Quantum dynamics of electronic excitations in biological chromophores: Models for the influence of the protein and solvent environment

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Statement of Originiality

Except where otherwise acknowledged and referenced in the customary manner, the material presented in this thesis is, to the best of my knowledge, original and has not been submitted in whole or part for a degree in any university.

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List of Publications

Papers forming part of this thesis


Papers related to this thesis but not forming part of it


Abstract

This thesis presents minimal quantum mechanical models for the interaction between electronic excitations in a chromophore with its surrounding environment, including protein, bound water and bulk solvent. The interaction of the chromophore’s electric dipole moment with the fluctuating electric dipole moments of the solvent and protein molecules is shown to be described by an independent boson model. An explicit microscopic derivation is given for the spectral density through a fluctuation-dissipation relationship. Continuum dielectric models are used to describe the protein and solvent. Several models are proposed for the structure of the protein and bound water around the chromophore, and spectral densities are obtained analytically for each case. These spectral densities depend only on measurable quantities, in particular the relaxation times of the environment, which are generally obtainable from experiment or simulation.

In most cases, the relaxation times of the solvent, bound water and protein are widely separated and it is shown that individual contributions to the total spectral density can then be identified for each of these features. Current methods for obtaining the spectral density from molecular dynamics simulations and experiments such as the dynamic Stokes shift and three pulse photon echo spectroscopy are examined, and a survey of recent results is undertaken. Minimal models are used to provide a natural explanation and model for the different time scales observed in the extracted spectral densities, and suggest physical processes corresponding to experimental peaks.

In many situations, it is found that only one aspect of the environment is important for the quantum dynamics. The relative contribution of each component is determined by the
time scale on which one is considering the quantum dynamics of the chromophore. Results are then compared to those obtained for specific chromophores in specific proteins. The effect of the protein on ultrafast solvation is also considered.

The models are then extended to two optically active molecules coupled by resonance energy transfer. When only a single excitation is present, the transfer dynamics of the excitation is shown to be described by the spin-boson model, with a spectral density given by the sum of the spectral densities of the individual chromophores. The dynamics of such systems are investigated and quantitative criteria are given for the presence of quantum coherent oscillations of excitations between the chromophores. Experimental tests to confirm these results, and to investigate the quantum-classical crossover between coherent and incoherent transfer, are proposed through the use of Fluorescent Resonant Energy Transfer (FRET) spectroscopy. The results are then applied to systems of coupled chlorophyll molecules in the photosynthetic reaction centre.

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4.1 Behaviour of $P(t) = \langle \sigma(z)(t) \rangle$ for the spin-boson model, which gives the state of the two level system as a function of time $t$, for $\epsilon = 0$ and $\Delta \ll \hbar \omega_c$, where $\Delta$ is the tunneling strength and $\omega_c$ is the high frequency cut-off of the spectral density $J(\omega)$. “loc” refers to localisation, “coh” to damped coherent oscillations and “inc” to incoherent behaviour i.e., exponential decay. $T$ is the temperature of the system and $\alpha$ is the dimensionless coupling constant of the chromophores to the environment as defined in Equation (1.16). $\tau$ refers to the relaxation rate in the expression $P(t) = \exp(-t/\tau)$. The analytic form of $P(t)$ is given where known, and is generally valid only for timescales longer than $1/\omega_c$. $\Delta_r = \Delta(\Delta/\hbar \omega_c)^{\alpha/(1-\alpha)}$. 

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List of Abbreviations

BChl  Bacteriochlorophyll
FRET  Fluorescent Resonance Energy Transfer
GFP   Green fluorescent protein
HOMO  Highest Occupied Molecular Orbital
LH-I  Light harvesting complex I
LH-II  Light harvesting complex II
LUMO  Lowest Unoccupied Molecular Orbital
PSU   Photosynthetic unit
PYP   Photoactive yellow protein
RC    Reaction centre
RET   Resonance Energy Transfer
TLS   Two level system