Russian Supercomputing Days 2019

Orange Carotenoid Protein Absorption Spectra Simulation Using the Differential Evolution Algorithm

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Outline

1. Photosynthetic Pigment-protein complexes, pigment molecules and their optical properties.

The theory of optical response and the multimode Brownian model.

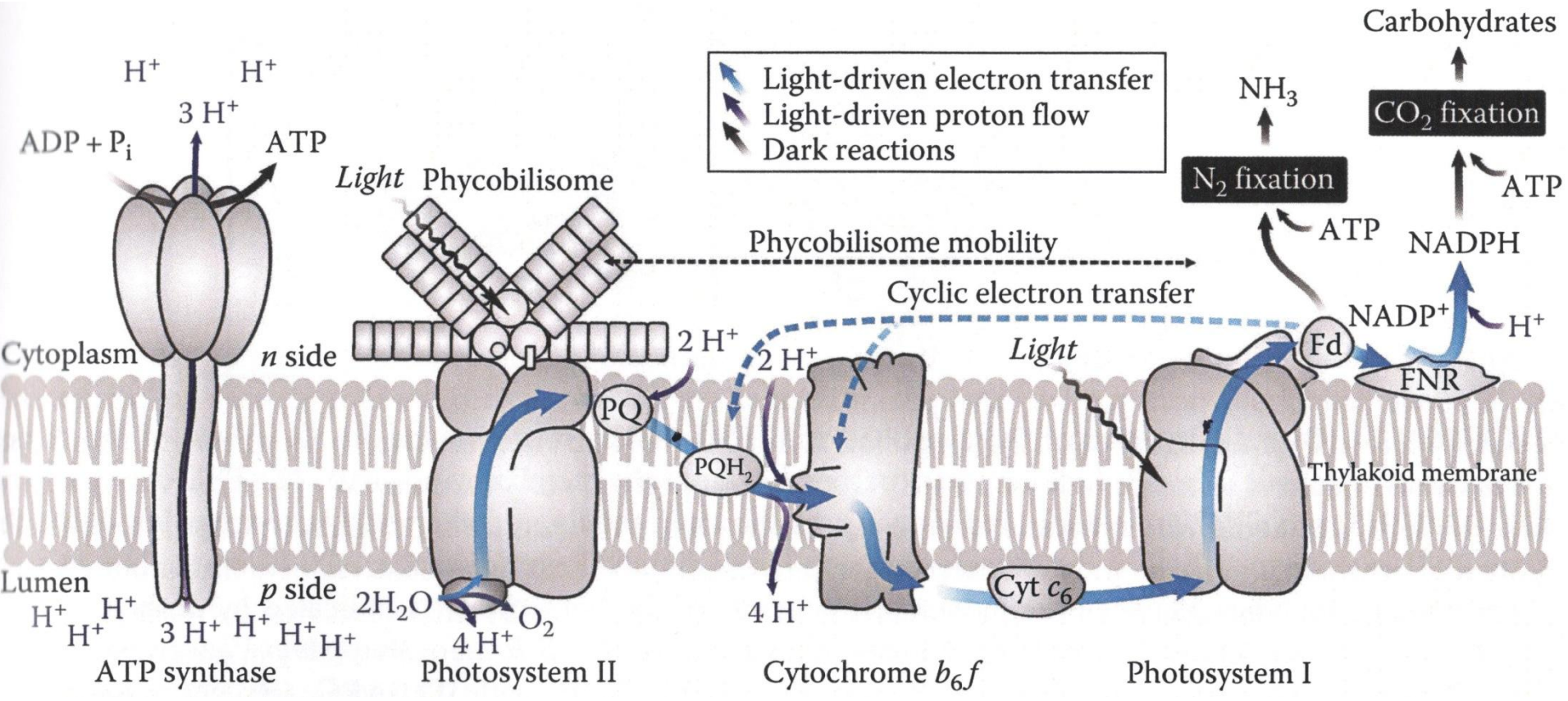
2. Genetic algorithms and The Differential evolution

3. The Differential evolution application:

Simulation of* Chlorophyll *a and* Bacteriochlorophyll a *absorption using the Multimode Brownian oscillator model

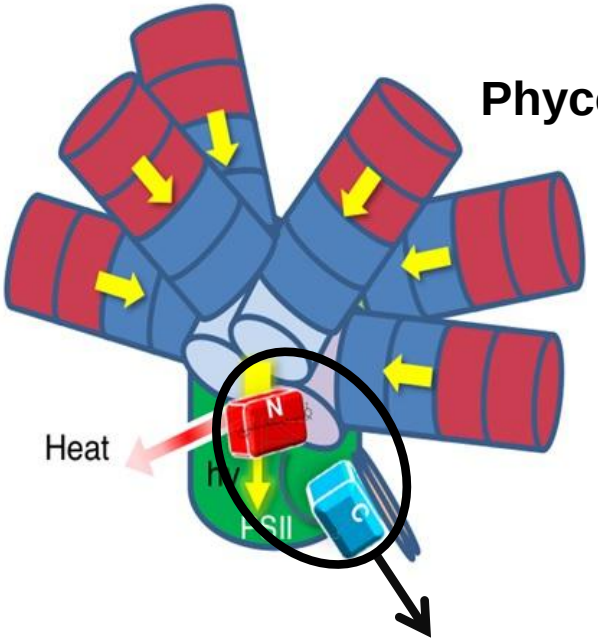
Simulation of Orange Carotenoid Protein absorption

Schematic representation of the protein complexes involved in light-induced electron and proton transfer reaction of oxygenic photosynthesis of cyanobacteria

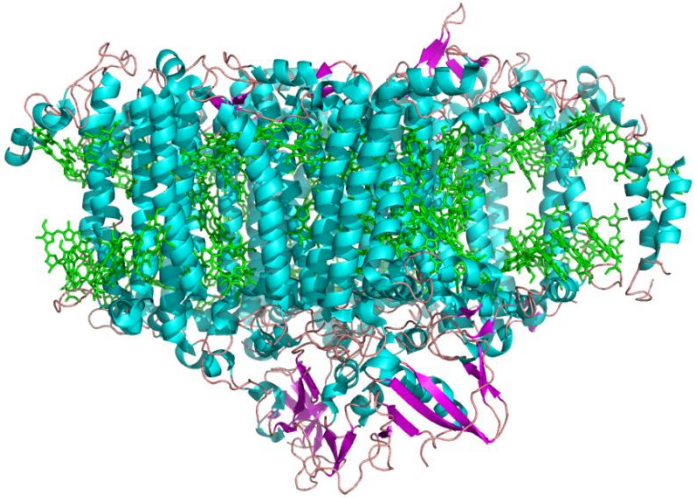


"Oxygenic photosynthesis in Cyanobacteria", **D. Shevela, R Pishchalnikov, L. Eichaker, Govindjee**, 2013, CRC Press Taylor & Francis Group

Photosynthetic pigment-protein complexes and Orange Carotenoid Protein

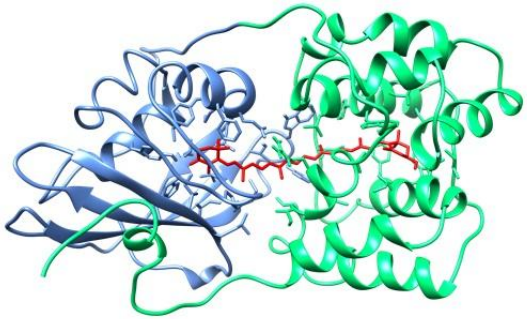


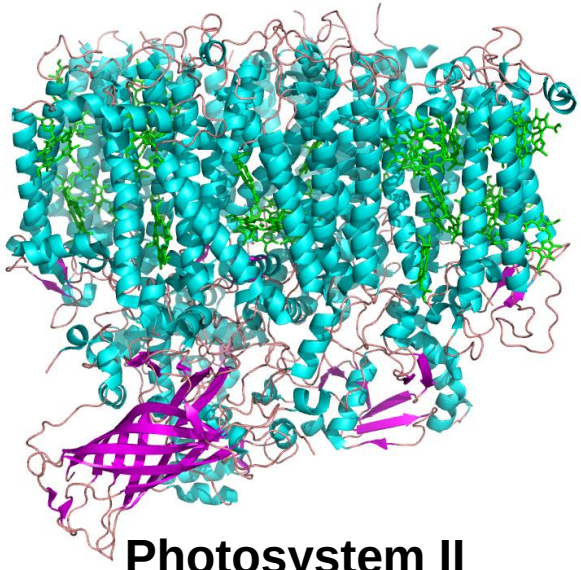
Phycobilisome



Photosystem I

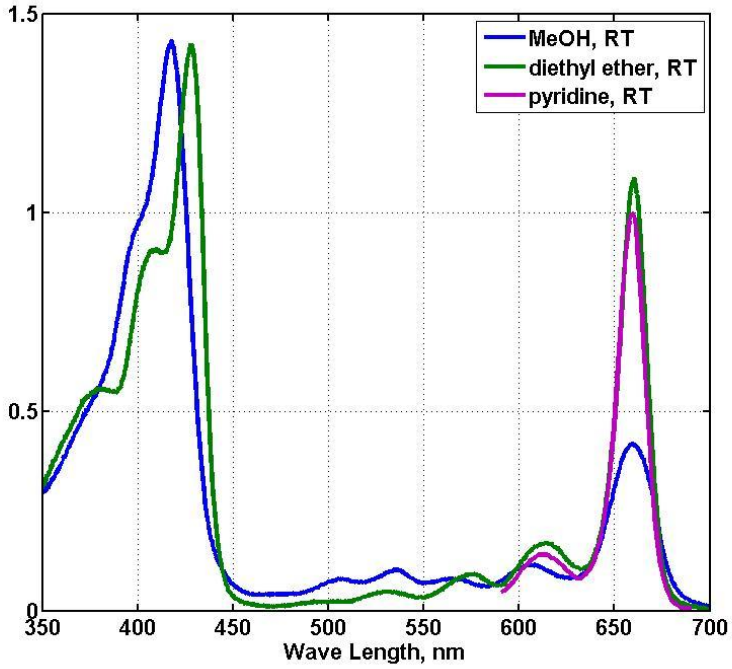
Orange Carotenoid Protein

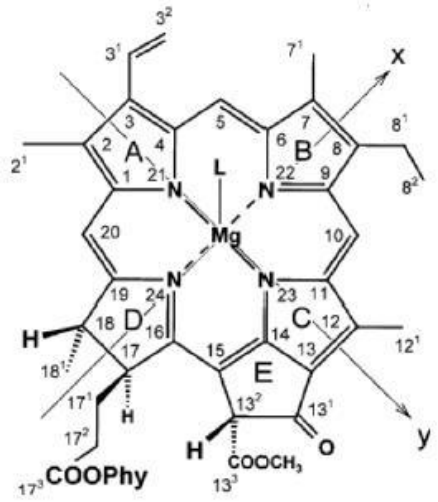


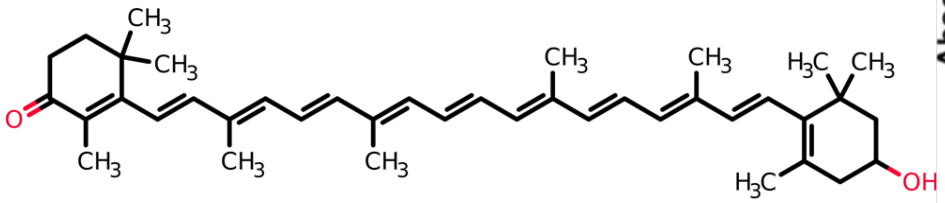


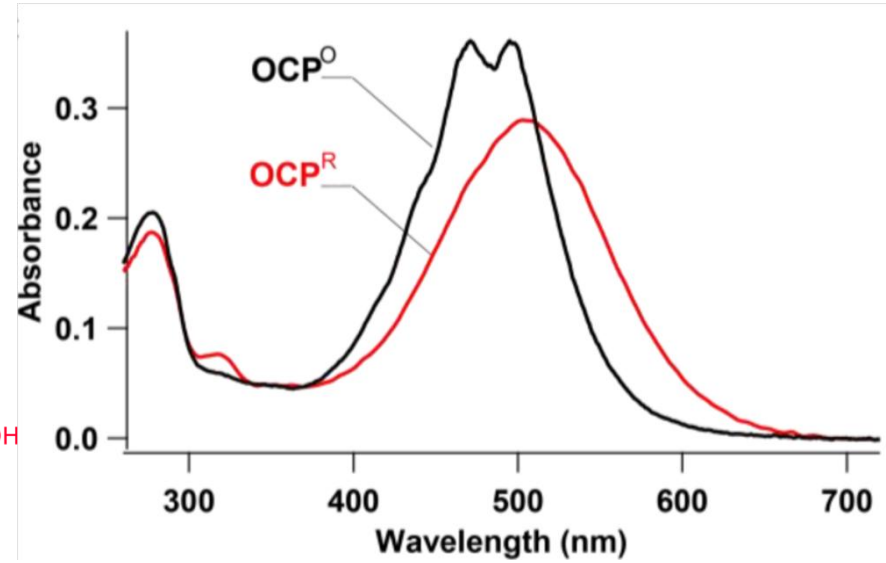
Photosystem II

Bacteriochlorophyll a and Carotenoid absorption spectra (echinenone)

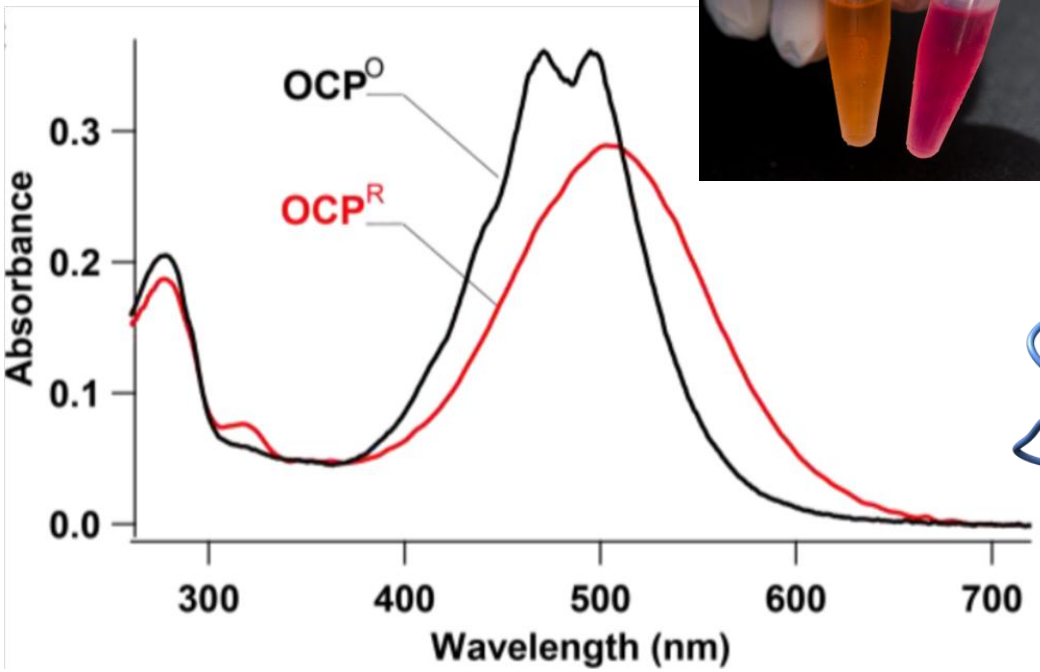


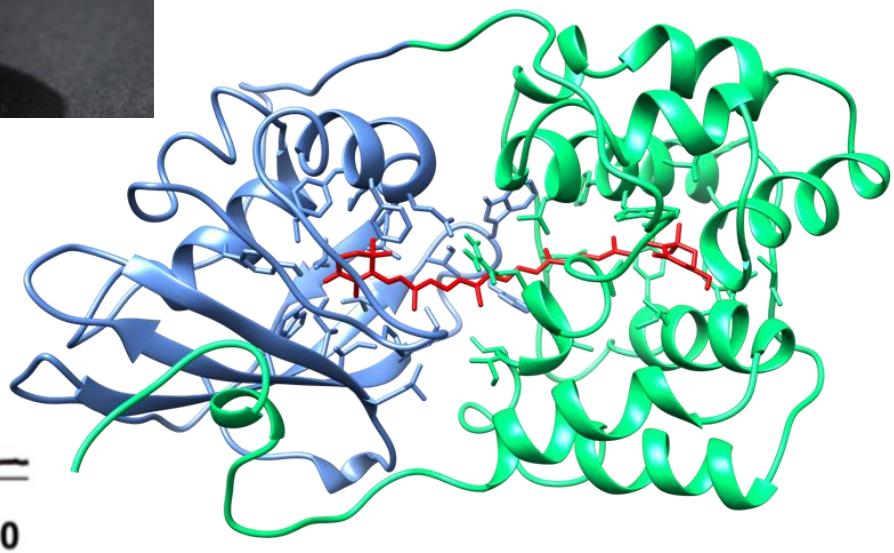




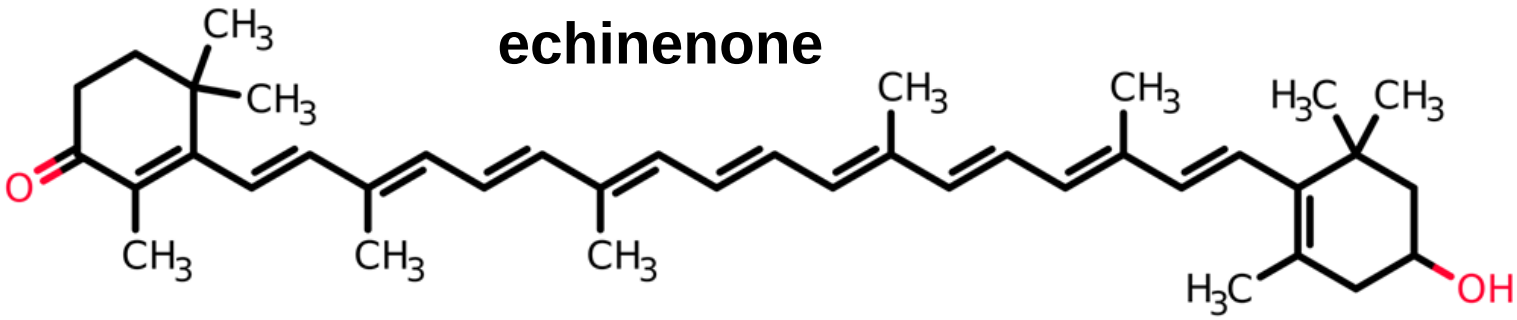


Orange Carotenoid Protein (OCP)



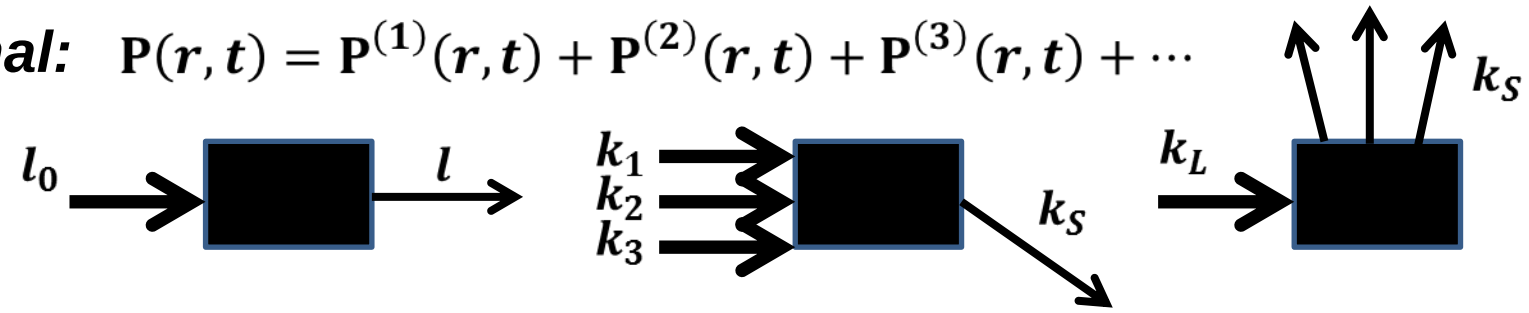


echinenone



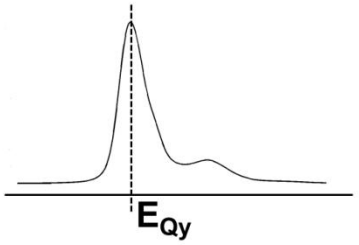
Three important points of linear and non-linear spectroscopy data quantum analysis

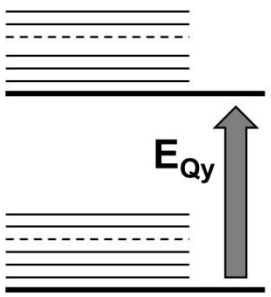
Signal: $\mathbf{P}(r,t) = \mathbf{P}^{(1)}(r,t) + \mathbf{P}^{(2)}(r,t) + \mathbf{P}^{(3)}(r,t) + \cdots$

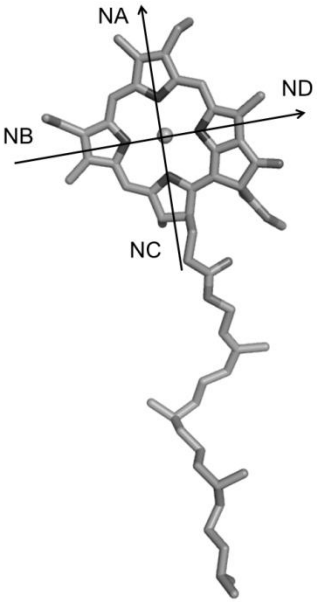


System: $H_S|v\rangle = \varepsilon_v|v\rangle$ Molecular aggregates of Frenkel excitons

$$H = H_S(q_S) + H_B(q_B) + H_{SB}(q_S, q_B)$$







Bath: Dimensionless spectral density

$$J_k(\omega) = \frac{\omega_k^2 \omega \gamma^2}{\left(\omega^2 + \omega_k^2\right)^2 + \omega^2 \gamma_k^2}$$ Lorentzian underdamped

$$J_k(\omega) = 2\frac{\omega \Lambda_k}{\omega^2 + \Lambda_k^2}$$ Overdamped Brownian

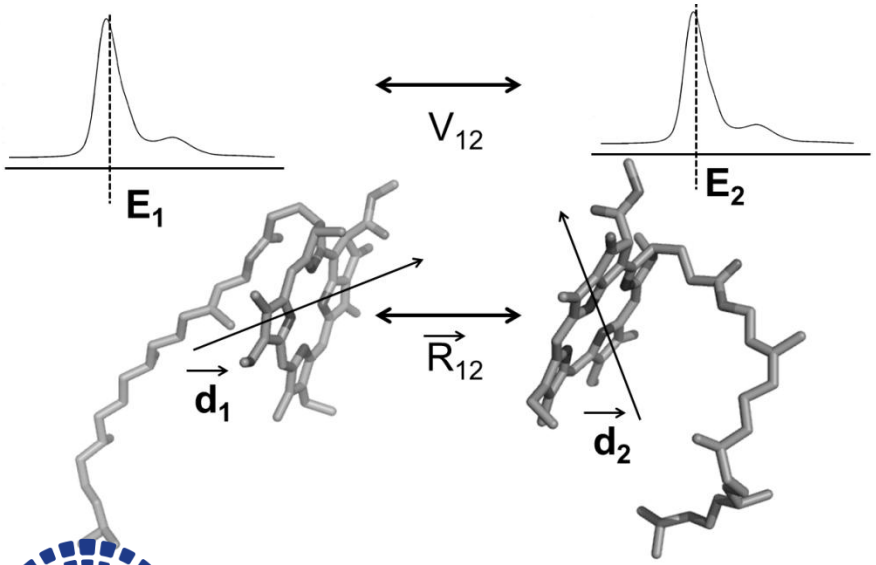
Density matrix equation of motion

$$H = H_S^{el}(q_S) + H_S^{Coup}(q_S) + H_B(q_B) + H_{SB}(q_S, q_B)$$

$H = H^0 + H'$, where H' is a perturbation

$$\frac{\partial \rho(t)}{\partial t} = -\frac{i}{\hbar}[H^0, \rho(t)] - \frac{i}{\hbar}[H', \rho(t)]$$

$$\frac{\partial \rho(t)}{\partial t} = -\frac{i}{\hbar}L^0\rho(t) - \frac{i}{\hbar}L'\rho(t)$$, the Liouville equation of motions



Förster: weak electronic coupling

$H_S^{Coup}(q_S)$ is a perturbation

Redfield: weak electron-phonon coupling

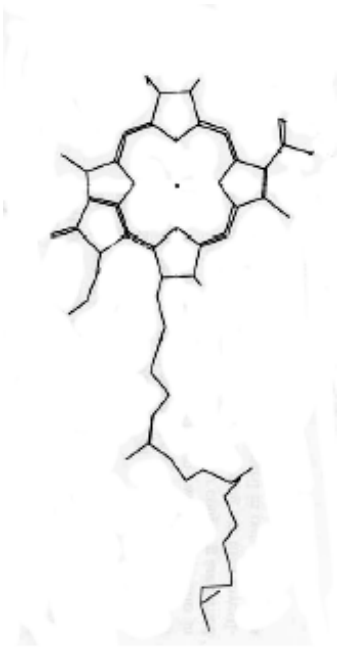
$H_{SB}(q_S, q_B)$ is a perturbation

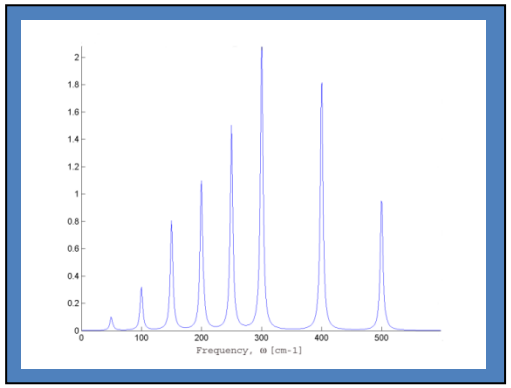
Modified Redfield: Intermediate case the Redfield regime

$H_{SB}^{\mu\nu}(q_S, q_B)$ is a perturbation

$H_{SB}^{\mu\mu}(q_S, q_B)$ is non-perturbative

The lineshape function and the spectral density





Correlation functions:

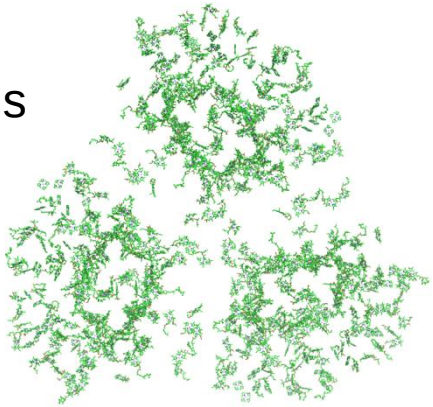
$$\tilde{C}(\omega) = \int_{-\infty}^{\infty} dt \exp(i\omega t) C(t)$$

$$\tilde{C}(\omega) = \tilde{C}'(\omega) + \tilde{C}''(\omega)$$

$$C(t) = \frac{1}{2\pi}\int_{-\infty}^{\infty} d\omega \cos(\omega t) \coth\left(\frac{\hbar\omega}{2kT}\right)\tilde{C}''(\omega) + i\int_{-\infty}^{\infty} d\omega \sin(\omega t)\tilde{C}''(\omega)$$

$$g(t) \equiv \int_0^t d\tau_2 \int_0^{\tau_2} d\tau_1 C(\tau_1)$$ Line-shape function of absorption

Photosystem I trimer; approximately 300 Chls



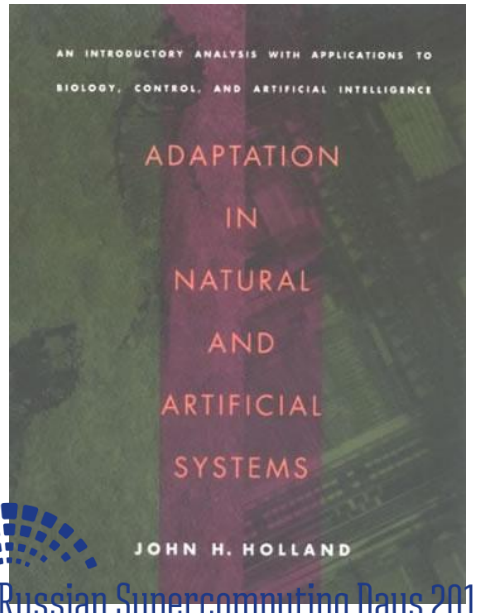
Green function of the generalized master equation for exciton hopping

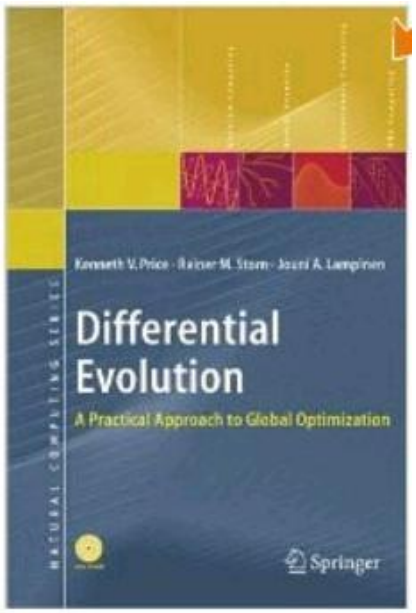
$$\frac{d}{dt}G_{\mu\nu}(t) = \sum_{\alpha}^{\alpha\neq\mu}\left[K_{\mu\alpha}G_{\alpha\nu}(t) - K_{\alpha\mu}G_{\mu\nu}(t)\right]$$

Eigenstate problems, matrix multiplication

Genetic Algorithms

Genetic algorithm is a heuristic algorithm of the best solution search which is used for solving of optimization problems and modelling by means of a random choice, combination and variation of the initial parameter set. This mechanism of manipulation resembles biological natural selection process.

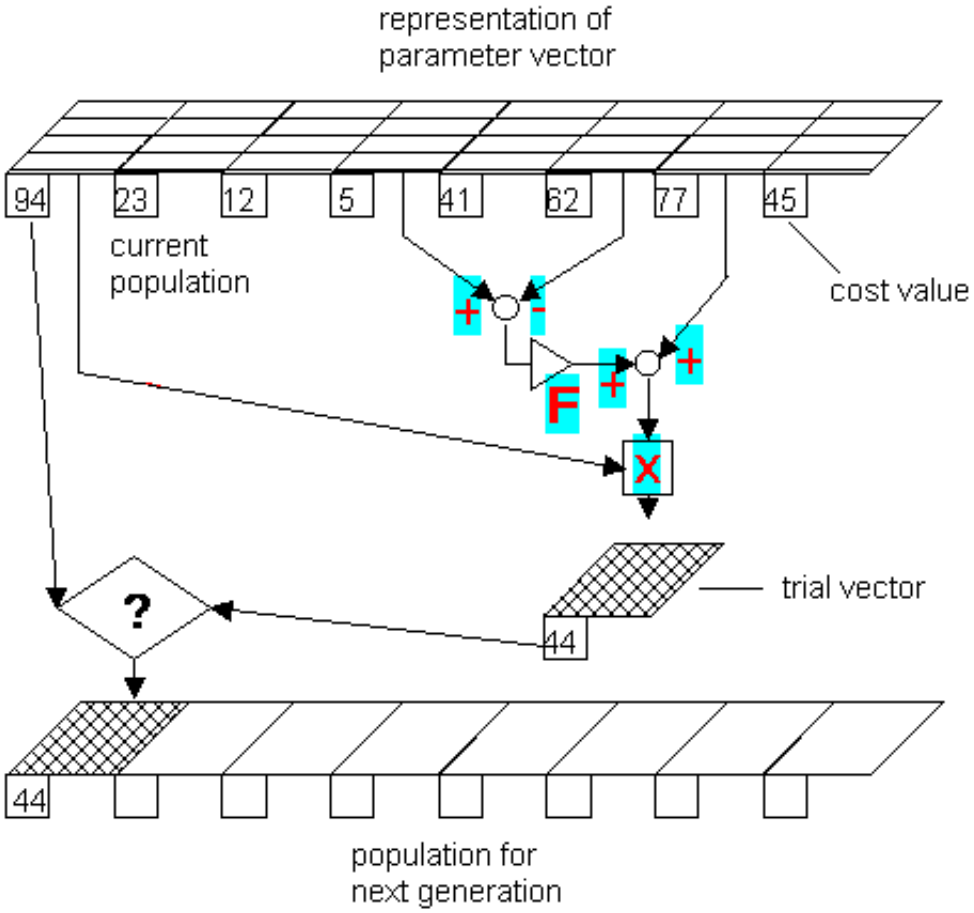




Differential Evolution - A Practical Approach to Global Optimization" by Ken Price, Rainer Storn, and Jouni Lampinen, 2005

J. H. Holland. “Adaptation in Natural and Artificial Systems.” The MIT Press, reprint edition, 1992.

Differential Evolution method



Differential evolution is a method of multidimensional optimization which implements some ideas of genetic algorithms.

Generation of a mutant vector:

F – a weighting factor

C – a crossover constant

$F(\omega)$ - the target function

$f_k(\omega)$ - A trial vector

The cost value $= \sum_{j=1}^{N} \left(F(\omega_j) - f(\omega_j) \right)^2$

http://www1.icsi.berkeley.edu/~storn/code.html

Applications of the Differential Evolution

1. Multiprocessor synthesis. Optimization of multithread systems (cluster supercomputers) http://www.cs.nthu.edu.tw/~isss98/isss98_slides.html

2. Crystallographic characterization. Problems of crystallography http://www.physik.uni-osnabrueck.de/nonlinop/sncfd.htm

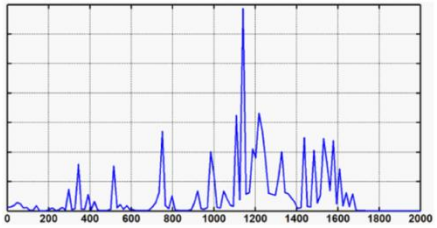
3. Scenario-Integrated Optimization of Dynamic Systems. Strategy optimizations in chemical industry. http://discovery.bits-pilani.ac.in/discipline/chemical/BVb/publications.html#39

4. Optimization of Non-Linear Chemical Processes. http://discovery.bits-pilani.ac.in/discipline/chemical/BVb/publications.html#46

http://www1.icsi.berkeley.edu/~storn/code.html

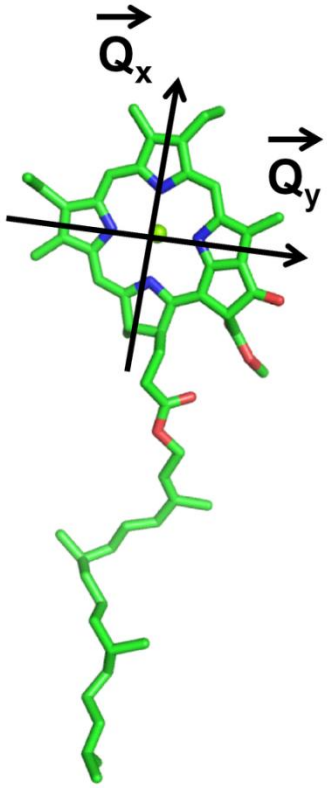
How to fit experimental data using the Differential evolution

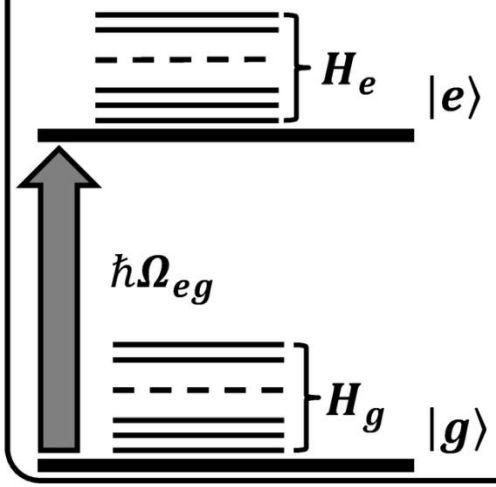
Chlorophyll Optical properties



$C''_k(\omega_k, S_k, \gamma_k)$ -
- correlation function

$g(t)$ -
- lineshape function





DE

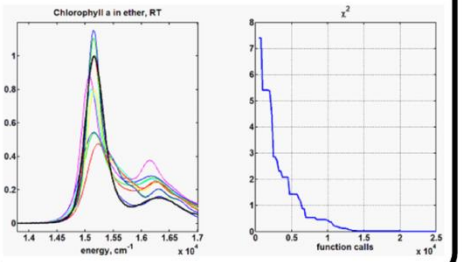
free parameters:

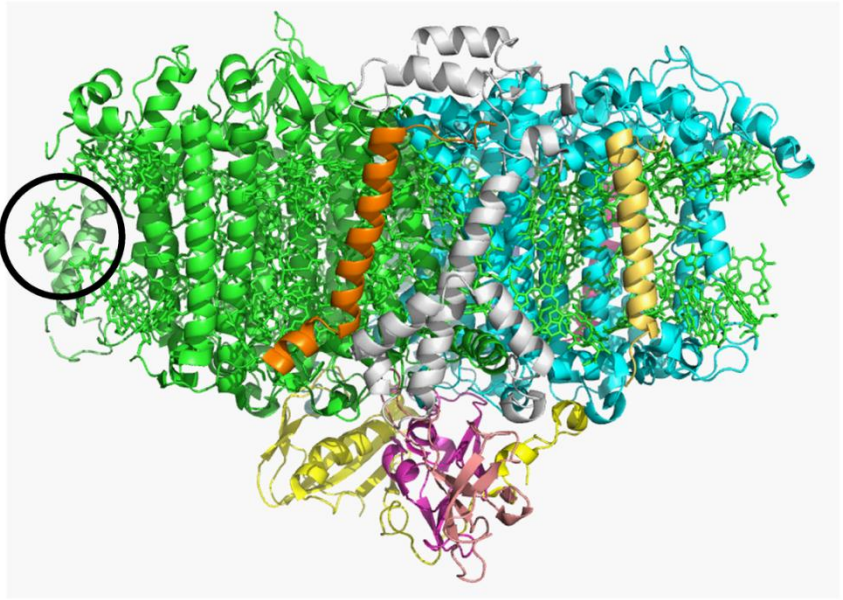
$\omega_k, S_k, \gamma_k, \Omega_{eg}, FWHM$

The cost value:

$$\chi^2 = \frac{1}{N}\sum_{n=1}^{N}\left(\frac{I(\omega_n) - \sigma_{abs}(\omega_n)}{I(\omega_n)}\right)^2$$

Fit of the Chl optical response





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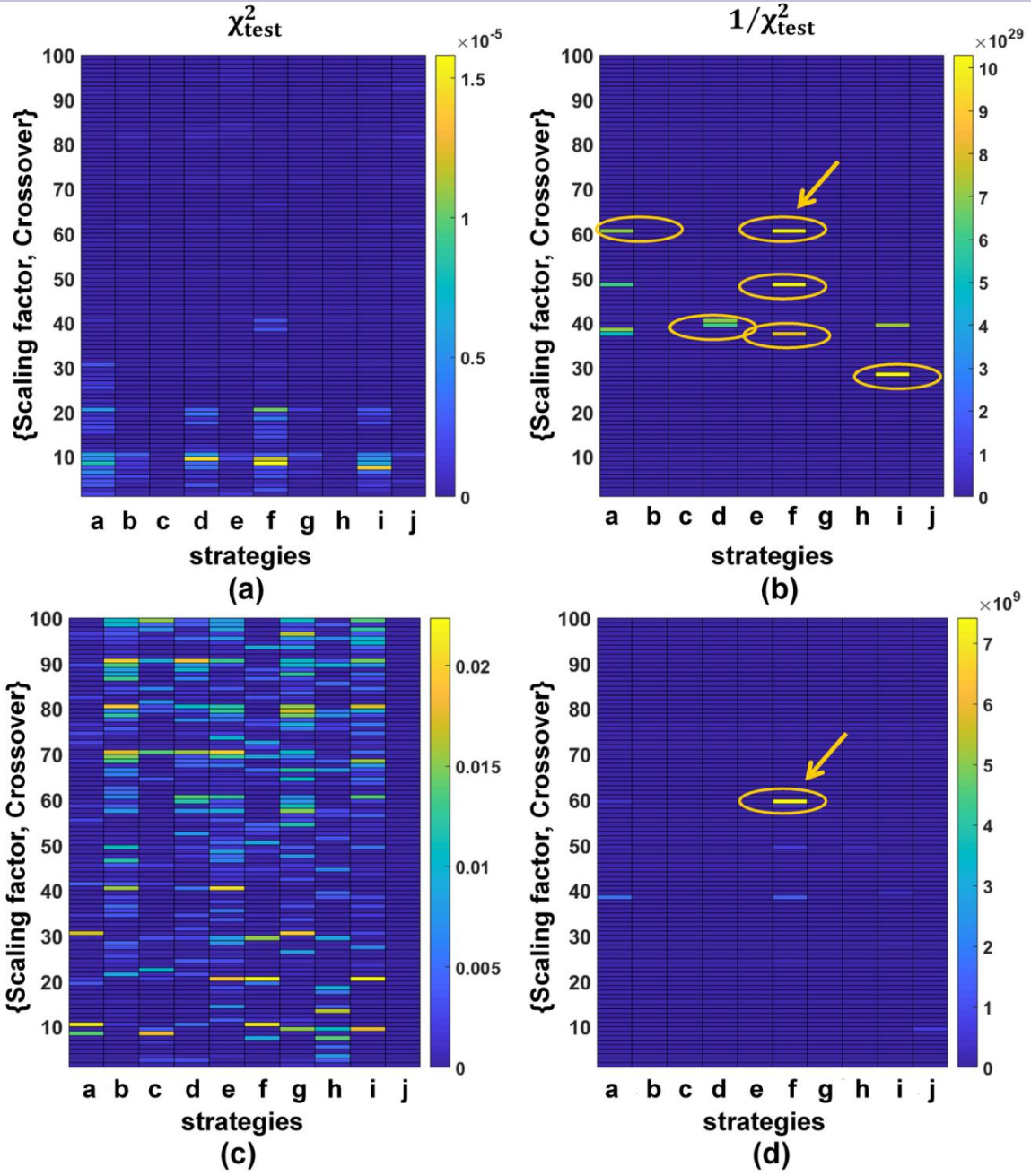
Roman Pishchalnikov, (2018) Journal of Computational Physics, 372, pp. 603-615

Optimum strategy search with the test spectra

Results of the fitting procedure for a chlorophyll absorption spectrum

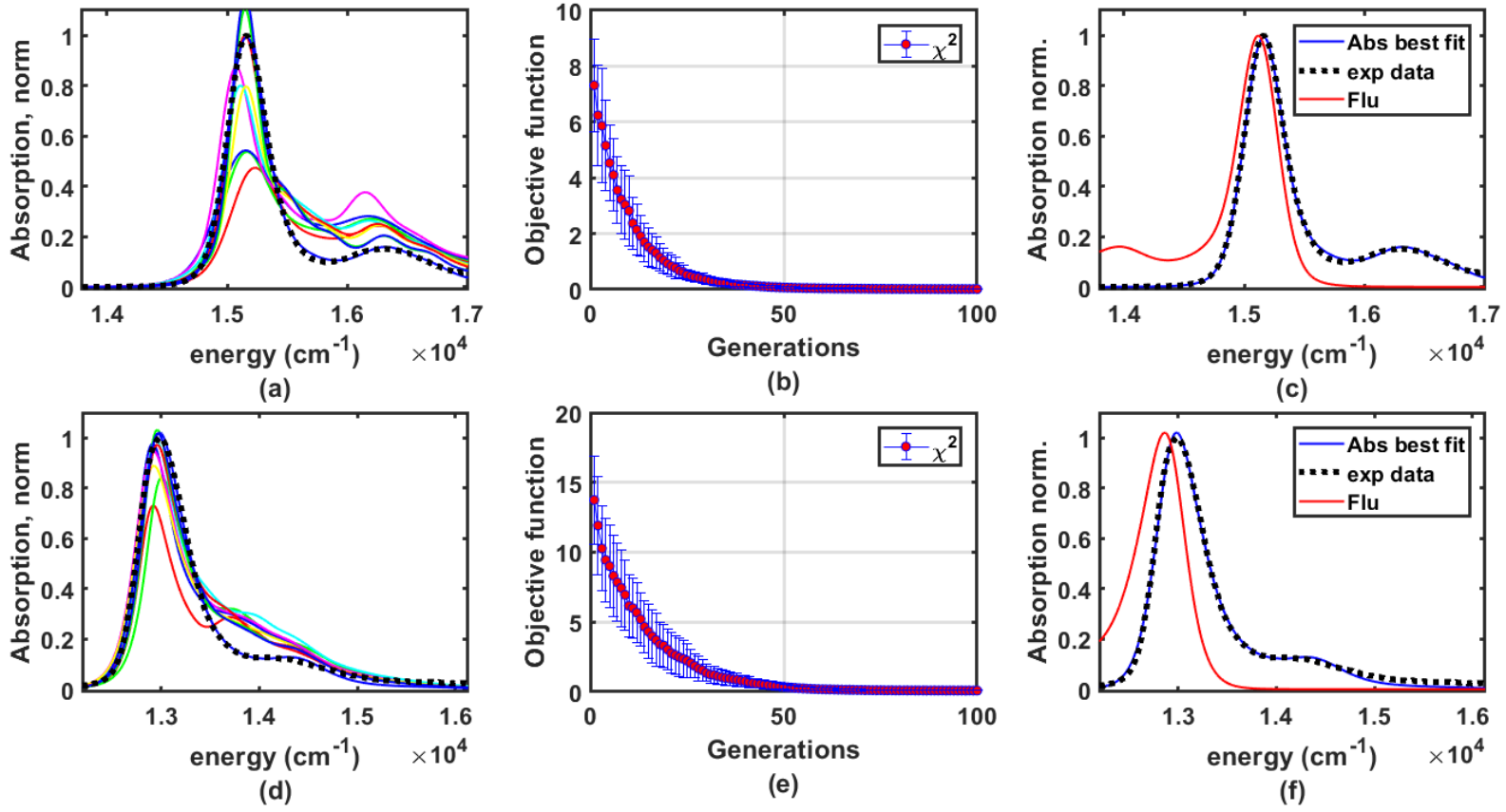
	Strategy	χ^2
a	DE/best/1/exp	6.0322e-10
b	DE/rand/1/exp	2.6456e-08
c	DE/rand-to-best/1/exp	2.6456e-08
d	DE/best/2/exp	3.8145e-08
e	DE/rand/2/exp	*2.4048e-07*
f	DE/best/1/bin	1.3473e-10
g	DE/rand/1/bin	1.6287e-08
h	DE/rand-to-best/1/bin	3.4160e-09
i	DE/best/2/bin	2.5890e-09
j	DE/rand/2/bin	1.6362e-09



Two sets of free parameters and the final values for the best fitting of the experimental data

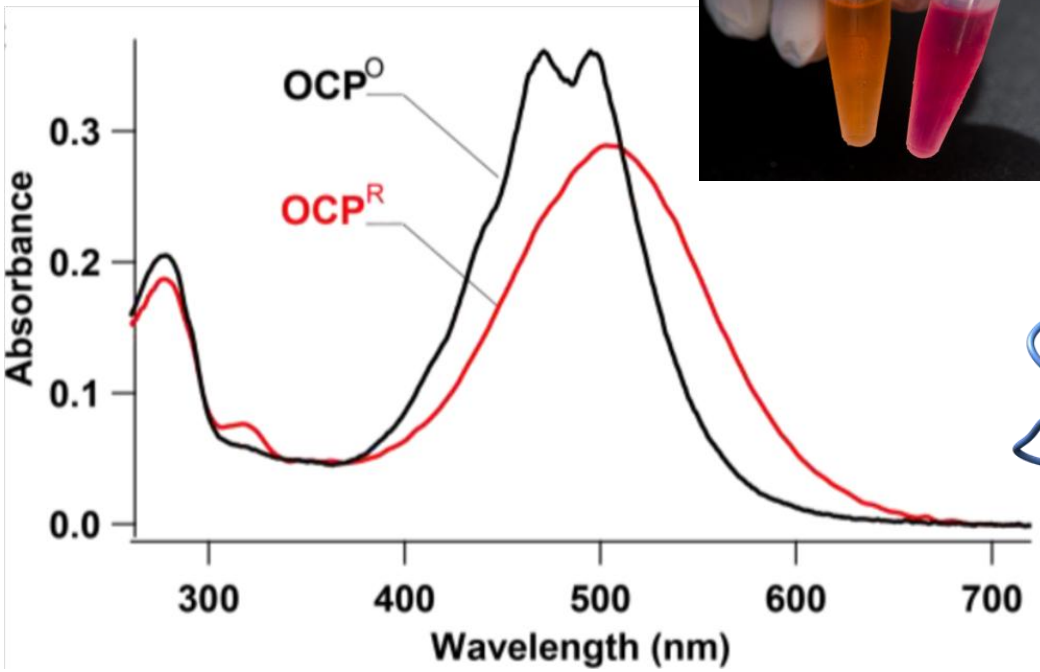
	Chlorophyll			Bacteriochlorophyll		
vector, x_j	initial constraints		the best fit	initial constraints		the best fit
	B_j^{lower}	B_j^{upper}		B_j^{lower}	B_j^{upper}	
Ω_{eg}	13500	17500	15544.89	12195	16130	13306.26
$FWHM_0$	50	450	305.78	50	350	298.48
ω_0	30	90	72.09	20	90	53.56
ω_1	60	140	134.14	80	150	143.99
γ_0	20	40	36.66	20	90	50.81
γ_1	1	10	7.02	1	10	1.7325
S_0	0.1	0.9	0.1674	0.05	0.9	0.1819
S_1	0.01	0.1	0.0657	0.001	0.1	0.0312
S_2	0.01	0.1	0.0266	0.001	0.1	0.0215
S_3	0.01	0.1	0.0331	0.001	0.1	0.0899
S_4	0.01	0.1	0.0001	0.001	0.1	0.0316
S_6	0.01	0.1	0.0002	0.001	0.01	0.0055
S_8	0.01	0.1	0.0000	0.001	0.01	0.0113
S_{10}	0.01	0.1	0.0001	0.001	0.01	0.0024
S_{12}	0.01	0.1	0.0000	0.001	0.01	0.0100
S_{14}	0.01	0.1	0.0006	0.001	0.01	0.0042
S_{16}	0.01	0.1	0.0003	0.001	0.01	0.0047
S_{18}	0.01	0.1	0.0011	0.001	0.01	0.0006

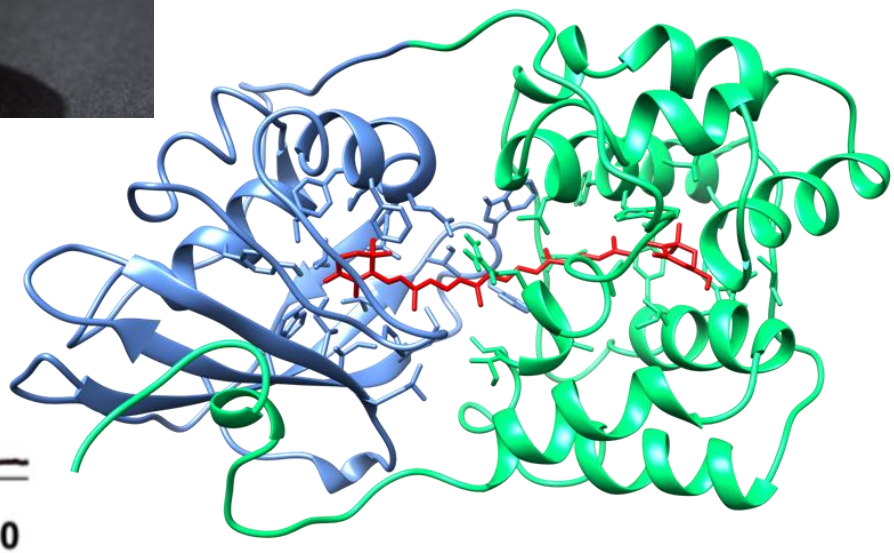
Results of Chlorophyll (upper plots) and Bacteriochlorophyll (lower plots) Qy band absorption spectrum modelling



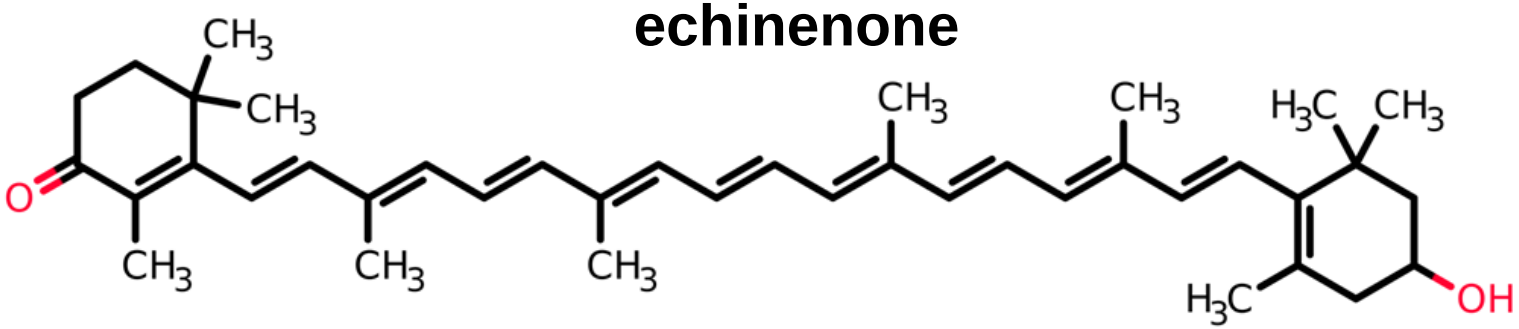
The best solution shown after 100 generations. The used strategy is DE/best/1/bin; F=0.6, Cr=0.9.

Orange Carotenoid Protein (OCP)



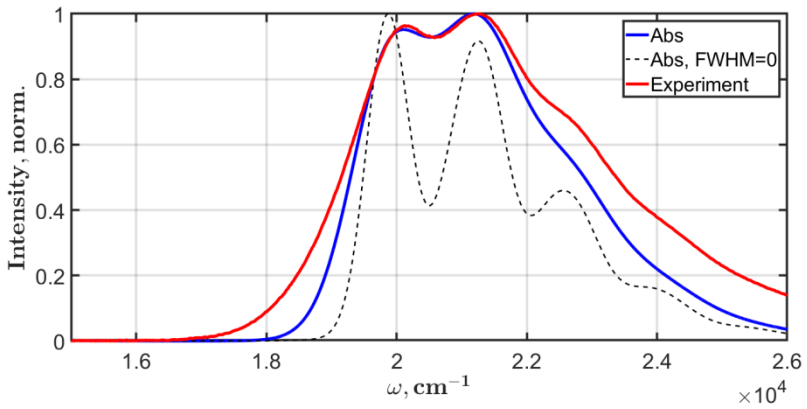


echinenone

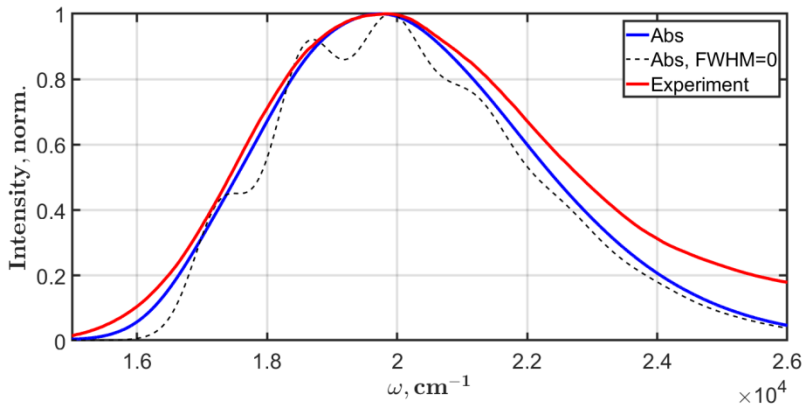


The best solution for the Orange Carotenoid Proteins in orange and red states

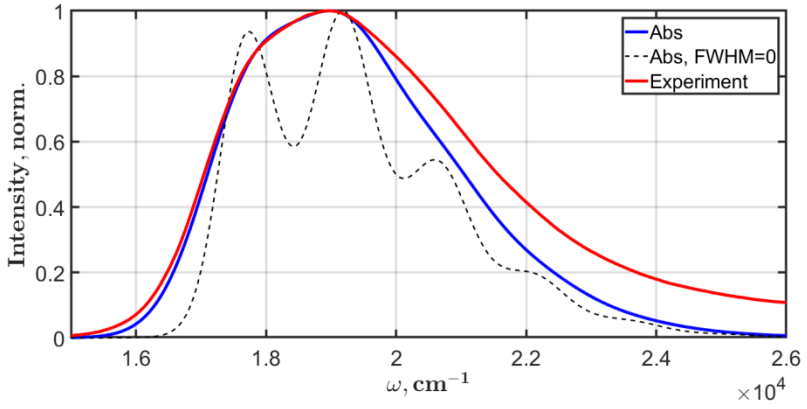
OCP orange (echinenone)



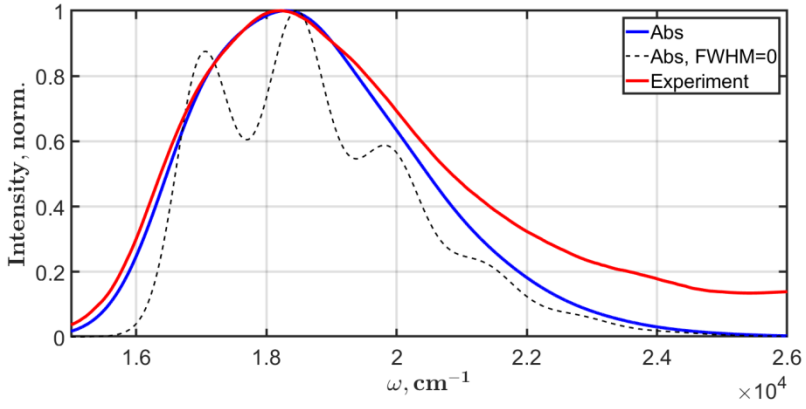
OCP red (echinenone)



OCP AA (canthaxanthin)



COCP (canthaxanthin)



	Ω_{eg}	$FWHM_0$	ω_{low}	S_{low}	γ_{low}	S_{γ_1}	S_{γ_2}	S_{γ_3}	S_{γ_4}
WT O	21402.0	1112.0	152.0	1.8	400.0	0.65	0.25	0.1	0.12
WT R	20310.0	1407.0	250.0	2.0	400.0	0.94	1.0	0.2	0.11
AA	19403.0	1420.0	260.0	1.8	400.0	0.9	0.1	0.1	0.04
COCP	18798.0	1506.0	260.0	1.8	400.0	0.88	0.2	0.1	0.05

Computational facilities

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http://parallel.ru

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