

COHERENT ENERGY TRANSFER IN THE FMO COMPLEX

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The Fenna-Matthews-Olson (FMO) pigment-protein complex of green sulfur bacteria is one of the most studied natural light harvesting complexes. Recently it has been found that its energy transfer mechanism features quantum phase coherence [1]. This energy transfer regime, due to non-negligible contributions from the electronic coupling between chromophores and from the electron-nuclear coupling characterized by the reorganization energy, is highly interesting, since it naturally interpolates between the classical and quantum behaviours. In fact case the excitation can still move in space in a deterministic, classical way, but a preferred path is chosen because the wavefunction is partially delocalized and phase information can be coherently transferred through space [2].

Standard theoretical approaches for treating the dynamics of these systems utilize semiclassical methods in which the excited state energy is assumed to “hop” between discrete energy levels, however these treatments inherently ignore the effects of coherence and ultimately fail to capture important aspects of the physics of these systems. More recently, several perturbation theory based methods have been developed to account for the effects of coherence in quantum systems. However they rely on the assumption that the relative magnitudes of the coupling between the chromophores and the environment can be quite disparate, while experiments suggest that both are appreciable and no such separation of scales should be possible.

In the group of Prof. Coker they have developed a new non-perturbative method [3] that makes no inherent assumptions about the relative magnitudes of the coupling involved. The Iterative Linearized Density Matrix (ILDm) approach, propagates the reduced density matrix non-adiabatically using a mixed quantum-classical approach. The result is a microscopic interpretation of the exciton evolution as described by the time-dependent reduced density matrix. The method allows to relax the model restrictions on the system-bath interaction, and gives a more realistic representation of the light harvesting systems discussed above.

The model Hamiltonian for the generalized excitonic system is given by:

$$\hat{\mathcal{H}} = \frac{1}{2} \sum_{n=1}^N (\hat{p}_n^2 + \omega_n^2 \hat{x}_n^2) + \sum_{\alpha} \left\{ \left[\epsilon_{\alpha} + \sum_n c_{n,\alpha} \hat{x}_n \right] |\alpha\rangle\langle\alpha| \right\} + \sum_{\alpha < \alpha'} \left[\Delta_{\alpha,\alpha'} + \sum_n c_{n,\alpha,\alpha'}^{\Delta} \hat{x}_n \right] (|\alpha\rangle\langle\alpha'| + |\alpha'\rangle\langle\alpha|),$$

in the exciton (or site) basis $|\alpha\rangle$; both site energies (ϵ_{α}) and inter-chromophore couplings ($\Delta_{\alpha,\alpha'}$) are expanded about the protein environment equilibrium

geometry to linear order in the bath oscillator coordinates \hat{x}_n . The system–bath linear coupling comes from the spectral densities $J_\alpha(\omega)$ using the fact that $J_\alpha(\omega) = \pi/2 \sum_{n=1}^N \delta(\omega - \omega_n) c_{n,\alpha}^2 / \omega_n$. $J_\alpha(\omega)$ is given by the Fourier Transform of the site energies correlation function $C_\alpha(t) = \langle \delta\epsilon_\alpha(0) \delta\epsilon_\alpha(t) \rangle$.

The objective of the research project started during my stay in Dublin is to obtain the spectral density from mixed MM and QM calculations. In particular, the MM stage consists in propagating the dynamics of the FMO trimer during few picoseconds (for the moment only 20 ps). Trajectories are stored every 5 fs and the site energy of each chromophore is then calculated with techniques dealing with excited states (see below). Since such kind of calculations are not affordable by considering the whole protein, QM calculations are performed only on the chromophores, and the effect of the protein environment is taken into account by computing the electric field produced by the MM charges of the environment.

The main concern about this project is related to finding a good compromise between the reliability of the technique for excited state calculations and the computational time required. In the two weeks of my stay in Dublin I made calculations both with semiempirical and time dependent DFT techniques. The latter is far more sound in terms of underlying theory, but it is also very time consuming. On the other hand, semiempirical calculations have proven to work satisfactorily and to be at least 10 times faster than TD-DFT. The two techniques give results in agreement both for the transition dipole moments and for the site energies correlation functions ($C_\alpha(t)$) but different absolute values for the site energies. Semiempirical calculations perform better in the comparison to experiment in determining the excitation energy.

I am now extending my studies to see if the two approaches lead eventually to similar features of the spectral density. Once devised a reliable and cheap way of making the calculations, we plan to apply it to all chromophores. It would be the first time that quantum dynamics is propagated using a different spectral density for each site. Eventually we expect to get a more realistic model of this system, which would be published on some physical chemistry journal.

Though my stay has been quite short, it has indeed been very productive for what concern the results obtained. The work environment in Prof. Coker's group is very nice and stimulating. I am currently applying for a Marie Curie fellowship to collaborate further on this exciting and innovative research field.

REFERENCES

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