Absorption spectra of protein chromophores

Miguel A. L. Marques1,2, Xabier López,3 Daniele Varsano,3 Alberto Castro,3 and Ángel Rubio3

1Institut für Theoretische Physik, Freie Universität Berlin, Arnimallee 14, 14195 Berlin, Germany
2Departamento de Física de Materiales, Facultad de Químicas, Universidad del País Vasco UPV/EHU and Donostia International Physics Center (DIPC), 20018 San Sebastián/Donostia, Spain
3Departamento de Química, Facultad de Ciencias, UPV/EHU, 20018 San Sebastián, Spain

Abstract

Not surprisingly, the theoretical understanding of biophysical processes is a very active field of research. In particular, there have been spectacular advances in the characterisation of structural and dynamical properties of complex biomolecules by a combination of quantum mechanical and classical molecular mechanics methods (QM-MM). However, and in spite of the large amount of experimental work in photo-active molecules, the theoretical description of the interaction of these molecules with external time-dependent fields is very much in its infancy. Photo-active molecules relevant for biology include retinal (responsible for the process of vision), the green fluorescent protein (GFP), and chlorophyll, etc. On the other hand, time-dependent density functional (TDDFT) theory has proved to be an invaluable tool for the calculation of excitation spectra of molecules. We will present a way to combined QM-MM methods (for the ground state) with TDDFT (for the description of the excited states) to calculate optical absorption spectra. Our first test case, the GFP, yielded remarkably good results.

Structure optimized in 3 steps.

- An initial optimization was performed with all backbone and chromophore atoms fixed at their crystallographic positions.
- In a second step we allowed relaxation only of the coordinates of the chromophore. These first two steps were done using empirical potentials to model the interaction between the atoms.
- The geometry of the chromophore is further optimized by using a QM/MM method.

QM/MM Methods

Most proteins are clearly too large to be handled in our current DFT codes. However, only a small part of the protein—the chromophore—is responsible for the optical absorption in the lower end of the spectrum.

QM/MM is an approximate framework that allows us to treat the important part of large biological molecules using quantum mechanics, while the rest is handled with empirical potentials.

- The QM part are the MM atoms as if they were external point charges.
- The QM/MM boundary sometimes has to run through a bond. In this case a hydrogen atom (H-bridge) is added to the QM system in order to saturate the bond.

The final geometry of the (QM) chromophore of the GFP (together with the closest MM residues) was obtained by running a series of optimization steps. The geometry was further optimized by using a QM/MM method.

To approximate the exchange-correlation potential we used the adiabatic LDA

\[ \epsilon^{\text{LDA}}(\mathbf{r}(t)) = \frac{1}{\text{dim}} \rho(\mathbf{r}(t)) \]

Our starting point for the time-dependent propagation we use the ground-state Kohn-Sham wavefunctions, \( \psi(\mathbf{r}) \), excited by a small perturbation of the form \( -q_0 \delta(\mathbf{r}) \).

The dynamical polarizability can be obtained from

\[ \alpha_\ell(\omega) = \frac{1}{\text{dim}} \int d\mathbf{r} \delta(\mathbf{r}) \mathbf{p}_\ell(\mathbf{r}, \omega) \]

where \( \mathbf{p}_\ell(\mathbf{r}, \omega) \) is the Fourier transform of \( \mathbf{r}(\mathbf{r}, t) = \psi(\mathbf{r}, t=0) \). The photo-absorption cross-section is then proportional to the imaginary part of the dynamical polarizability

\[ \sigma(\omega) \propto \text{Im} \alpha_\ell(\omega) \]

Our Tool

http://www.tddft.org/programs/octopus

Results - GFP

The dashed line corresponds to the neutral chromophore, the dotted line to the anionic state, whereas the green and blue curves are the experimental results of Nielson et al.[PNAS, 2001] and of Creemers [PRL, 2000] respectively. For comparative purposes, we divided the anionic results by 4 with respect to the neutral results. Just decomposition of the computed spectra of the neutral species in the three directions, showing the inherent anisotropy of the GFP molecule.