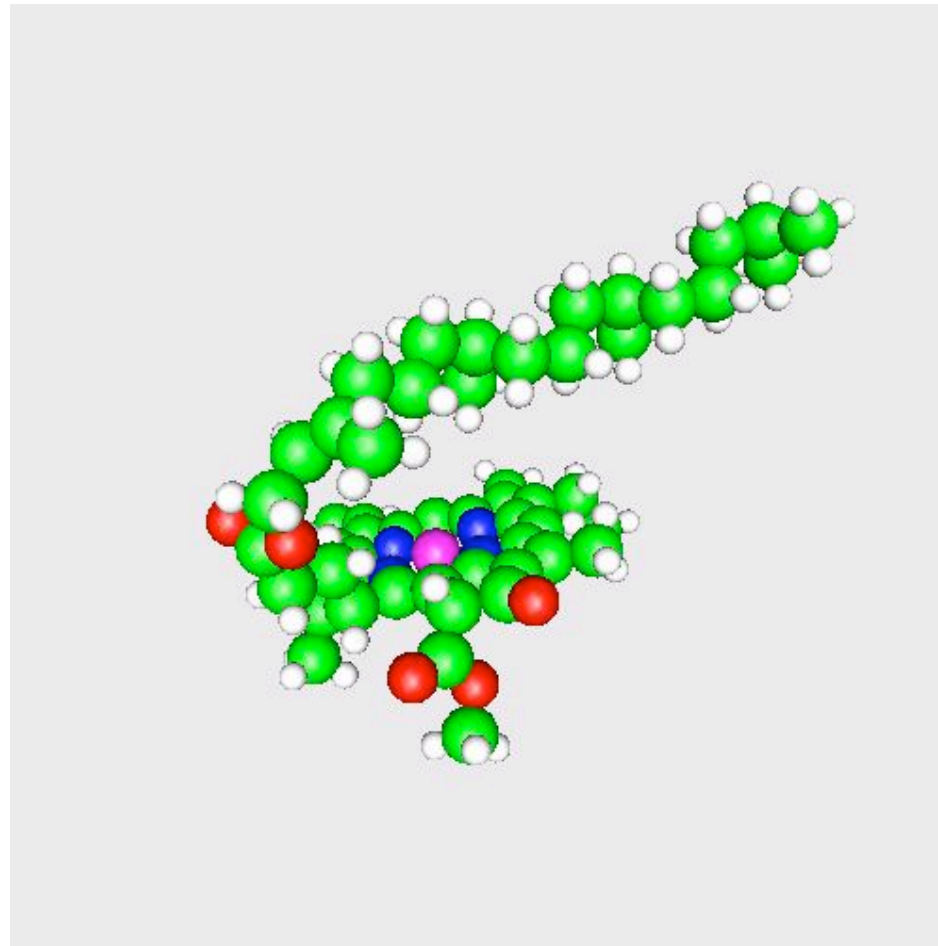# Speeding up the convergence
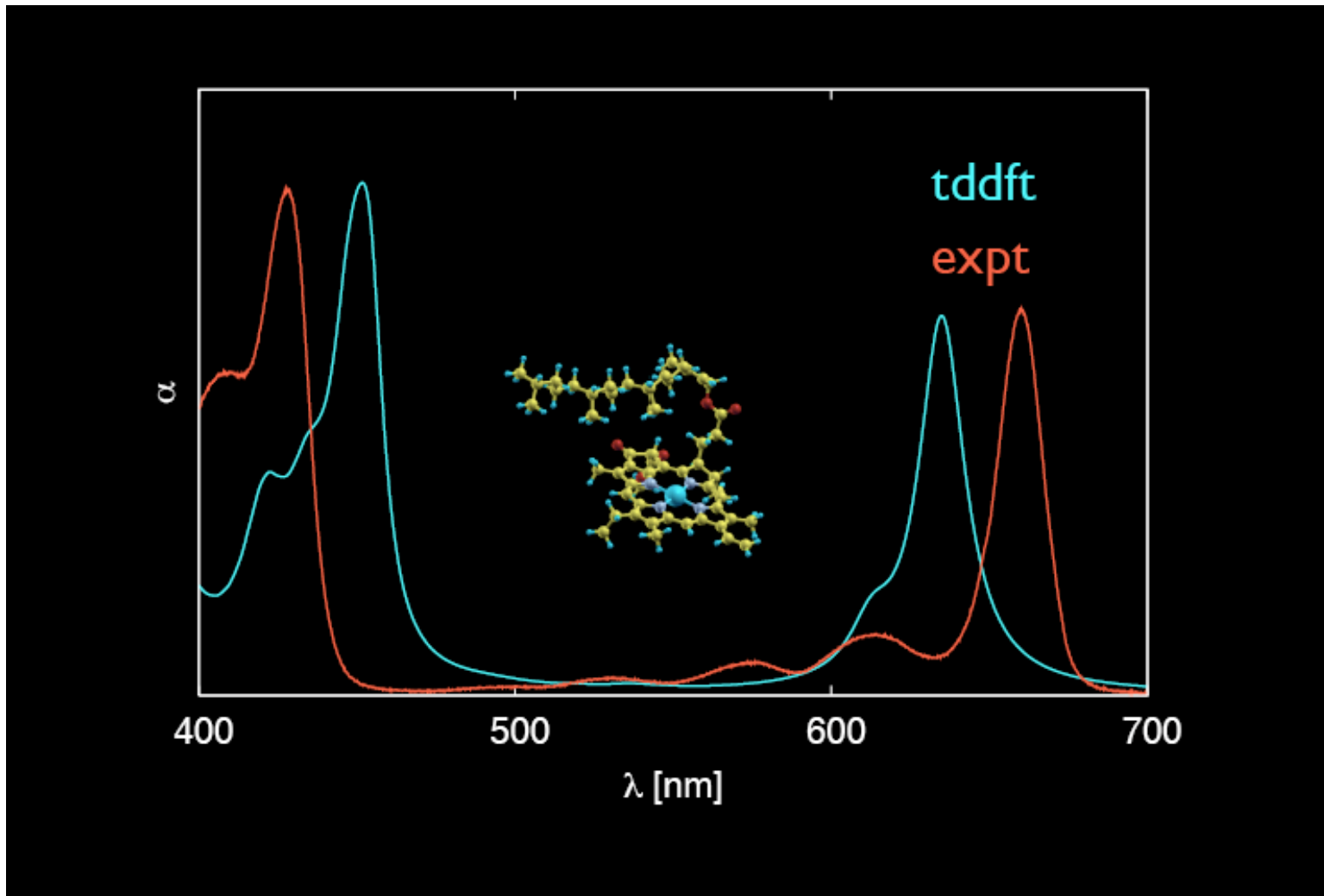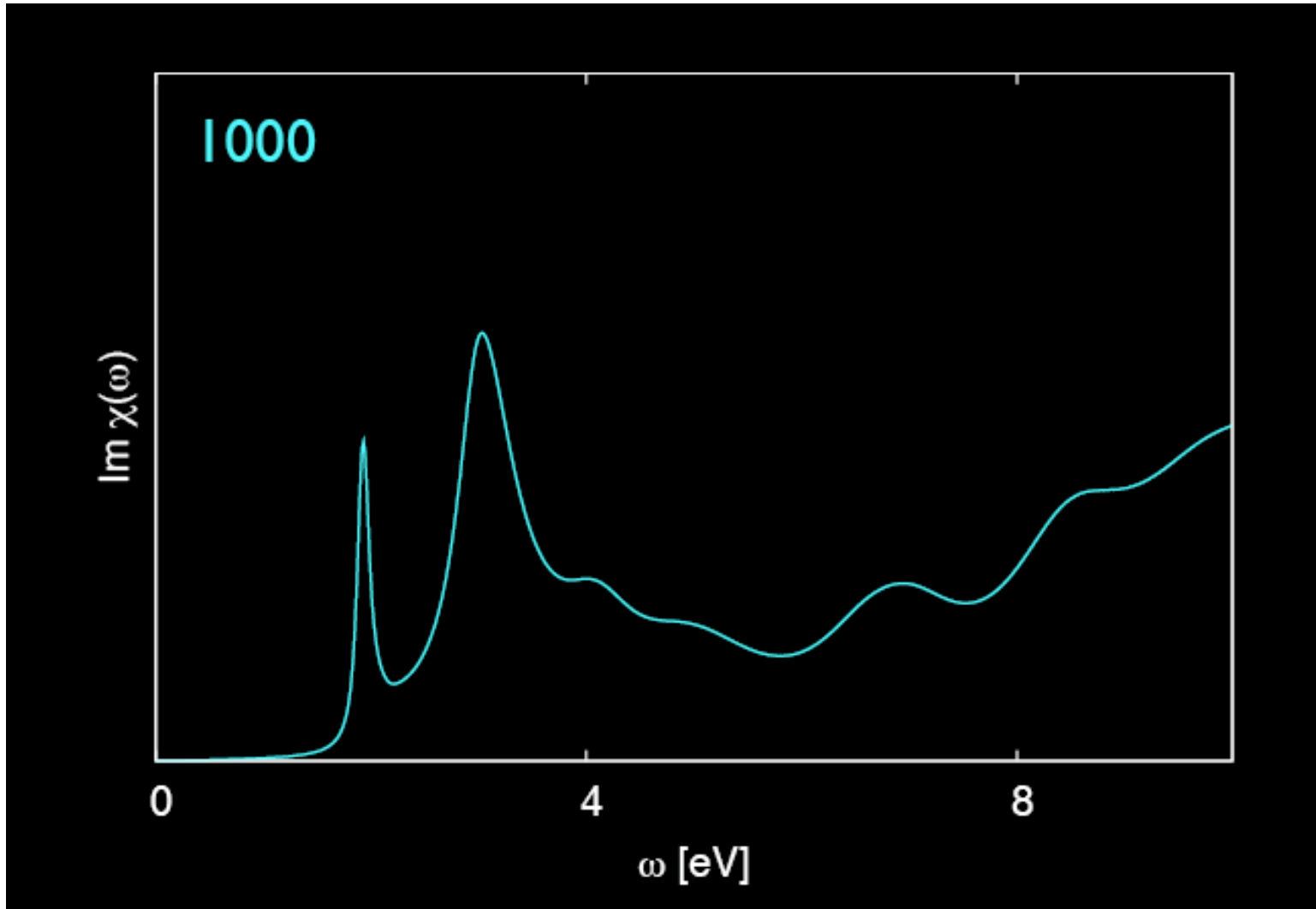
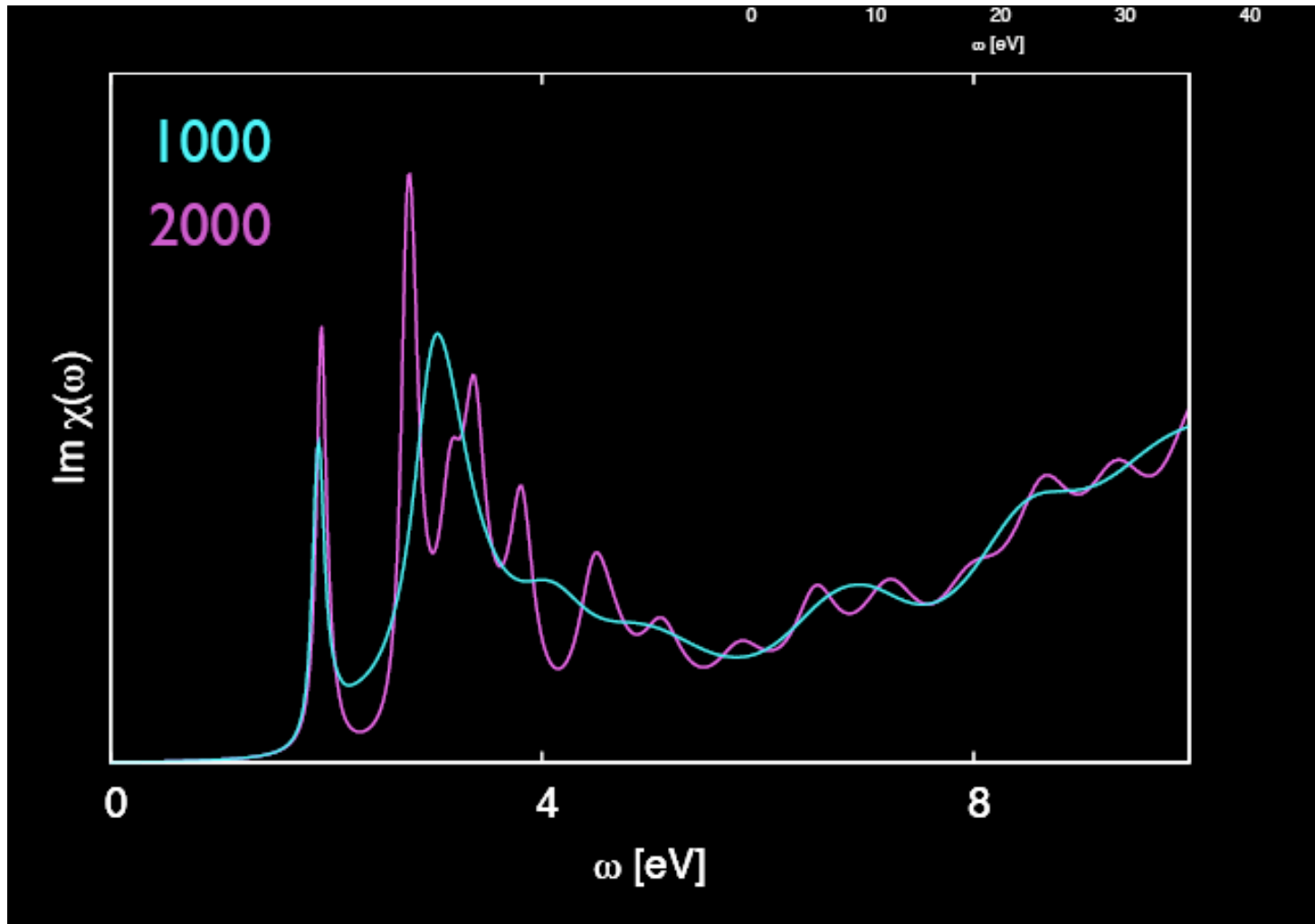# Speeding up the convergence
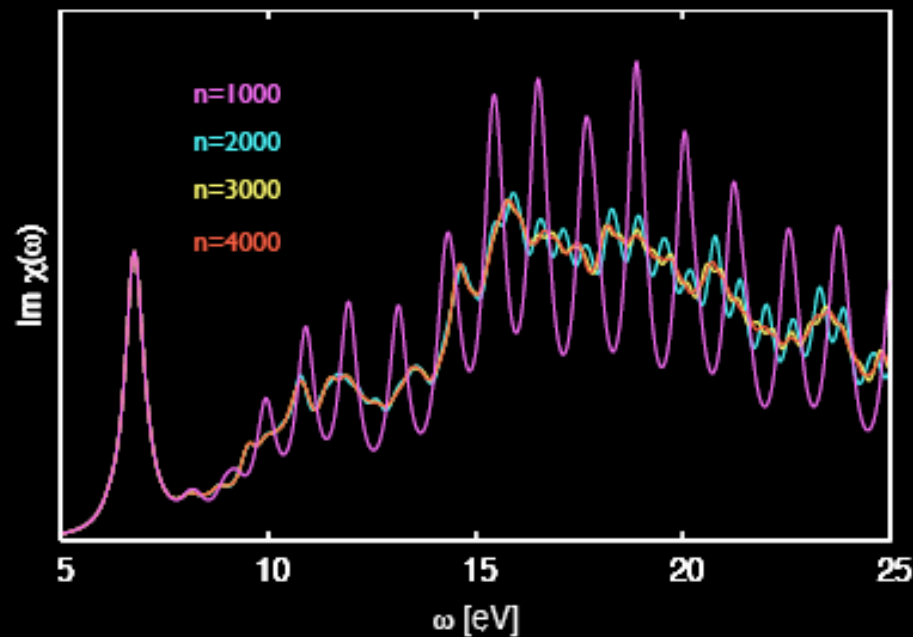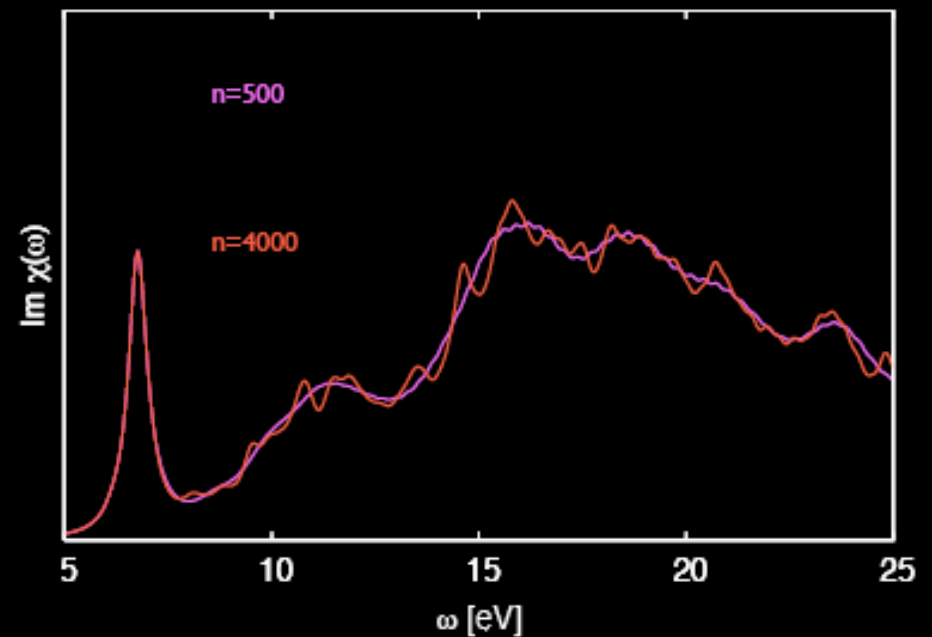
# Another example: Chlorophyll a

137 atoms

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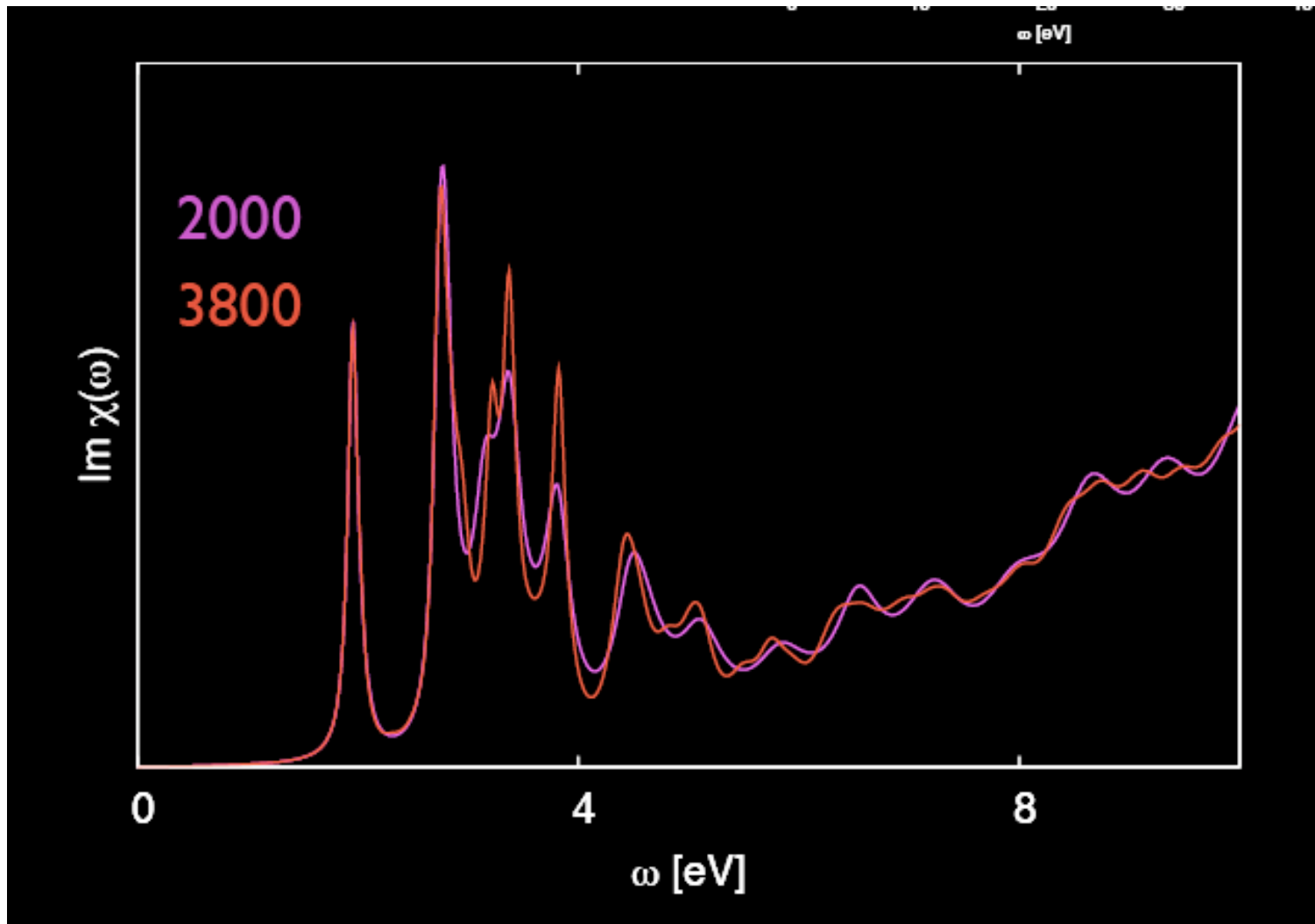# Another example: Chlorophyll a

137 atoms

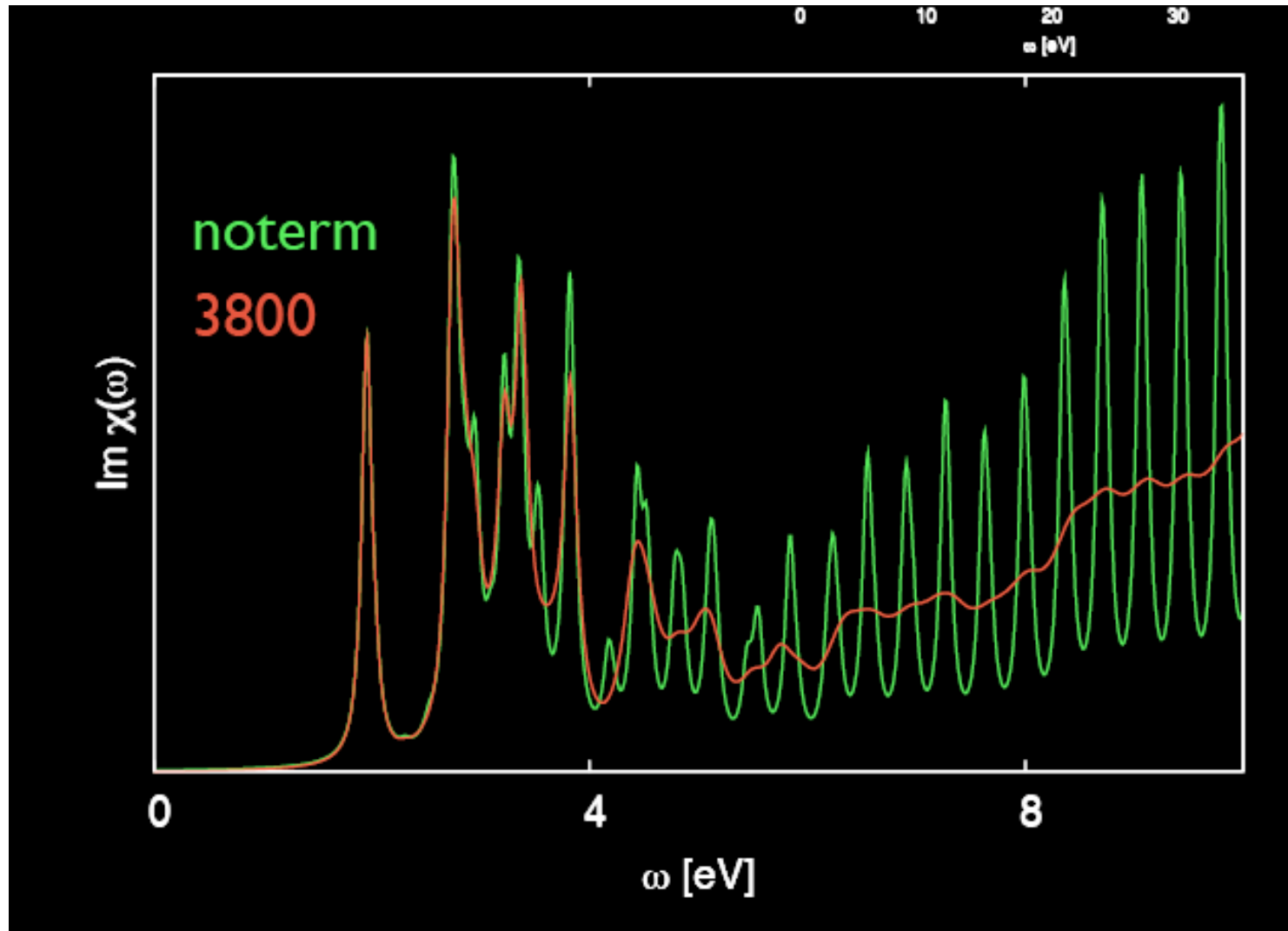# Another example: Chlorophyll a

137 atoms

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137 atoms

# Another example: Chlorophyll a

137 atoms

# This afternoon's hands-on tutorial

3 hours of "optics in QE"

      1h TDDFPT (me) + 2h GW (P. Umari)

TDDFPT example: optical spectrum of a benzene molecule

To learn more in depth about optical properties and Quantum Espresso:

SISSA-DEMOCRITOS tutorial 18-22 October 2010

# Conclusions

- Lanczos recursions can be useful if

  One is interested in the spectrum, not in the eigenvector of one given excitation

  Has either huge basis sets or very large systems (or both)

- Lanczos recursions are independent of frequency: Only one chain is needed for the whole specrum

  No calculation of eigenvectors for huge Liouvillian matrix

- Possible to extend to other observables, like dichroism spectra

- Possible to calculate response densities for a given frequency

- Applications show the feasibility in large systems with large basis sets

# Thanks to:

- Stefano Baroni (SISSA & DEMOCRITOS, Trieste)

- Brent Walker (University College, London)

- Dario Rocca (UC Davis)

- Filippo De Angelis (Perugia)

- O. Baris Malcioglu (Trieste)

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)