Photosynthetic pigment-protein complexes optical response modeling optimized by Differential evolution: algorithm convergence study

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Abstract. Photosynthetic pigment-protein complexes are the essential parts of thylakoid membranes of higher plants and cyanobacteria. Besides many organic and inorganic molecules they contain pigments like chlorophyll, bacteriochlorophyll, and carotenoids, which absorb the incident light and transform it into the energy of the excited electronic states. The semiclassical theories such as molecular exciton theory and the multimode Brownian oscillator model allows us to simulate the linear and nonlinear optical response of any pigment-protein complex, however, the main disadvantage of those approaches is a significant amount of effective parameters needed to be found in order to reproduce the experimental data. To overcome these difficulties we used the Differential evolution method (DE) that belongs to the family of evolutionary optimization algorithms. Based on our preliminary studies of the linear optical properties of monomeric photosynthetic pigments using DE, we proceed to more complex systems like the reaction center of photosystem II isolated from higher plants (PSIIRC). PSIIRC contains only eight chlorophyll pigments, and therefore it is potentially a very promising subject to test DE as a powerful optimization procedure for simulation of the optical response of a system of interacting pigments. Using the theoretically simulated linear spectra of PSIIRC (absorption, circular dichroism, linear dichroism, and fluorescence), we investigated the dependence of the algorithm convergence on DE settings: strategies, crossover, weighting factor; eventually finding the optimal mode of operation of the optimization procedure.

1. Introduction

The study of optical properties photosynthetic pigment-protein complexes (PPC) requires knowledge of three different areas: physics, biology, and mathematical modeling [1]. These PPCs are found in membranes of bacteria, algae, and higher plants. Generally, they take part in the energy conversion processes of photosynthesis transforming absorbed light quanta into the energy of chemical bonds [2]. PPCs are of great interest from the point of view of optical response modeling because their structures are very complex and non-symmetrical; as a result, many important properties of these complexes
remain unexplored. Since the exact analytical solutions are impossible for quantum models of PPCs, the semiclassical methods are preferable in fitting the experimental data. There are many experimental techniques allowing linear optical response investigation: such as measurement of absorption, fluorescence, linear and circular dichroism. By simulating the optical response and fitting the measured spectra, we can estimate and analyze the cooperative effects occurring within these complexes. In this study we examine optical properties of the reaction center of Photosystem II (PSIIRC) [3], which is shown in Figure 1.

Figure 1. Cofactors of the reaction center of Photosystem II

PSIIRC is the key structural unit of photosystem II – a PPC of oxygenic photosynthetic species containing the oxygen evolving complex. PSIIRC accepts the energy of absorbed light quanta from light-harvesting antenna and initiates three consecutive steps of charge separation processes. It consists of 6 bacteriochlorophylls, two of which form a dimer where charge separation starts, and 2 bacteriopheophytins, which is an electron acceptor in the transport chain in the reaction center. Bacteriopheophytin has the same structure as bacteriochlorophyll, but differs in the absence of a magnesium atom in the middle of the porphyrin ring [4].

Despite of many studies in the field, there is still a challenging task of how to interpret large amount of experimental data. Our work is devoted to modeling the linear optical response of PSIIRC with high accuracy (without sticking at local minima) in an acceptable time. To solve it, we will use Differential Evolution (DE) algorithm that includes a method that optimizes a problem by iteratively improving a candidate solution with regard to a given measure of quality [5]. One of the advantages of DE algorithm is that the cost function could be non-differentiable on the researching range [6, 7].

2. Theory

To demonstrate the potential of DE to be an effective optimization procedure when modeling the PPC optical response, the following assumption was made: instead of performing the real experimental data fitting, we used artificially created spectra as target functions. This trick allows DE to find a set of
desired model parameters with high accuracy and to analyze the rates of convergence for different strategies. To simulate absorption, fluorescence, circular and linear dichroism, we applied the modified Redfield theory (MRT) for interacting pigments and the multimode Brownian oscillator model (MBOM) [8]. MRT allows us to get a realistic of profile spectra of exciton states and with the help of MBOM we can properly take into account the influence of phonons on electronic excitation. To simplify calculation routines, the inhomogeneous broadening of exciton states was not included in the simulation. The expressions for the linear optical response are as follows:

\[
\begin{align*}
\sigma_{ab}(\omega) & \approx \frac{\omega}{\pi} \sum_{\alpha} d_{\alpha}^2 \Re \int_0^\infty dt e^{i(\omega - \epsilon_{\alpha})t} e^{-i\alpha(\omega - \epsilon_{\alpha})} e^{-0.5K_{aa}t}, \\
\sigma_{CD}(\omega) & \approx \frac{\omega}{\pi} \sum_{\alpha} R_{\alpha} \Re \int_0^\infty dt e^{i(\omega - \epsilon_{\alpha})t} e^{-i\alpha(\omega - \epsilon_{\alpha})} e^{-0.5K_{aa}t}, \\
\sigma_{LD}(\omega) & \approx \frac{\omega}{\pi} \sum_{\alpha} (d_{\alpha}^2 - (d_{\alpha}^2 + d_{\alpha}^2)/2) \Re \int_0^\infty dt e^{i(\omega - \epsilon_{\alpha})t} e^{-i\alpha(\omega - \epsilon_{\alpha})} e^{-0.5K_{aa}t}, \\
\sigma_{fl}(\omega) & \approx \frac{\omega^3}{\pi} \sum_{\alpha} (\delta_{\alpha}^2 e^{\epsilon_{\alpha}}) \Re \int_0^\infty dt e^{i(\omega - \epsilon_{\alpha} + 2\Delta_{\alpha} + 4\epsilon_{\alpha})t} e^{-i\alpha(\omega - \epsilon_{\alpha} + 2\Delta_{\alpha} + 4\epsilon_{\alpha})} e^{-0.5K_{aa}t},
\end{align*}
\]

where \(d_{\alpha}, d_{\alpha}', \) and \(d_{\alpha}''\) are the components of exciton transition moments; \(d_{\alpha}^2\) are squared values of the exciton transition moments; \(R_{\alpha}\) is the matrix of rotational strength applied for circular dichroism spectra, \(\alpha\) are the indexes of exciton states, and \(\epsilon_{\alpha}\) are the eigenvalues of the system Hamiltonian. And there are also two important elements of the modeling: \(\gamma_{\alpha\alpha\alpha\alpha}(t)\) is the lineshape function for the nth exciton state and \(K_{aa}\) are the diagonal elements of the relaxation matrix. Full expressions for the lineshape function and the relaxation matrix are given in [9].

The system Hamiltonian usually is written in the following form:

\[
H = \sum_n \Omega_n B_n^+ B_n + \frac{1}{2} \sum_{n,m} J_{mn} (B_n^+ B_m + B_m^+ B_n)
\]

where \(B_n^+\) and \(B_n\) are creation and annihilation operators, which obey the following commutation rules \([B_n, B_n^+] = 1\). \(\Omega_n\) are the transition energy between the ground and the excited states of PSIIRC cofactors. \(J_{mn}\) is a matrix of interaction energies calculated in the extended dipole approximation. The interaction energies are calculated based on the latest crystal structure. Diagonalizing this Hamiltonian, we get the eigenstates and eigenvalues that are necessary to evaluate the expressions (1-4), particularly \(\gamma_{\alpha\alpha\alpha\alpha}(t)\) and \(K_{aa}\).

The spectral density \(C(\omega)\) is another key function in the modeling of linear spectra of PSIIRC. This semiclassical expression allows us to estimate the phonon contribution to the optical response of the pigments introducing a set of vibronic modes, each of which is characterized by three parameters: \(\omega_j, S_j, \) and \(\gamma_j\).

\[
C(\omega) = \sum_j \frac{2S_j \omega \gamma_j^2}{(\omega_j^2 - \omega^2)^2 + \omega^2 \gamma_j^2}
\]

here \(\omega_j\) and \(\gamma_j\) are the frequencies and the damping factors of a mode; these are parameters that can be meaured in the experiments. \(S_j\) are the Huang-Rhys factors, the parameters responsible for the exciton-phonon interaction.

3. Results and Discussion

Finally, we have a following set of model parameters \(\{\Omega_n, \omega_j, S_j, \gamma_j\}\) to be optimized, where \(n\) indexes pigments of PSIIRC, and \(j\) indexes the vibronic modes (chlorophyll molecule requires 48 vibronic modes). PSIIRC contains 8 pigments; considering that all cofactors of PSIIRC have the same spectral density, the number of free parameters has to be 56, however, for the sake of simplicity; we consider only transition energies \(\Omega_n\) as free in our simulations.
DE has 10 strategies and two parameters to adjust the performance of each strategy, which have a big impact on work the algorithm. One of them is $F$ – the weighting factor and $Cr$ – the crossover probability. We choose the range of $F$ if $0.6 - 0.9$ and $Cr$ is $0.8 - 1.0$ for our calculations. The discrete step is $0.05$. The total number of combinations equals 35 for each strategy. All values were fitted using 4 experimental spectra: absorption, linear dichroism, circle dichroism, and fluorescence. All results obtained after 100 generations by averaging the best fitting results after 10 DE runs. The results of DE algorithm for strategies $DE/rand-to-best/1/exp$ (red) and $DE/best/1/bin$ (blue) are shown in Figure 2. The minimum of objective function for each pair $(F, Cr)$ and type of strategy are also shown.

![Figure 2](image.png)

Figure 2. The results of DE test runs for two strategies $DE/rand-to-best/1/exp$ (red) and $DE/best/1/bin$ (blue).

We can see that values of the objective function for $DE/best/1/bin$ strategy are better than for $DE/rand-to-best/1/exp$ strategy. The minimum of the objective function is with $F = 0.6$ and $Cr = 1.0$. It is equal to $8.33 \times 10^{-19}$, which is computer zero. It can be argued that for these parameters, the best solution was completely found. The biggest difference between two strategies is approximately 3-4 orders of magnitude when $F = 0.6$. Therefore, the rate of convergence for $DE/best/1/bin$ is significantly more than for $DE/rand-to-best/1/exp$ strategy. With an increase of $F$, this difference slightly decreases.

Thus, as a result of our simulations, the artificially created experimental data were fitted with high accuracy using a strategy and a pair of numbers $(F, Cr)$ found in the test runs of the optimization procedure. Using these settings of algorithm for fitting the real experimental data, we can determine the full set of MRT and MBOM parameters $\{\Omega_n, \omega_j, S_j, \gamma_j\}$, which in the future will help us to predict the results of certain nonlinear optical spectroscopy experiments with PSIIRC.

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