Electronic Energy transfer in light-harvesting antenna complexes

by

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Abstract

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The studies presented in this thesis explore electronic energy transfer (EET) in light-harvesting antenna complexes and investigate the role of quantum coherence in EET. The dynamics of energy transfer are investigated in three distinct length scales and a different formulation of the exciton transport problem is applied at each scale. These scales include: the scale of a molecular dimer, the scale of a single protein and the scale of a molecular aggregate.

The antenna protein phycoerythrin 545 (PE545) isolated from the photosynthetic cryptophyte algae *Rhodomonas* CS4 is specifically studied in two chapters of this thesis. It is found that formation of small aggregates delocalizes the excitation across chromophores of adjacent proteins, and that this delocalization has a dramatic effect in enhancing the rate of energy transfer between pigments. Furthermore, we investigate EET from a donor to an acceptor via an intermediate site and observe that interference of coherent pathways gives a finite correction to the transfer rate that is sensitively dependent on the nature of the vibrational interactions in the system.

The statistical fluctuations of a system exhibiting EET are investigated in the final chapter. The techniques of non-equilibrium statistical mechanics are applied to investigate the steady-state of a typical system exhibiting EET that is perturbed out of equilibrium due to its interaction with a fluctuating bath.
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Chapter 1

Photosynthetic light-harvesting and evidence of coherent energy transfer

1.1 Introduction

Photosynthesis is the process by which plants and algae convert solar energy into biomass thereby generating the bio-fuel required for sustaining life on the planet. The details of the process vary in different species of plants, algae and photosynthetic bacteria, but several common features can be attributed to all photosynthetic species. The first step in solar light-harvesting is the absorption of sunlight by special macro-molecules known as light-harvesting antenna complexes. These are pigment-protein complexes that are comprised of a number of light-absorbing molecules embedded in a protein scaffold. The antenna is an integral part of the photosynthetic machinery and acts much like a satellite dish: capturing the sunlight, storing it as electronic excitations, and transferring the excitation to the photosynthetic reaction centre (RC), as depicted in Fig. 1.1. The excitation is transported over distances of tens of nanometers via a process known as resonant energy transfer (RET). In the reaction centre the excitation is quenched, releasing an electron, and creating a charge gradient across the photosynthetic
membrane. Electron transfer across the membrane is accompanied by proton transfer (from the lumen to the stroma), and the resulting electrochemical potential provides the energy source for ATP synthesis.

Antenna complexes are remarkably diverse, to the extend that photosynthetic organisms can be classified based on the structure of their antennas [1]. There are a number of antennas which bare no resemblance to each other, as far as structure and pigment-types are concerned, suggesting that there must have been independent evolutionary origins leading to the development of light-capturing units. This is an example of ‘convergent evolution’: the ability for organisms evolved in isolation to arrive at the same survival strategies, and highlights the importance of light-absorbing units in photosynthesis.

Figure 1.1: Schematics of energy absorption, transfer and delivery in photosynthetic cryptophyte algae. Energy is absorbed by special pigments in the light-harvesting complex and transferred to the reaction centre via a series of hops. In the reaction centre the excitation is quenched, releasing an electron and creating a charge gradient across the membrane.

Transfer of energy between the light-absorbing macro-molecules is promoted via a long-range resonant interaction between the electrons in the excited state of the donor
molecule and the ground state of the acceptor molecule. This is an electrodynamic interaction and will be explained in some detail in the section 1.2.1. When the molecules are sufficiently far apart, the interaction can be approximated by a dipole-dipole coupling. The interaction is referred to as the coupling matrix element or the electronic coupling in the literature. For resonant molecules, the electronic coupling alone is sufficient to promote the transfer of energy. For off-resonant molecules however, the process would violate energy conservation, and a second compensating interaction is required. This second interaction is between the electronic and the environmental degrees of freedom, and has the effect of broadening the electronic spectra, or inducing uncertainty in the energy of the molecules. If the spectra are sufficiently broadened such that there is an overlap between the emission spectra of the donor and the absorption spectra of the acceptor, electronic energy transfer (EET) can still take place. The normal (vibrational) modes of the chromophores, as well as the vibrations of the surrounding solvent and the protein backbone, are the two major contributors to the spectral broadening. For this reason electronic energy transfer is often refereed to as a ‘phonon-assisted’ process.

Förster resonance energy transfer was the first successful quantitative description of EET between nearby molecules [2] and can describe the characteristic features of EET in photosynthetic antenna. It provides a phenomenological description of energy transfer and an associated expression for computation of the transfer rates. The Förster formula for the rate of energy transfer between two molecules in the simplest case can be expressed as

\[ k = \frac{2\pi}{\hbar} |J|^2 S \]  

where \( J \) is the electronic coupling and \( S \) is the spectral overlap between the emission spectrum of the donor molecule and the absorption spectrum of the acceptor. The electronic coupling in the dipole approximation is given by

\[ J = \frac{1}{4\pi\epsilon_0} \frac{\mu_1 \cdot \mu_2}{R^3} \]
where $R$ is the centre to centre separation between the molecules, and $\mu_i$ is the transition dipole moment of molecule $i$.

Owing to the fact that all parameters pertaining to the influence of the solvent and the vibrational modes can be obtained from an spectral overlap, transfer rates can be computed without a knowledge of the microscopic attributes of the system. This has led to the wide popularity of Förster theory in spectroscopic studies of energy transfer, and the theory has successfully been applied to describe EET in a variety of systems including conjugated polymers, quantum dots and organic solar cells [3]. An early application of the theory to EET in photosynthetic purple bacteria was reported in 1951 [4]. The theory has since been modified to describe energy transfer not only between individual pigments [5], but also among extensive light-harvesting networks with hundreds of proteins and thousands of pigments [6, 7].

Modifications to the theory were necessary as the original derivation by Förster made a number of key assumptions that are almost never met in natural light-harvesting complexes [8]. The first assumption is with regards to the electronic coupling: the theory assumes that the molecules are sufficiently far apart for the interaction between them to be approximated by a dipole-dipole coupling. Moreover, it assumes that this coupling is sufficiently small such that the resulting perturbation in the emission spectra of the donor or the absorption spectra of the acceptor is negligible. The second assumption is with regards to the nature of the energy transfer process. Förster theory assumes that energy transfer is an incoherent hopping process and the excitation is localized on individual molecules at any instant of time.

In many photosynthetic systems groups of pigments can be closely packed, such that the distance between the molecules is of the order of the molecular size. Under such circumstances the excitation is shared (delocalized) among a number of pigments. This invalidates a number of assumptions invoked in the Förster formula. Generalizations of the Förster theory where the donor and the acceptor are assumed to be groups of
molecules can still be applied in many of these circumstances [9, 10, 5]. Generalized Förster theories (GFTs) assume that the transfer is still incoherent, but provide a concrete recipe for computation of transfer rates under realistic conditions, where energy migrates between groups of molecules. In this approach the coupling within an aggregate can take any value, whereas the inter-aggregate coupling is still weak to rationalize the incoherent hopping mechanism. Moreover, failure of the dipole approximation implies that more sophisticated treatments are required to compute the electronic coupling between the molecules [5].

Although GFT remains to be the most successful quantitative EET theory as far as the computation of the transfer rates are concerned, it provides little insight with regards to the dynamics of the transfer process. Moreover, at the heart of Förster theory - and all its generalizations - lies the fundamental assumption of incoherent dynamics. In other words, EET is assumed to proceed via a sequence of random, uncorrelated hops among the pigments. There are, however, examples of EET in photosynthesis where the very notion of an incoherent hopping mechanism has been challenged; suggesting that new ways of thinking may be required to understand their intricate machinery.

This chapter is organized as follows: in section 1.2 we review the physics of RET from a quantum electrodynamical perspective and derive the Förster rate as the short-range limit of a unified theory of EET. Theoretical modelling of photosynthetic networks is briefly discussed in 1.2.3. The chromophore-solvent interactions are introduced in 1.2.4. In section 1.3 we highlight some of the intriguing experimental evidence which point to the importance of non-trivial quantum effects in photosynthesis. The lessons learnt from these experiments ultimately motivate the idea of modelling photosynthetic antennas as open quantum systems, the prime objective of the present thesis. Much of the investigations in this thesis have been focused on modelling the antennas protein phycoerythrin 545 (PE545), isolated from the photosynthetic cryptophyte algae *Rhodomonas* CS24. Antenna complexes in cryptophyte algae are discussed in some detail in section 1.4.
Organization of the remaining chapters are as follows: in chapter 2 we focus on a system of two molecules exhibiting EET and provide a solution for the dynamics of the reduced density matrix of the electronic subsystem. In chapter 3 we consider the role of path interference in EET within the framework of a perturbative treatment and apply the formalism to the photosynthetic protein, phycoerythrin 545 (PE545). In chapter 4 we consider EET on the scale of a molecular cluster and provide a comparison of two different formulations of EET. In chapter 5 we consider a typical system exhibiting EET and investigate the statistical fluctuations that arise from environmental perturbations. Chapter 6 is a summary of the conclusions.

1.2 Förster theory and modeling of photosynthetic complexes

1.2.1 The QED nature of the electronic coupling

Energy transfer over distances beyond wavefunction overlaps demands a resonant transfer mechanism whose correct description can only be obtained within the framework of quantum electrodynamics (QED). QED states that EET is mediated via the emission and absorption of virtual photons: messenger particles that cannot be detected directly, but facilitate the donor decay and the acceptor excitation [11, 12, 13]. Following the approach of Andrews and Bradshaw [12], in this section we discuss how a unified theory of EET can be achieved within the framework of QED.

The non-relativistic Hamiltonian of a system consisting of atoms or molecules is given by

$$H = H_{\text{mat}} + H_{\text{rad}} + H_{\text{int}}$$  \hspace{1cm} (1.3)

where $H_{\text{mat}}$ is the matter Hamiltonian, $H_{\text{rad}}$ is the radiation Hamiltonian, and $H_{\text{int}}$ represents the interaction of the radiation field with the molecules, which in turn mediates
the interaction between the donor and the acceptor. The exact form of the interaction is given by

\[ H_{\text{int}} = \frac{e^2}{4\pi \epsilon_0} \sum_{pq} \frac{1}{|r_{pq}|} \tag{1.4} \]

where the summation is carried out over the charge distribution of the electrons as illustrated in Fig. 1.2. The separation between the electrons is related to the position vectors via the relation

\[ r_{pq} = (R_i - R_j) - (r_q - r_p). \tag{1.5} \]

Assuming that \(|R_i - R_j| \gg |r_p - r_q|\) the interaction can be written in a multipolar expansion \([14, 15]\)

\[ H_{\text{int}} = -\sum_i \mu_i.E^\perp(r_i) - \sum_i m_i.B(r_i) + ... \tag{1.6} \]

where \(\mu_i(m_i)\) is the electric (magnetic) dipole moment operator for molecule \(i\), \(E^\perp(r_i)\) is the transverse electric field operator at \(r_i\), and \(B(r_i)\) is the magnetic field operator at \(r_i\). This approximation states that the charge distribution of molecule A generates an electric field which induces a transition dipole moment on molecule B. EET is often associated with the electric dipole transitions in both the donor and the acceptor. In instances where the donor and acceptor transitions are dipole forbidden, the magnetic dipole coupling becomes the principle transfer mechanism \([16]\). In this section we suffice on considering the electric dipole coupling. The formalism can equivalently be applied to magnetic dipole transitions \([12]\).

In an EET process involving the electric dipole allowed transitions, the initial and final states may be written as

\[ |i\rangle = |\psi_\alpha^A; \psi_0^B\rangle \otimes |0\rangle \tag{1.7} \]

\[ |f\rangle = |\psi_0^A; \psi_\beta^B\rangle \otimes |0\rangle \tag{1.8} \]

where the superscript 0 indicates the ground energy level, with \(\alpha\) and \(\beta\) representing the excited states for the donor and acceptor respectively. The zero ket indicates the state of the radiation field. The process thus involves the creation and annihilation of a single
Figure 1.2: Schematic diagram of the donor, the acceptor and the relevant position vectors. \( r_p \) and \( r_q \) are the position vectors of the electrons with respect to the centre of mass of the molecules.

photon, described by the field operators \( a_k^\dagger \) and \( a_k \), where the subscript \( k \) indicates the particular field mode into which the photon is emitted. There are two Feynman diagrams associated with this process corresponding to the different orderings of the operators: a) creation of a virtual photon at A and its subsequent annihilation at B, b) vice versa. The Feynman diagrams of these two pathways are represented in Fig. 1.3. The latter pathway appears somewhat implausible as it indicates the propagation of a photon from the acceptor to the donor. Due to the virtual nature of the photon, this property is not problematic and the theory demands the addition of the quantum amplitudes of both pathways. The coupling matrix element that enables the transfer of energy is given by

\[
J = \langle i | H_{\text{int}} | f \rangle. \tag{1.9}
\]

In second order time-dependent perturbation theory, the coupling is approximated as

\[
J = \sum_r \frac{\langle f | H_{\text{int}} | r \rangle \langle r | H_{\text{int}} | i \rangle}{E_i - E_r} \tag{1.10}
\]

where \( \sum_r \) represents a summation over all intermediate states. \( E_i \) and \( E_r \) are the energies of the initial and the intermediate states respectively. After expressing the electric field as a summation of field modes and performing the necessary sums (over the two intermediate states as well as all possible modes into which the photon may be emitted), it can be
demonstrated that the coupling $J$ takes the form

$$J = \mu_0^{\alpha}(A) U_{ij}(k, R) \mu_0^{\beta}(B)$$

(1.11)

where the transition dipole moment is defined to be

$$\mu_0^{\alpha}(A) = \langle \psi_0^A | \mu_A | \psi_0^A \rangle.$$  

(1.12)

$U_{ij}(k, R)$ is the dipole-dipole coupling tensor and includes the orientational factors,

$$U_{ij}(k, R) = \frac{e^{ikR}}{4\pi\epsilon_0 R^3}\left\{ (\delta_{ij} - 3 \hat{R}_i \cdot \hat{R}_j) - (ikR)(\delta_{ij} - 3 \hat{R}_i \cdot \hat{R}_j) - (kR)^2(\delta_{ij} - \hat{R}_i \cdot \hat{R}_j) \right\}.$$  

(1.13)

In this expression $R$ is the centre to centre separation between the molecules and direction of the unit vectors $\hat{R}_i$ and $\hat{R}_j$ are illustrated in Fig. 1.2. We are now in a position to compute the transfer rate $k_{A\rightarrow B}$. By Fermi’s golden rule the transfer rate is given by

$$k_{A\rightarrow B} = \frac{2\pi}{\hbar} |J|^2 \delta(E_A - E_B)$$

(1.14)

Due to the vibrational motion of the surrounding environment at finite temperature, the delta function may be replaced by the spectral overlap factor $S$ [17]

$$S = \int_{-\infty}^{\infty} F_d(\epsilon) A_d(\epsilon) d\epsilon$$

(1.15)
where \( F_d(\epsilon) \) is the normalized emission spectra of the donor and \( A_a(\epsilon) \) is the normalized absorption spectra of the acceptor. Note that the terminology ‘spectral overlap’ could be misleading, since \( J \) does not equate the overlap integral of the two spectra, although it does vanish if the overlap integral is zero. For two freely rotating molecules Eq. (1.14) also demands a rotational averaging [18]. We arrive at the following expression for the transfer rate

\[
k_{A \rightarrow B} = \frac{4\pi}{9\hbar} \left( \frac{9\hbar}{(4\pi \epsilon_0 R^3)^2} \right) S \cdot \left( 3 + (kR)^2 + (kR)^4 \right)
\]

The first term dominates at short-range and is the Förster rate for ‘radiation-less’ transitions. The last term dominates at large separations and has the \( R^{-2} \) dependence of the classical inverse square law of radiative transfer. The radiative and radiation-less transfer are thus the limiting cases of a single unified description.

### 1.2.2 Failure of the multipolar expansion

The derivation in section 1.2.1 assumes that the molecules are sufficiently far apart for the interaction to be expressed as a multipolar expansion. This approximation becomes problematic in instances where the donor-acceptor separation is comparable to the molecular size. In extended molecular assemblies such as light-harvesting complexes [19, 17], or elongated systems such as carbon nano-tubes [20], conjugated polymers [21] and quantum rods [22], the geometry and the relative orientations must be carefully considered and multipolar approximations are to be entirely avoided. In such instances the coupling matrix element \( J = \langle \psi_A^\alpha; \psi_B^0 | H_{\text{int}} | \psi_A^0; \psi_B^\beta \rangle \) must be computed directly from the Coulomb interaction

\[
H_{\text{int}} = \frac{e^2}{4\pi \epsilon_0} \sum_{pq} \frac{1}{|\mathbf{r}_{pq}|}
\]

The electronic coupling is therefore given by the following integral

\[
J = \frac{1}{4\pi \epsilon_0} \int d\mathbf{r}_p d\mathbf{r}_q \rho_D(\mathbf{r}_q) \rho_A(\mathbf{r}_p) \frac{\rho_D(\mathbf{r}_q) \rho_A(\mathbf{r}_p)}{|\mathbf{r}_{pq}|}
\]
where $\rho_A(r_p)$ and $\rho_B(r_q)$ are the transition densities

$$\rho_A(r_p) = e\psi_A^0(r_p)\psi_A^\alpha(r_p)$$

(1.19)

$$\rho_B(r_q) = e\psi_B^0(r_q)\psi_B^\alpha(r_q)$$

(1.20)

Given the spatial distribution of the molecular wavefunctions, Eq. (1.18) can be evaluated computationally. Given the molecular wavefunctions, and a knowledge of the crystal structure of the molecules, the electronic couplings can be computed with arbitrary precision.

### 1.2.3 Modelling of EET in multi-chromophoric systems

**Electron-nuclear Hamiltonian in EET**

Photosynthetic complexes can be modelled by considering the electronic degrees of freedom, the environmental (bath) degrees of freedom, and the interaction between the two. The environmental degrees of freedom describe the electron-nuclear interactions where the nuclei can be those of the chromophores, or of the surrounding solvent, or the protein scaffolding. The combined Hamiltonian is therefore a summation of these contributions

$$H = H_e + H_b + H_{int}.$$  

(1.21)

The electronic degrees of freedom constitute the ground and the first excited electronic state of the individual chromophores. Higher excited states are short-lived and relax non-radiatively to the lowest excited state which then emits. This effect that only the lowest excited state lives long enough to emit fluorescence is called Kasha’s rule [23].

For instance when the Soret band of chlorophyll is excited in the blue, the emission is observed in the red. This lowest excited state is a spin singlet ($S_1$), and is involved in the primary photochemical processes of photosynthesis (from absorption of a photon to charge transfer in the reaction centre) [1]. Triplet states are important in photo-protective
processes but are not involved in the primary events and will not be discussed in this thesis.

It can be shown that under illumination by sunlight, the probability of having more than one excitation in the system is negligible. The active subspace is thus the subspace in which one molecule is excited and the rest are in the ground state. The single excitation can, however, be coherently shared between multiple molecules. The interaction $J_{ij}$ couples the ground state of molecule $i$ to the excited state of molecule $j$ and vice versa. The electronic and the electron-nuclear interactions are described by the following Hamiltonian [24]

$$H_e + H_{int} = \sum_i \epsilon_i(x)|i\rangle\langle i| - \sum_{i \neq j} J_{ij}|i\rangle\langle j|$$

where $x$ represents the nuclear coordinates and $\epsilon_i(x)$ is the nuclear-dependent energy gap between the ground and excited state potentials at molecule $i$. The ket $|i\rangle$ is the state in which molecule $i$ is excited and the rest of the molecules are in the ground state. In general, the interaction $J_{ij}$ is also dependent on the nuclear coordinates, but the changes in $J_{ij}$ tend to be small and variations in the energies are the dominant electron-nuclear interactions. The nuclear dependent electronic energy can be expanded for small nuclear perturbations

$$\epsilon_i(x) \simeq \epsilon_i + \frac{\partial \epsilon_i}{\partial x_i}|_{\bar{x}_i} x_i + \sum_{j \neq i} \frac{\partial \epsilon_i}{\partial x_j}|_{\bar{x}_i} x_j$$

where $\bar{x}_i$ is the equilibrium nuclear configuration of the ground electronic state of molecule $i$, and $\epsilon_i$ is the electronic energy difference between the ground and the excited electronic state of molecule $i$ evaluated at $\bar{x}_i$ (Fig. 1.4). In the literature this energy is referred to as the site energy. The third term represents variations of the electronic energy of molecule $i$ due to changes in the nuclei of molecule $j$. This change is comparatively small and can be neglected. The electronic and the electron-nuclear Hamiltonians can therefore be identified

$$H_e = \sum_i \epsilon_i|i\rangle\langle i| - \sum_{i \neq j} J_{ij}|i\rangle\langle j|$$
$H_{\text{int}} = \sum_{i} |i\rangle \langle i| \sum_{k} c_{ik} x_k$ \hfill (1.25)

The summation over $k$ indicates that a molecule can interact with multiple nuclear modes, and $c_{ik}$ is the coupling between site $i$ and the nuclear mode $x_k$. The variations in energy are therefore assumed to be linear with respect to small nuclear perturbations. This is a harmonic oscillator property and states that the nuclear potentials are harmonic for small deviations from the equilibrium nuclear position. The influence of the nuclei is thus modelled as a thermal bath of harmonic oscillators

$$H_b = \sum_{k} \left( \frac{p_k^2}{2m_k} + \frac{m_k\omega_k^2 x_k^2}{2} \right)$$ \hfill (1.26)

The nuclear (environmental) degrees of freedom include the stretching of the bonds within the individual chromophores, the interaction of the solvent and the biological fluids with the chromophores, and the vibrations of the protein scaffold. The frequencies and spectral densities of these modes can be determined via a combination of Raman spectroscopy (for inter-molecular vibrations) and spectral fitting (for solvent interactions). Normal modes of the chromophores appear as narrow peaks in the vibrational spectra. The remaining interactions appear as a broadband contribution to the spectra over a range of frequencies. Environmental interactions are discussed in more detail in the next section.

It is often convenient to identify the relevant nuclear coordinate(s), such as the bond length, and express the ground and the excited electronic potentials in terms of this coordinate

$$V_g(x) = \frac{1}{2} m \omega^2 (x - \bar{x}_g)^2$$ \hfill (1.27)

$$V_e(x) = \frac{1}{2} m \omega^2 (x - \bar{x}_e)^2 + (\epsilon_i - E_R)$$ \hfill (1.28)

Note that the ground and the excited state potentials have different equilibrium nuclear coordinates as indicated in Fig. 1.4. For the case of inter-molecular vibrations, for instance, this corresponds to stretching of the bonds upon electronic excitation. $E_R$ is the reorganization energy and indicates that due to the displacement of the two potentials, an electronically excited molecule finds itself in an excited vibrational state. The molecule
relaxes to the ground vibrational state of the excited state potential before it fluoresces to the ground electronic state. The reorganization energy often has two contributions, one due to the solvent and the other due to the vibrational modes of the chromophores

\[ E_R = E_R^{\text{sol}} + E_R^{\text{vib}} \]  

Both contributions result in broadening of the electronic spectra and a shift between the absorption and the fluorescence spectra. The solvent contribution will be discussed in detail in the section 1.2.4.

![Potential energy curves indicating absorption and fluorescence for a two-level molecule.](image)

**Figure 1.4:** Potential energy curves indicating absorption and fluorescence for a two-level molecule. \( V_g(x) \) and \( V_e(x) \) are the ground and the excited electronic surfaces, approximated as harmonic potentials. Excitations are vertical in accordance to the Franck-Condon principle. After excitation the molecule relaxes to the new equilibrium nuclear position, dissipating the excess energy. This energy difference is known as the reorganization energy \( E_R \).

The Hamiltonian is often represented in the second quantized notation, where the bath coordinates are replaced by the corresponding bosonic operators \( b \) and \( b^\dagger \), satiating the commutation relation \([b, b^\dagger] = 1\). The bath coordinate \( x_k \) is replaced by

\[ x_k = \frac{1}{\sqrt{2m_k\omega_k}} \left[ b_k + b_k^\dagger \right]. \]  

(1.30)
In this notation the total Hamiltonian is given by

\[ H = \sum_i |i\rangle \langle i| \left[ \epsilon_i + \sum_k \phi_{ik} \omega_k (b_k + b_k^\dagger) \right] - \sum_{i \neq j} J_{ij} |i\rangle \langle j| + \sum_k \omega_k b_k^\dagger b_k \]  \hspace{1cm} (1.31)

where \( \phi_{ik} \) is a dimensionless displacement that represents the strength of the coupling between mode \( k \) of the bath and molecule \( i \) and is related to the displacement of the ground and the excited state potentials. A convenient alternative notation is to replace the kets by exciton creation and annihilation operators:

\[ a_i^\dagger a_i = |i\rangle \langle i|, \text{ and } a_i^\dagger a_j = |i\rangle \langle j|, \]

where \( \{a_i^\dagger, a_i\} \) are the raising and lowering operators for site \( i \). This notation has been used in chapters 2, 3 and 4.

Eq. (1.31) is the starting point of modelling EET. Solving this equation in various limits and investigating the consequences of strong, weak and intermediate electronic coupling, are the prime objectives of the present thesis. Throughout this thesis we have assumed that the bath associated with different sites are identical and independent. Eq. (1.31) is however general and includes the possibility of shared bath modes. If each molecule is coupled to \( p \) bath modes, the summation \( \sum_k \) runs from \( k = 1 \) to \( k = np \), where \( n \) is the number of molecules. The bath modes \( b_k \), and the bath frequencies \( \omega_k \), therefore do not carry a site index.

In this notation, the reorganization energy associated to site \( i \) is given by

\[ E_R = \sum_k \phi_{ik}^2 \omega_k \]  \hspace{1cm} (1.32)

In spectroscopy, reorganization energy is proportional to the energy shift between the absorption and florescence of a molecule (stokes shift is twice the reorganization energy). The bath reorganization energy quantifies the electron-nuclear interaction and its size in comparison to the electronic coupling determines the operating regime of EET.
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Reduced density matrix

The reduced density matrix of the electronic degrees of freedom $\sigma(t)$, can be obtained by averaging over the environmental degrees of freedom

$$\sigma(t) = \text{Tr}_b\{\rho(t)\}$$  \hspace{1cm} (1.33)

where $\rho(t)$ is the total density matrix and $\text{Tr}_b$ indicates averaging over the environmental modes. For the Hamiltonian of Eq. (1.21) the reduced density matrix can be obtained from the Heisenberg equation of motion [25]

$$\frac{\partial \sigma(t)}{\partial t} = -i[H_e, \sigma(t)] - i\text{Tr}_b\left\{[H_{\text{int}} + H_b, \sigma(t)]\right\}$$  \hspace{1cm} (1.34)

Perturbative treatments are often utilized to solve Eq. (1.34). In the weak (electronic) coupling limit where excitations are localized to individual pigments, energy migration can be described as a sequence of uncorrelated hops among the pigments, with rates determined by the Förster formula. In this limit Eq. (1.34) is reduced to the classical rate equation,

$$\frac{dp_i(t)}{dt} = \sum_j k_{ji}p_j(t) - \sum_k k_{ik}p_i(t) - \left[ k_{\text{diss}} + \delta_{i,R}k_{cs}\right] p_i(t)$$  \hspace{1cm} (1.35)

where $p_i(t)$ is the probability that pigment $i$ is excited at time $t$, $k_{ij}$ are the Förster rates, $k_{\text{diss}}$ is the dissipation rate due to fluorescence decay, and $k_{cs}$ is the charge separation rate at the reaction centre. $k_{\text{diss}}$ and $k_{cs}$ are phenomenological loss terms that are added to the rate equation and are not present in Eq. (1.34). In this limit coherences are neglected and the bath influences the transfer rates through the spectral overlap factor.

In the opposite limit where the electronic coupling is strong, the eigenstates of the electronic Hamiltonian (excitons) are delocalized over a number of pigments. In this limit the influence of the bath is to induce jumps between the excitonic states. The dynamics are therefore a combination of coherent evolution of phases and incoherent jumps between the excitons. This limit will be discussed in chapters 4 and 5.
In a typical pigment-protein complex there are a range of electronic couplings, and the appropriate description must be chosen depending on our knowledge of the electronic and vibrational interactions. In many instances, however, the electronic and the vibrational parameters are of the same order and formulations of EET in the limiting cases are of little applicability. In general, one must chose a formulation depending on the time scale of interest: on the scale of a few femtoseconds, the system has not reached the steady-state and coherent effects are likely to be important. On the scale of a few hundred picoseconds however, the system has reached the steady-state and the average population of different sites, or the average rate of trapping, can be obtained via a course-graining approach.

In chapters 2 we consider EET between two molecules, and in chapter 3 we look at the dynamics at the scale of single proteins. On such scales coherent effects are important and a non-Markovian description of the environment is required. In chapter 4 energy transfer on the scale of a molecular cluster is considered, where the time taken for the excitation to diffuse is of interest. On this scale a course-grained treatment of the bath is adequate and the important factor is an accurate estimation of the transfer rates between the pigments.

1.2.4 Chromophore-bath interactions

The coupling of the electronic transitions to the nuclear degrees of freedom gives rise to dephasing in the time domain, or spectral broadening in the frequency domain. The nuclear degrees of freedom can be those of the chromophores, the protein scaffolding, or the solvent. Intra-chromophore electron-nuclear couplings are due to the interaction of the electronic transitions to the normal vibrational modes of the chromophores. As these modes correspond to stretching of specific bonds at well-defined frequencies, it comes as no surprise that the corresponding vibrational bath can be described as a set of harmonic oscillators. Vibrational coherence is created when superpositions of these modes are excited, and can only be described correctly if the normal vibrational modes
are included in the system Hamiltonian. However, a more common, and mathematically simpler formalism is to include them as part of the bath. Although this approach cannot reproduce vibrational coherence, it can still describe the influence of these modes on the spectral broadening. This is the approach that we will follow in the present thesis.

The electron-nuclear interactions arising from the solvent are less intuitive and demand further elaboration. In the previous section the solvent was modeled as a harmonic bath, but the physical origin of the harmonic modes was left undiscussed. In this section we discuss the origin of the harmonic approximation in the solvent Hamiltonian, asking the question: is the harmonic approximation merely an effective way of modeling friction, or do the harmonic modes correspond to physical oscillators? We begin by introducing the linear response theory, and demonstrating how the combination of this theory and the fluctuation-dissipation theorem, provides a framework for describing solvent relaxation. We then move on to state why a harmonic description of the bath recovers the results of the linear response theory.

The physical origin of harmonic oscillator modes are then discussed in the context of the instantaneous normal mode theory of solvation - a theory aimed at providing a molecular understanding of solvation by approximating the short-time motions in the molecular configurations as harmonic. The results of the instantaneous normal mode theory for water are subsequently discussed. As water is the relevant solute in photosynthetic proteins, the findings of this theory have direct validity to modeling of chromophore-solvent interactions.

The electron-nuclear interactions arising from the protein scaffolding have much the same character as the solvent interactions, expect that they constitute a medium of much higher viscosity. These interactions will not be discussed in this section as the solvent is expected to dominate the spectral broadening. However, much of the discussion on solvent relaxation can be applied to electron-nuclear interactions between the chromophores and the proteins coils.
Quantum linear response theory

To describe the linear response theory we change our viewpoint: we will not ask in what manner a system is influenced by a bath, but how the bath dynamics are modified by the system (see chapter 3 in Ref. [25]). The action of the system on the bath is thus viewed as a perturbation that is sufficiently small for linearization. Consider the following system-bath interaction

$$H_{\text{int}}(t) = \sum_u K_u(t) \Phi_u$$ (1.36)

where $\Phi_u$ are the bath operators, and $K_u(t)$ are the perturbative forces on the bath due to the system. The bath Hamiltonian plus the interaction assumes the form

$$H(t) = H_b + H_{\text{int}}(t)$$ (1.37)

where $H_b$ is unspecified. As a consequence of the action of the forces, the bath is driven out of equilibrium, but if the non-equilibrium state only deviates slightly from equilibrium, the deviation can be linearized with respect to the external perturbation, that is

$$\langle \Phi_u(t) \rangle = \sum_v \int_{t_0}^t dt' \chi_{uv}(t, t') K_v(t')$$ (1.38)

where $\langle \Phi_u(t) \rangle$ denotes the fluctuations of a bath observable induced by the system, and $\chi_{uv}(t, t')$ is the linear response function or the linear susceptibility. This result is known as the linear response theory. It can subsequently be shown that the linear susceptibility is given by [25]

$$\chi_{uv}(t, t') = \langle [\Phi_u(t), \Phi_v(t')] \rangle$$ (1.39)

where the angled brackets indicate an averaging with respect to the equilibrium bath fluctuations. By comparison with the bath correlation function $C_{uv}(t, t')$, a relation between the linear response function and the bath correlation function can be established

$$C_{uv}(t, t') = \langle \Delta \Phi_u(t) \Delta \Phi_v(0) \rangle$$ (1.40)

$$\Delta \Phi_u = \Phi_u(t) - \langle \Phi_u \rangle$$ (1.41)
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\begin{equation}
\chi_{uv}(t,t') = -2i\text{Im}[C_{uv}(t,t')]
\end{equation}

One can also consider the change in the internal energy \( W(t) \) of the bath, as a result of the external perturbation

\begin{equation}
W(t) = \langle U^\dagger(t - t_0)H_{\text{int}}(t)U(t - t_0) \rangle
\end{equation}

It can be shown that the rate of change of this energy is determined by

\begin{equation}
\frac{\partial}{\partial t}W(t) = \sum_u \langle \Phi_u(t) \rangle \frac{\partial}{\partial t} K_u(t)
\end{equation}

This equation states that the fluctuations of certain operators of the bath lead to a change in its internal energy, and is known as the fluctuation-dissipation relation. By assuming a functional form for the bath correlation function, linear response theory and the fluctuation-dissipation theorem completely characterize the linear and non-linear spectra of the solute [26].

Linear response assumes that the forces responsible for the return of the reservoir to equilibrium depend linearly on the deviation from equilibrium. As this is a harmonic oscillator property, it comes as no surprise that theories that treat the bath as a collection of harmonic oscillators reproduce the results of linear response, and in fact, fluctuation-dissipation theorem can be rigorously derived within the framework of the displaced harmonic oscillator Hamiltonian [27]. Moreover, by approximating the environment as a bosonic bath, one can derive analytic expressions for the bath (or solvation) correlation function in terms of the bath spectral density. A knowledge of the solvent frequencies, which can be obtained from the instantaneous normal mode theories for instance, can then lead to the computation of the solvation correlation function. This point will be illustrated further in the next section.

Linear response theory enables us to write an expression for the solvation function, which is defined to be [28]

\begin{equation}
S(t) \equiv \frac{E(t) - E(\infty)}{E(0) - E(\infty)}
\end{equation}
In this expression $E(t)$ is the non-equilibrium solvation energy and $E(\infty)$ is the equilibriated solvation energy, where solvation energy is the energy released as a solute dissolves in a solvent. In linear response this becomes

$$S(t) = \frac{\langle \Phi(t) \rangle - \langle \Phi(\infty) \rangle}{\langle \Phi(0) \rangle - \langle \Phi(\infty) \rangle} \tag{1.46}$$

One can show by simple manipulations that Eq. (1.46) can be written as

$$S(t) = \frac{\langle \Delta \Phi(0) \Delta \Phi(t) \rangle}{\langle (\Delta \Phi)^2 \rangle}. \tag{1.47}$$

Eq. (1.47) can be identified as the correlation function of the bath

$$S(t) = C(t). \tag{1.48}$$

If the solvent is modeled as a polarizable dielectric medium, the function $\Phi(t)$ corresponds to the electrostatic potential at a given point in the solvent, and the perturbing force is the charge distribution of the solute. For a continous distribution of charge, the perturbation can be identified as $H_1 = \int d^3r \Phi(r)(r,t)$, where $\rho(r,t)$ specifies the charge distribution of the solute.

Therefore, in the linear response approximation, the non-equilibrium solvation function $S(t)$, is equal to the equilibrium correlation function $C(t)$. The solvation function is directly observable by monitoring the dynamic line-shift as the solvent responds to the electronic excitation of a solute (see Fig. 1.5). The solvation energy $E(t)$, then corresponds to the non-equilibrium energy difference between the excited state and the ground state of the solute, as the solvent relaxes and re-orient itself to accommodate the new charge distribution of the solute [26].

**Instantaneous normal mode theory and the molecular dynamics of solvation**

The discussion presented in the previous section establishes the mathematical foundation of the harmonic approximation of a solvent. The question still remaining is whether the harmonic modes are mere mathematical tools, or if they correspond to physical...
oscillators. This question has been addressed from different perspectives, two of which will be discussed in this section. The first perspective views the solvent as a polarizable dielectric with a frequency dependent susceptibility. The dielectric responds to a change in the charge distribution of the solute, and the harmonic modes are interpreted as local changes in the polarization field.

Dielectric continuum models (DCMs) have become increasingly elaborate over the years, as they have incorporated more and more information with regards to the frequency dependence of the susceptibility and charge distribution of the solute [29]. Despite their success in reproducing fluorescence dynamics, these models do not provide a molecular level description of the solvent dynamics.

The second perspective is offered by the instantaneous normal mode (INM) theories, and offers a molecular level description of solvation [30, 31, 32]. The idea behind INMs is that the displacement of a solution’s configuration $R_t$ at any time $t$, from what it was in its initial configuration $R_0$, can be decomposed into a set of independent collective modes $\{q_\alpha(t)\}$, where $\alpha$ ranges from 1 to the number of degrees of freedom of the system. Different initial configurations lead to different sets of INMs, but the insight lies in the realization that for sufficiently short $t$, these modes have simple harmonic dynamics.

To illustrate the idea further, suppose that the potential energy $V$ of a liquid differs at sometime $t$, from what it was at $t = 0$. As the difference is due to the change in the liquid configuration $R_t - R_0$, for sufficiently short time intervals the potential energy difference can be expanded in the powers of this change [31], that is

$$V(R_t) \approx V(R_0) - F.(R_t - R_0) + \frac{1}{2}(R_t - R_0).D.(R_t - R_0)$$

(1.49)

where $F$ is the instantaneous force (at $t = 0$) and $D$ is the dynamical matrix that characterizes a given configuration. The eigenspectrum of $D$ constitutes the instantaneous normal modes of the solvent. The energy difference between the two configurations can
now be written as a sum of independent harmonic contributions

\[ V(R_t) \approx V(R_0) + \sum_\alpha \left\{ f_\alpha q_\alpha(t) + \frac{1}{2} \omega_\alpha^2 q_\alpha^2(t) \right\} \]  

(1.50)

where \( \{f_\alpha\} \) are components of the transformed force, \( \{\omega_\alpha\} \) and \( \{q_\alpha(t)\} \) are the eigenvalues and the eigenvectors of the matrix \( D \) respectively. The index \( \alpha \) runs from 1 to \( 3N \) where \( N \) is the number of particles. INMs can be applied to compute the solvation correlation function by expanding the solvation energy in powers of the harmonic modes [30], that is

\[ E(t) - E(0) = \sum_\alpha \epsilon_\alpha q_\alpha(t) + O(q_\alpha, q_\beta) \]  

(1.51)

where the coefficients \( \{\epsilon_\alpha\} \) act as a set of susceptibilities that quantify the ability of each mode to solvate the solute. Therefore by computing the instantaneous normal modes over many sets of initial configurations, the solvation correlation function \( C(t) \), can be directly computed. Once the normal modes are computed, their nature (rotational, translational, etc) can also be determined. By projecting specific portions of the solvation spectrum, one is therefore able to quantify the contribution of different sets of modes to the solvation dynamics.

INM analysis on liquid water reveals that the first stage of solvation involves low frequency modes associated with ballistic motion of individual solvent molecules [32]. This inertial motion occurs on a time scale of \( \sim 100 \text{ fs} \), during which the motions of individual molecules are largely uncorrelated, and the corresponding decay in the solvent correlation function has a Gaussian profile. The molecular picture associated with this phase of solvation is stretching of specific bonds in the solute as a result of electronic excitation. The water molecules are subsequently pushed away to accommodate this change. Translational, or centre of mass modes, are thus the dominant contributors in the first stage of solvation.

Following the initial inertial motion, the solvent molecules re-orient to respond to the new charge distribution of the solute (see Fig. 1.5). Rotational motions of the molecules
Figure 1.5: a) Schematic illustration of the potential energy surfaces involved in the solvation dynamics. The solute is assumed to have no permanent dipole moment in its ground electronic state, but acquires a dipole moment upon excitation. The water molecules reorient themselves to accommodate the new charge distribution. b) Solvent relaxation can be probed by detecting the time-dependent fluorescence stokes shift. c) Solvent relaxation also leads to decay of the solvation correlation function on a sub-picosecond time-scale.
within the first solvation shell (\( \sim 6.8 \) Å for water), dominate the dynamics during this relaxation period. The relaxation process occurs on a sub-picosecond timescale and is more significant for polar solvents such as water. Solvent relaxation is characterized by collective molecular motions, and an exponential decay of the correlation function. The average number of molecules involved in a given mode is estimated to be \( \sim 80 \). Another set of modes that contribute to this phase of solvation are the so-called librational modes. Librational motion is the back-and-forth oscillation of a molecule about a fixed axis, much like the small amplitude oscillations of a simple pendulum. In water, any given molecule is attracted to the neighboring molecules, so that it has a fixed orientation and may not be able to rotate freely, but it can exhibit small amplitude oscillations about the molecular axis. Of course, over time the molecules move and the axis is changed.

The translational modes span a frequency range of \( 0 < \omega < 350 \text{ cm}^{-1} \) and make up about 24\% of the total modes in the solvation spectrum of water. Despite this, for both polar and non-polar solvents, 70 – 80\% of the decay of the correlation function occurs during the first stage of solvation. The rotational and librational modes span a frequency range of 400 – 1000 cm\(^{-1}\). Between the two frequency limits the motion is a combination of all three modes.

Due to the short time harmonic approximation, INM theories agree with the full molecular dynamics simulations on a sub-picosecond timescale, but deviate over longer times. Luckily, correlation functions decay on this timescale, and an accurate computation of \( C(t) \) over \(< 1 \text{ ps} \) is sufficient for mapping the solvation dynamics. Most notably the theory can predict short time oscillations in the correlation function, attributing the oscillatory features to superpositions of the instantaneous normal modes of the solvent molecules.
1.3 Evidence for coherent dynamics

The evidence for coherent dynamics in photosynthetic pigments comes from two-dimensional electronic spectroscopy (2D ES). In 2D ES the electronic properties of a sample (an optically non-linear medium) are probed by means of its third-order optical response to incident electric fields [33]. In contrast to linear spectroscopy that probes only the energy levels of a system, 2D ES builds up a picture of the evolution of the density matrix; both populations and coherences can therefore be probed and mapped out. In this section we will discuss a number of important and highly cited articles on spectroscopic studies of photosynthetic complexes.

The first series of 2D ES experiments were performed by the Fleming group in Berkeley and the first results were reported on the Fenna-Matthews-Olson (FMO) bacteriochlorophyll a complex, a pigment-protein complex found in photosynthetic green sulfur bacteria isolated from Chlorobium tepidum [34]. The bacteria is found in anoxic and sulfide-rich waters and is well adapted to energy collection under low-light conditions [1]. The FMO complex is the first photosynthetic complex whose molecular structure was determined by X-ray crystallography, thus allowing the computation of the dipole moments and the electronic couplings [35]. The complex is unique among photosynthetic antennas, as it rarely absorbs photons, but instead connects a large light-harvesting peripheral antenna, the chlorosome, to the reaction centre. The structure of the complex is shown in Fig. 1.6. In the original experiment by the Fleming group, dilute solutions of the FMO protein were probed by a number of femtosecond pulses in a four-wave mixing setup. Short pulses create coherent superpositions of the excitonic eigenstates of the complex, and the decay of coherence of this superposition state was investigated. The original set of experiments were performed at cryogenic temperatures of 77 K, and revealed evidence of coherences lasting up to 660 fs [34]. The surprising feature of this observation was that theoretical models indicated that coherences must vanish on the time scale of the initial population transfer time of 250 fs. A previously unforeseen mechanism was therefore concluded to
Figure 1.6: FMO protein is a molecular wire connecting a large peripheral antenna complex, the chlorosome, to the bacterial reaction centre.

be responsible for the protection of electronic coherence.

Inspiring as these findings may have been, there were several shortcomings in the original article. Firstly, the justification behind the electronic (as opposed to vibrational) nature of the oscillatory component of the spectrum was shown to be insufficient [36]. Vibrational modes are localized on single chromophores, and vibrational coherence between two localized modes can be created via resonant pulses [37]. Electronic coherence, on the other hand, is a collective excitonic effect, involving multiple pigments. As the electronic degrees of freedom are coupled to the environmental modes, electronic coherence is expected to dephase rapidly. Vibrational coherence however, involves the much slower motion of the nuclei and is comparatively long-lived. The main claim of the article was therefore largely unsubstantiated. Secondly, regardless of the operating temperature of the experiment, coherences are expected to damp out with time. In the reported data, however, the amplitude of the coherent oscillations grows with time! (Fig. 2 b. in Ref. [34] ) This is an odd feature and was left undiscussed in the article. Thirdly, in this article
a number of claims were made with regards to ‘wave-like energy transfer’ and ‘sampling of different pathways to find the fastest route to the trapping site’. These claims were wildly speculative as the experiments did not probe the EET pathways in the system. The article nonetheless established the potential of 2D ES for spectroscopic studies of coherent phenomena in photosynthetic complexes, spearheading an effort towards a better understanding of the dynamics of such systems at ultra-fast timescales.

The second series of 2D ES experiments were performed by the same group on the reaction centre complex of the photosynthetic purple bacteria *Rhodobacter sphaeroides* [38]. Coherences between two excitonic eigenstates were observed to last for 440 fs at 77 K and 310 fs at 180 K. The important conclusion drawn from the data was the influence of the protein environment in inducing correlations in the nuclear motion of the molecules. It is a common assumption in theoretical models of energy transfer to take the bath-induced correlations at different sites to be independent. The evidence here, however, suggested that in closely packed pigment-protein complexes, this assumption is not correct, and correlated nuclear motion may indeed be the mechanism responsible for slow dephasing.

Similar experiments were later performed on different antenna proteins, namely the two water-soluble pigment-protein complexes known as phycoerythrin 545 (PE545) isolated from *Rhodomonas* sp. strain CS24 [39] and phycocyanin 645 (PC645) isolated from *Chroomonas* sp. The sample was prepared by isolating the protein from the cell and preparing a dilute solution of the complex. The optical density of these samples is so low that the interaction between the protein units can be neglected. The data was taken at room temperature and similar conclusions with regards to persistent coherence between electronic eigenstates was drawn [39]. This was the first published report on the observation of coherent dynamics in a light-harvesting complex at ambient temperatures, and led to the intriguing speculation that if the coherent features are to be believed, they might be of relevance for the living organism after all. However, ambient temperatures
imply a large line-broadening, which obscured the oscillating features of the spectrum. Moreover the electronic nature of the beats was still unsubstantiated.

The first experimental attempt to verify the electronic nature of the oscillatory beats was published by the Scholes group on the antenna protein PC654, isolated from the cryptophyte algae *Chroomonas* sp [40, 41]. In this report a protocol for distinguishing the origin of the oscillatory contributions to the spectrum was devised and implemented. The premise of this protocol is that electronic coherence occurs between two excited electronic states, in a system of multiple coupled molecules, but vibrational coherence arises between the ground and excited vibrational states of a single molecule (Fig. 1.7). Since the electronic and vibrational frequencies are close, the difference between the two spectra is subtle, and measurements of the oscillatory frequencies alone does not determine their origin. Instead, features that are unique to each scheme must be extracted from the spectra.

Although most of the Liouville pathways that can be constructed for the two energy level schemes are identical, there are a few pathways that are unique to each model. For instance in Fig. 1.7, pathways involving the doubly excited state $|f\rangle$, are unique to the excitonic model, and can be used to discriminate the excitonic and the vibrational contributions. The analysis suggested that both electronic and vibrational coherences can be excited and observed in the antenna complex PC645 at ambient temperatures. The protocol assumes a purely excitonic description of the coupled molecules, neglecting the vibronic progression of the excitonic states. In other words, the influence of the discrete vibrational modes on the energy level of the coupled system has been neglected. Vibronic progressions are significant when the Huang-Rhys factors of the vibrational modes are large. Under these circumstances interactions between higher energy vibronic states can alter the transfer rates and the relaxation mechanisms [42].

In an interesting study Hayes and colleagues took a different approach to discriminate the electronic and vibrational features: they investigated the sensitivity of the 2D
Figure 1.7: a) Energy level diagram of an electronic two-level system coupled to a single vibrational mode. The vibrational mode is present in both the ground and the excited electronic state. b) Energy level diagram of a molecular dimer, formed by resonant coupling of two two-level systems. The coupling splits the first excited state into $|e_1\rangle$ and $|e_1\rangle$. $|f\rangle$ is the second excited state formed by simultaneous excitation of both molecules. If $\omega_a = \omega_b$, the superposition states $|e, 1\rangle + |e, 0\rangle$ and $|e_1\rangle + |e_1\rangle$ cannot easily be distinguished. Arrows represent processes that are common to both systems and cannot be distinguished experimentally [36].
spectra to structural modifications in the protein and the light-absorbing units in the FMO complex [43]. The structure of the FMO complex was altered by near-complete substitution of Carbon-12 by Carbon-13. The structure and arrangement of the bacteriochlorophyll a chromophores were also modified. The modifications were observed not to effect the frequency or the amplitude of the beats observed in the 2D spectra. As structural modifications are expected to alter the vibrational frequencies of the chromophores, the authors conclude that the beating must arise from electronic coherence and not vibrational wavepacket motion. Unfortunately the authors did not include the corresponding change in the vibrational spectra of the protein upon structural modifications. Had the structural adjustments resulted in detectable change in the vibrational spectra of the protein, and a clear shift of the vibrational frequencies, the evidence would have been strongly supportive of the electronic nature of the coherent components.

In summary, the inherent complexity of 2D ES, the multiple degrees of freedom that can interact with the exciting fields, and the large degree of line-broadening and noise in the system, render the task of drawing solid conclusions from the experimental data a near impossible one. There is certainly room for experimental improvements. Experiments on single molecules, for instance, do not suffer from inhomogeneous broadening of the optical absorption lineshapes, and present a step in the right direction [44, 45, 46, 47, 48, 49]. Moreover, there is a need for development of experimental techniques other than 2D ES for investigation of biological systems. There have been breakthroughs in probing photosynthetic proteins in optical cavities [50], although cavity QED is best suited for studies in the gas phase, and has proven difficult for molecules in solution [51].

From a more critical perspective, the question still remains that to what extend in 
vitro studies of isolated proteins are informative in understanding the in vivo function of a complex antenna structure. For instance the different initial conditions created in spectroscopy and by sunlight, and the relevance of the conclusions drawn from one scenario to the other, have been the subject of recent attention [52, 53, 54]. A more
conservative viewpoint is perhaps to recognize that the experiments serve as a tool to probe the operating conditions of photosynthetic antennas, leaving the matter of the biological significance of such operating conditions an open question. On a positive note, it is hoped the lessons learned from photosynthesis would find technological applications in artificial light-harvesting [55], fluorescent-based sensors [56] and excitonic circuits [57].

In the meantime much theoretical work has been carried out to better understand the underlying mechanism of EET in photosynthetic complexes. Most theoretical work in this field is not aimed at simulating the experiments, but wish to investigate whether a coherent wiring of pigments under natural conditions could have any advantageous consequences for photosynthesis.

Much of the work presented in this thesis has been focused on the antenna complex PE545 isolated from the photosynthetic cryptophyte algae Rodomonas CS24. Photosynthetic cryptophytes are introduced in the next section.

### 1.4 Photosynthetic cryptophyte algae

Algae are plants with no stems, leaves or roots, and constitute a major form of oxygenic photosynthetic organisms. In aquatic environments algae are the dominant photosynthetic life forms, but they can also be found in dry habitats. Different forms of algae are often classified based on their antenna structure and the type of pigments they contain. The major constituents of the light-harvesting antennas in algae are a combination of different chlorophyll types, as well as special pigment-protein complexes known as phycobiliproteins [1].

There are three types of phycobiliproteins known as allophycocyanin (APC), phycocyanin (PC) and phycoerythrin (PE). The combination of these three complexes absorbs light in a major part of the spectrum that is largely uncovered by chlorophylls, as indicated in table 1.52. The reason for this spectral selectivity is as follows: the intensity
of light is rapidly reduced in aquatic environments; this decrease however is not uniform in wavelength. Water absorbs light in the red portion of the spectrum, and scatters light primarily in the blue part. Red and blue photons are thus rapidly depleted, and at depths over a few tens of meter, most available light is in the green part of the spectrum. Chlorophylls do not absorb green light very well, whereas other photosynthetic pigments, such as carotenoids and phycobiliproteins have intense absorption in this region and are found in abundance in many marine photosynthetic organisms. Different species of algae use different combinations of phycobiliproteins depending on the wavelengths of light available in their environment.

\[
\text{Phycobiliproteins} = \begin{cases} 
\text{Allophycocyanin (APC)} & 590-654 \text{ nm} \\
\text{Phycocyanin (PC)} & 575-645 \text{ nm (PC645)} \\
\text{Phycoerythrin (PE)} & 545-575 \text{ nm (PE545)} 
\end{cases} 
\]

The abundance of different phycobiliproteins, and the arrangement of the antennas within the cell, can vastly vary from one organism to another. In red algae, for instance, all three types of phycobiliproteins are used. The antenna are positioned outside the thylakoid membrane of the cell, such that the highest energy proteins capture the sunlight, and the lowest energy ones are closest to the reaction centre (Fig. 1.8 b.). This is an example of a classic energy funnel: the difference in energy is the primary drive behind the directional flow of electronic excitation. A funnel structure demands energetic and spacial ordering of the pigments around the trap. As elegant as it may seem, such an arrangement is not entirely necessary as sufficient thermal energy for moderate uphill transfer is readily available.

The organized antenna structures formed by phycobiliproteins (in red algae for instance) are known as phycobilisomes. In unicellular cryptophyte algae, in contrast, phycobiliproteins are not organized into phycobilisomes, but are located inside the thylakoid lumen (Fig. 1.8 c.). Note that antenna complexes in both red and cryptophyte algae are examples of peripheral antenna: antenna that do not cross the lipid bilayer, but are at-
tached to one particular side of the protein membrane. In higher plants, in contrast, the antenna system is an integral part of the membrane (Fig. 1.8 a.), and is located adjacent to the reaction centre (which is always within the membrane). The funnel concept seems to be particularly suitable for peripheral membrane antenna that directly interact with the reaction centre, and not so useful for integral membrane systems that demand the uphill energy step.

Figure 1.8: Arrangement of the antenna complexes with respect to the thylakoid membrane in a) higher plants, b) red algae and c) cryptophyte algae.

*Rhodomonas* CS24 is an example of a marine cryptophyte algae utilizing only one type of phycobiliprotein, namely phycoerythrin 545 (PE545). PE545s are the primary antenna
complexes in *Rhodomonas* CS24, and are packed closely inside the lumen of the cell (Fig. 1.9 e.). They do not appear to exhibit any preferred orientations relative to each other or the thylakoid membrane of the cell, although there is evidence of aggregation among the units [58, 59]. The protein concentration inside the lumen depends on the intensity of sunlight available in the environment: at lower light intensity a higher concentration of the antenna is required. The cell has the capability to adjust the protein concentration conditioned on the light intensity. The excitation is eventually funneled to the reaction centre complex, located on the thylakoid membrane of the cell. The energy funnel can involve up to 200 molecules, and the excitation is transported over a total length of 20-100 nm via a series of hops among the proteins [60].

The structure of PE545 was determined via X-ray crystallography with a resolution of 0.97 Å in 2004 [61]. The structure of a single unit of PE545 is shown in Fig. 1.9 f.). It contains eight light-absorbing molecules (chromophores), or four pairs of molecular dimers. The lowest energy chromophores are a pair of dihydrobiliverdin (DBV) bilins. There are additionally two pairs of phycoerythrobilin (PEB) chromophores with a single covalent bond to the protein, and a dimer of doubly bound PEB chromophores (central dimer).

One of the distinctive features of PE545 is the relatively large separation between the light-absorbing molecules. The average separation between the chromophores is of the order of 1 nm, which is twice that of higher plants. This appears to be a peculiar optimization strategy: the rate of energy transfer between the pigments drops as $R^{-6}$, and the lower light intensity in marine environments demands a faster, more efficient mechanism of energy transport. One would thus naively expect a closer positioning of the light-absorbing molecules. This thought is, of course, somewhat simplistic, as biological organisms are complex environments and the genetic mutations dictating the design of the photosynthetic apparatus have been influenced by many factors other than the transport efficiency. The chromophores, for instance, are covalently bound to the
Figure 1.9: a) Optical micrograph of cryptophyte algae *potomonas sulcata* [62]. b) Transmission electron micrograph displaying a cross section of the cryptophyte. The nucleus of the cell (dark circle) and the thylakoid membranes (narrow lines) can be identified [62]. (c) and d) Scanning electron micrograph images of the cryptophytes with a resolution of 20 µm and 5 µm respectively [62]. e) Schematics of the thylakoid disk within the chloroplast. Light-absorbing proteins (PE545) are drawn as green circle. Reaction centres are located within the thylakoid membrane. f) Chromophores from the structural model of PE545.
protein matrix, and the structure of the protein and how tightly it can fold, influences the positioning of the chromophores. In other words, biological designs need to be robust before they can be optimized. Moreover, resonant energy transfer is mediated via a long-range interaction. If the molecules are too close the wavefunction overlap would favour electron transfer, suppressing excitation transfer. Optimization thus requires a distance that inhibits unwanted electron transfer, but enables sufficiently fast excitation transfer.

Another example of completing optimization factors in antenna complexes are the absorption strength and the excited state lifetime. Light absorption is most efficient if the excited state has an intense absorption band. This, however, creates a short-lived excited state, placing an upper bound on the exciton diffusion time. The subsequent processes that store the energy must therefore occur at an ultra-fast timescale.

The large inter-pigment separations, together with the remarkable ability of the antenna at photon scavenging at low light conditions, has nonetheless fuelled the curiosity of researchers in this field. The hypothesis that non-trivial quantum effects may be the missing piece of the jigsaw, has motivated the researchers in our group to investigate the electronic structure of this protein via 2D ES.

1.5 List of previously published articles included in this thesis

Most of the material presented in this thesis is based on previously published work. In this section I clarify my contribution to these publications.

Chapter 2 is based on the ideas presented in the article H. Hossein-Nejad and G. D. Scholes. *Energy transfer, entanglement and decoherence in a molecular dimer interacting with a phonon bath* New J. Phys. 12 065045 (2010). A mistake in the calculations was found after publication of the article. The results presented in chapter 2 are the corrections to the original calculations. Victor V. Albert (visiting student) performed the
analytic calculations presented in appendix C.

Chapter 3 is the results of the article H. Hossein-Nejad, A. Olaya-Castro, G. D. Scholes. *Phonon-mediated path-interference in electronic energy transfer* J. Chem. Phys. 136, 024112 (2012). I had the idea of applying time-dependent perturbation theory to EET to investigate path-interference in antenna complexes following discussions with G. D. Scholes with regards to the relevance of phase coherence in EET. I did all analytic calculations presented in this article and wrote the article with guidance from the co-authors.

Chapter 4 is based on the article H. Hossein-Nejad, C. Curutchet, A. Kubica, G. D. Scholes, *Delocalization-enhanced long-range energy transfer between cryptophyte algae PE545 antenna proteins*. J. Phys. Chem. B. 10.1021 (2011). In this work the Hamiltonian of the PE545 tetramer was computed by C. Curutchet. I computed the transfer rates between all pigments from the Hamiltonian and wrote a Monte-Carlo program to simulate the energy transfer. I wrote the paper with guidance from C. Curutchet and G. D. Scholes. The formalism presented in this work was also applied in another article by C. Curutchet [C. Curutchet, Jacob Kongsted, A. Munoz-Losa, H. Hossein-Nejad, G. D. Scholes and B. Mennucci. *Photosynthetic light-harvesting is tuned by the heterogeneous polarizable environment of the protein*. J. Am. Chem. Soc. 133(9) 3078-3084 (2011)]

Chapter 5 is based on the article H. Hossein-Nejad, F. Fassioli, G. D. Scholes, A. Olaya-Castro. *Dynamical transitions in Markovian exciton transport*. The idea behind this calculation came from A. Olaya-Castro. I did all calculations presented in this article, and wrote the article with guidance and advise from the co-authors.
Chapter 2

Energy transfer on the scale of a molecular dimer: An analytic solution

2.1 Introduction

In this chapter we review the reduced density matrix approach, one of the most commonly employed tools in theoretical modelling of open quantum systems in general and EET in particular. To demonstrate the method we first consider a single molecule and obtain the reduced dynamics of the electronic degrees of freedom. A molecular dimer is subsequently considered and the decoherence and population transfer time of a prototype system is investigated. Molecular dimers are the smallest units exhibiting EET and an appreciation of their dynamics is a first step in understanding the dynamics of larger systems. Although this simple system does not capture the correlations present in larger systems, it serves as a starting point in understanding the EET dynamics. The tools and ideas developed in this chapter are used in all subsequent chapters.

We specialize to a scenario where a dimer of identical molecules undergoes dephas-
ing due to the coupling of the electronic degrees of freedom to its vibrational modes. This case is of current experimental importance as the collective vibrational modes in multichromophoric systems are believed to play the role of a dephasing bath, influencing the dynamics of energy transfer. We pursue a (mathematically) non-standard route and strive to obtain an analytic solution for the dynamics of the dimer by reducing the dimer Hamiltonian to that of a single molecule, for which exact analytic solutions are known. The Fulton-Gouterman diagonalization recipe [63, 64] is employed to achieve this goal. The reduced dynamics of the system is subsequently obtained by applying multiple small-polaron transformations, in an approach similar to the calculations of Reichman and Silbey [65] for single molecules. Energy transfer time scale and decoherence time can subsequently be investigated by computing the diagonal and the off-diagonal elements of the reduced density matrix.

Our treatment assumes that the interaction between the electronic and the vibrational degrees of freedom can be modelled via the spin-boson Hamiltonian. The spin-boson model is a well-investigated Hamiltonian, and there are many solutions of this model for two coupled molecules [66, 67, 68, 69, 70]. There are however limitations with all current treatments that restrict their applicability to a limited regime under certain key assumptions. In general there are two important parameters which determine the regime of validity of a given theory: the strength of the electronic coupling between the pigments, and the strength of the electron-phonon coupling. The latter parameter is specified through the reorganization energy of the vibrational bath. Reorganization energy arises due to the fact that the ground and the excited electronic states have differing equilibrium nuclear coordinates. As a result, upon electronic excitation the molecule finds itself in an excited vibrational state. The molecule subsequently relaxes to the new ground vibrational state, releasing the excess reorganization energy. If the reorganization energy is significantly larger than the electronic coupling, the system operates in the Förster regime [2], where coherent effects are minimal and energy transfer proceeds via a sequence
of hops. On the other hand if the reorganization energy is significantly smaller than the electronic coupling, the system is in the Redfield limit [71, 72] and the dynamics are a combination of coherent evolution and incoherent hopping. Many light-harvesting complexes, however, operate in an intermediate regime where the two time scales are of the same order [8]. For instance in the FMO complex the typical value of the electronic coupling spans the range 1-100 cm$^{-1}$ while the reorganization energy is of the order of 35 cm$^{-1}$ [73, 74]. The lack of a clear separation of time scales is therefore one of the major challenges in the theoretical modelling of light-harvesting systems.

Moreover, there are a number of other approximations within most perturbative treatments which impose further constrains on the regimes of their validity. The Markov and the secular approximations are the most well-known examples and will be discussed further in this chapter. Motivated by these observations we aim to avoid the routine sequence of approximations and instead utilize the symmetries of a homodimer to solve the model as exactly as possible. We are able to avoid the Markov and the secular approximations, but the regimes of applicability of the analytic solution will still turn out to be limited. This calculation nonetheless offers some insight into dynamics of the prototype dimer, and highlights the difficulties of solving the model for larger systems. Physical systems that may be adequately described by our model include dimers of organic molecules in the gas phase, where the ground and excited electronic states are known to exhibit different torsional motion along the symmetry axis of the molecules [75, 76]. The torsional degrees of freedom constitute a shared phonon bath which may be suitably described within the framework of the current model.
2.2 Dephasing in a single molecule

2.2.1 Reduced density matrix

We begin by reviewing the dephasing process between the ground and the excited electronic states of a single molecule. To model the coherent evolution of the electronic states one must consider the electronic and the vibrational modes of the molecule and the interaction between them. The former is modeled as a two-level system (spin), where the two levels correspond to the ground and the excited electronic states. The vibrational modes of the molecule are modeled as a ladder of harmonic oscillators (boson). Such models have been studied extensively in the EET literature [66, 67, 68, 69, 70], and were introduced in section 1.2.3. For a single molecule the interaction between the electronic and the vibrational degrees of freedom is described via the following Hamiltonian

\[
H = \left[ \epsilon + \sum_k h_k(b_k + b_k^\dagger) \right]a^\dagger a + \sum_k \omega_k b_k^\dagger b_k
\]

where \(\epsilon\) is the energy splitting between the electronic ground and excited state, \(\omega_k\) and \(h_k\) are the frequency and the electron-phonon coupling for the mode \(k\) of the bath respectively, \(\{a^\dagger, a\}\) are the excitonic raising and lowering operators and \(\{b_k^\dagger, b_k\}\) are the bosonic operators for the mode \(k\) of the bath (see Fig. 1.4). Following the approach of Reichman and Silbey [65], we compute the dynamical evolution of the subsystem by solving for the reduced density operator.

We assume that at \(t = 0\) an excitation pulse promotes the system to a superposition of the ground and the excited electronic states. The duration of this pulse is taken to be too short to cause disturbances in the vibrational modes, i.e. the vibrational modes relax to the thermal distribution on a time scale that is much faster than the dephasing time of the electronic states. Upon this assumption the state of the subsystem and bath is initially separable

\[
\rho(0) = \sigma(0)\rho_b,
\]
where $\sigma(t)$ is the reduced density operator of the electronic degrees of freedom and $\rho_b$ is the density operator of the bath as governed by a thermal distribution,

$$
\rho_b = \frac{e^{-\beta H_b}}{\text{Tr}_b[e^{-\beta H_b}]}.\quad (2.3)
$$

The vibrational bath is therefore assumed to remain at thermal equilibrium throughout. The subsequent evolution of $\sigma(t)$ is given by

$$
\sigma(t) = \text{Tr}_b[e^{-iHt}\rho_b\sigma(0)e^{iHt}]\quad (2.4)
$$

where $\text{Tr}_b$ indicates an averaging over thermally equilibrated phonon modes, and $H_b = \sum_k \omega_k b_k^\dagger b_k$. By exponentiating the Hamiltonian of (2.1), it is straightforward to show that the diagonal elements of the reduced density matrix remain stationary. The evolution of the off-diagonal elements is determined by

$$
\sigma_{21}(t) = \sigma_{21}(0)e^{-i\bar{\epsilon}t}\text{Tr}_b[e^{-i(H_b+\Delta)t}\rho_b e^{iH_b t}],\quad (2.5)
$$

where $\Delta = \sum_k h_k(b_k + b_k^\dagger)$. In other words the influence of the vibrational bath is solely to dephase the electronic coherence between the ground and the excited state. The eventual loss of the electronic energy and the subsequent relaxation of the molecule to the ground electronic state occurs on a longer time scale and is not described within the current model.

We evaluate Eq. (2.5) by applying a small-polaron (displacement) transformation [77, 24]. The action of the transformation can be written as

$$
Me^{-i(H_b+\Delta)t}M^\dagger = e^{-i(\sum_k b_k^2/\omega_k)t}e^{-iH_b t}.\quad (2.6)
$$

where $M$ is a displacement operator and $\bar{\epsilon}$ is the shifted energy.

$$
M(t) = \exp \left[ \sum_k \frac{h_k}{\omega_k} (b_k^\dagger e^{i\omega_k t} - b_k e^{-i\omega_k t}) \right] \quad (2.7)
$$

$$
\bar{\epsilon} = \epsilon - \sum_k \frac{h_k^2}{\omega_k}.\quad (2.8)
$$
The quantity $\sum_k \frac{\hbar^2}{\omega_k}$ is the reorganization energy of the bath. Note that we use the small-polaron transformation merely as a mathematical tool: we have not changed basis and the off-diagonal term still refers to the coherence between the ground and the excited electronic states. Upon this transformation we obtain

$$\sigma_{21}(t) = \sigma_{21}(0)e^{-i\bar{\epsilon}t}\text{Tr}_b[M^\dagger(t)M\rho_b]$$

(2.9)

Eq. (3.6) is linear in exponentials of bosonic operators. The averaging over the bath degrees of freedom may be carried out by expanding the bath modes in the Fock basis [78]. We arrive at the following expression for the time evolution of coherence

$$\sigma_{21}(t) = \sigma_{21}(0)e^{-\gamma(t)}e^{-i\varphi(t)}$$

(2.10)

where $\gamma(t)$ and $\varphi(t)$ are the time-dependent decay function and phase function respectively

$$\gamma(t) = \sum_k [1 - \cos(\omega_k t)]\coth(\beta\omega_k/2)(h_k/\omega_k)^2$$

(2.11)

$$\varphi(t) = \bar{\epsilon}t - \sum_k (h_k/\omega_k)^2 \sin(\omega_k t)$$

(2.12)

The decay function has all the thermal dependence, and the phase part is independent of temperature. This equation states that the total dephasing rate is a summation of oscillatory contributions from different bath modes, where the thermal factor $\coth(\beta\omega_k/2)$, ensures that dephasing is dominated by lower frequency modes. These oscillations are characteristics of non-Markovian dynamics and would not appear if the Markov assumption had been invoked. For a macroscopic bath with a continuum of modes, the different oscillatory contributions interference destructively and the dynamics will be dominated by the thermal factor. For a mesoscopic bath with a finite, discrete number of modes, the oscillations lead to reversible dynamics. This is a general result we shall revisit in the next section where we study the dynamics of a dimer.

Note that $g(t) = \gamma(t) + i\varphi(t)$ is closely related to the line-broadening function [79], as dephasing and line-broadening have the same physical origin. Optical spectra computed
with this function appear as vibronic progressions in which individual transitions exhibit identical line-broadening.

### 2.2.2 Spectral density

In many instances the vibrational modes of a molecule can be probed via Raman spectroscopy. The resulting spectra tend to be broad at low frequencies and can more conveniently be described via a spectral density. We consider the continuum limit of Eq. (2.11) and Eq. (2.12) to rewrite the equations of motion in terms of a spectral density $J(\omega) = \sum_k \hbar^2 \delta(\omega - \omega_k)$. In this limit the decay function and the phase function are found to be

$$\gamma(t) = \int_0^\infty d\omega \frac{J(\omega)}{\omega^2} \left[1 - \cos(\omega t)\right] \coth(\beta\omega/2)$$

$$\varphi(t) = \bar{\epsilon} t - \int_0^\infty d\omega \frac{J(\omega)}{\omega^2} \sin(\omega t)$$

The reorganization energy $E_R$, is in turn related to the spectral density $J(\omega)$, via the expression

$$E_R = \int_0^\infty d\omega \frac{J(\omega)}{\omega}.$$  

A number of different forms of the spectral density are often utilized to model different system-environment interactions. They are often characterized by a power law rise for small frequencies, and an exponential decay for large frequency. The transition between the two regions occurs at a cut-off frequency $\omega_c$. An Ohmic spectral density, for instance, takes the form

$$J(\omega) = \frac{E_R}{\omega_c} \omega e^{-\omega/\omega_c}.$$  

A different frequency dependence is given by the Debye (also known as the Brownian oscillator) spectral density

$$J(\omega) = \frac{2E_r}{\pi} \frac{\omega \omega_c}{\omega^2 + \omega_c^2}.$$  

This form is often used to characterize the coupling between a solute and a polar solvent [25] and is reduced to the Ohmic form if the cut-off frequency is large. Note that the
time constant of the function $\gamma(t)$ is determined by the cut-off frequency of the spectral density. For a Brownian oscillator spectral density, for instance, a large cut-off frequency implies rapid decay of $\gamma(t)$, that is $\gamma(t) \approx \delta(t)$. This is the Markov limit where the bath correlations occur on a time scale much faster than all other relevant time scales of the system, and can thus be regarded as instantaneous.

### 2.3 Dephasing in a dimer: analytic solution

#### 2.3.1 FG versus site basis

We now extend the methodology of the previous section to study the dephasing dynamics of a dimer. Under excitation by weak light, only the states with a single excited state need to be considered. We can therefore restrict the analysis to the single excitation subspace, i.e.: $\{|e\rangle_A \otimes |g\rangle_B, |g\rangle_A \otimes |e\rangle_B\}$. In this subspace, the effective Hamiltonian of two coupled two-level systems \cite{24, 80} is identified to be

$$H = -J(a_1^\dagger a_2 + a_2^\dagger a_1) + \sum_{i=1}^{2} a_i^\dagger a_i \left[ \epsilon + \frac{1}{2} \sum_k h_{ik}(b_k^\dagger + b_k) \right] + \sum_k \omega_k b_k^\dagger b_k$$  \hspace{1cm} (2.18)

where $J$ is the electronic coupling and $\{a_i^\dagger, a_i\}$ are the raising and lowering operators for the $i$th molecule. The exciton-phonon couplings of the two molecules satisfy the relation $h_{1k} = -h_{2k}$, because the fluctuations are specified as stretching vibrational modes in the coordinate system of the two interacting molecules. For example, if the dephasing bath is an interchromophore vibrational mode of the dimer, then the second-quantized bath coordinate $x \propto (b^\dagger + b)$, quantifies the separation between the molecules. We next write the Hamiltonian in the single excitation subspace as a matrix in the site basis

$$H = \begin{pmatrix} H_b + \epsilon + \frac{1}{2} \Delta & -J \\ -J & H_b + \epsilon - \frac{1}{2} \Delta \end{pmatrix},$$ \hspace{1cm} (2.19)

where $\Delta = \sum_k h_{1k}(b_k^\dagger + b_k)$. At this point we drop the subscript $k$ and focus on one mode of the bath only. Extension to many modes is straightforward and the multimode
result is quoted at the end of this section. The dimer Hamiltonian can be diagonalized in the electronic basis by applying the following Fulton-Gouterman (FG) transformation [81, 63, 64]

\[ U = \frac{1}{\sqrt{2}} \begin{pmatrix} 1 & R \\ -R & 1 \end{pmatrix}, \]  

where \( R = (-1)^{b^b} \). R is a parity operator that adds a phase factor of +1 (-1) to states with an even (odd) number of phonons, whereby dividing the Hamiltonian into subspaces of even and odd parity. The transformed Hamiltonian \( D = UHU^\dagger \), is found to be

\[ D = \begin{pmatrix} A & 0 \\ 0 & B \end{pmatrix}, \]

\[ A = H_b + \frac{1}{2}\Delta - J(-1)^{b^kb_k} + \epsilon, \]

\[ B = H_b - \frac{1}{2}\Delta + J(-1)^{b^kb_k} + \epsilon. \]

This Hamiltonian is diagonal in the electronic basis, but infinite dimensional in the vibrational basis. Diagonalization via the FG transformation implies the following relations,

\[ e^{-iDt} = U e^{-itH} U^\dagger \]  

\[ e^{-iHt} = U^\dagger e^{-itDU} \]

These expressions can be used to transform the density matrix from the site to the FG basis and vice versa. We now focus on computing the reduced density matrix in the FG basis analytically, the corresponding calculation in the site basis is discussed in Appendix B. The FG basis is analogous to the eigenstate basis, as the electronic Hamiltonian is diagonal in this basis.
2.3.2 Density matrix in the FG basis

The evolution of the reduced density matrix in the FG basis is relatively straightforward to compute, and is determined by

\[
\bar{\sigma}(t) = \text{Tr}_b\{\bar{\rho}(t)\} = \text{Tr}_b\{U\rho(t)U^\dagger\} = \text{Tr}_b\{Ue^{-iHt}\rho(0)e^{iHt}U^\dagger\}
\]

(2.26)

(2.27)

(2.28)

where we have used bars to denote states in the FG basis. Assuming separable initial conditions in the site basis, we arrive at the following expression for evolution of \(\bar{\sigma}(t)\)

\[
\bar{\sigma}(t) = \text{Tr}_b\{Ue^{-iHt}\rho_b\sigma(0)e^{iHt}U^\dagger\}
\]

(2.29)

Using (2.24) and (2.25) we next replace exponentials of Hamiltonian with exponentials of \(D\),

\[
\bar{\sigma}(t) = \text{Tr}_b\{e^{-itD}U\rho_b\sigma(0)U^\dagger e^{itD}\}
\]

(2.30)

\[
= \text{Tr}_b\{e^{-itD}\rho_b\sigma(0)e^{itD}\}. 
\]

(2.31)

The last line could have be written from the outset, as it merely states that the evolution of the transformed density matrix is determined by the diagonalized Hamiltonian. The populations and coherences can be evaluated by writing Eq. (2.31) in the matrix form. That is,

\[
\bar{\sigma}(t) = \text{Tr}_b\left\{\begin{pmatrix} e^{-itA} & 0 \\ 0 & e^{-itB} \end{pmatrix} \begin{pmatrix} \bar{\sigma}_{11}(0) & \bar{\sigma}_{12}(0) \\ \bar{\sigma}_{21}(0) & \bar{\sigma}_{22}(0) \end{pmatrix} \rho_b \begin{pmatrix} e^{iAt} & 0 \\ 0 & e^{iBt} \end{pmatrix} \right\}
\]

(2.32)

We arrive at the following expressions for the evolution of population and coherence

\[
\bar{\sigma}_{11}(t) = \text{Tr}_b\left\{\bar{\sigma}_{11}(0)\rho_b\right\}
\]

(2.33)

\[
\bar{\sigma}_{12}(t) = \text{Tr}_b\left\{e^{-iAt}\bar{\sigma}_{12}(0)\rho_b e^{iBt}\right\}. 
\]

(2.34)
Populations thus remain invariant in the FG basis, and provided that multiple bath modes participate in the dynamics, coherences are expected to decay with time. However, as the initial conditions in the FG basis are unknown, we rewrite these equations in terms of the initial density matrix in the site basis. Recalling that

$$\bar{\sigma}(0) = U\sigma(0)U^\dagger$$

we write $U$ in the matrix form and substitute Eq. (2.35) into Eq. (2.32), thereby converting the initial conditions to the site basis. The final solution reads

$$\bar{\sigma}_{11}(t) = \frac{1}{2} + \text{Re} \left[ \sigma_{12}(0) \right] \text{Tr}_b \{ R\rho_b \}$$

$$\bar{\sigma}_{12}(t) = \left[ \frac{1}{2} - \sigma_{11}(0) \right] \text{Tr}_b \left\{ e^{-iAt} \rho_b e^{iBt} \right\} + i\text{Im} \left[ \sigma_{12}(0) \right] \text{Tr}_b \left\{ e^{-iAt} \rho_b e^{iBt} \right\}.$$  (2.37)

where $\text{Re}$ and $\text{Im}$ indicate the real and imaginary parts respectively. The problem is thus reduced to the evaluation of the traces over the bath. The details of the calculations presented in this section may be found in Appendix A.1.

**Approximated solution in the FG basis**

All calculations up until this point have been exact. The trace $\text{Tr}_b \{ R\rho_b \}$ can readily be evaluated analytically. The remaining traces however are notoriously difficult, and cannot be evaluated unless an approximation is introduced. In order to do this, we expand the parity operator and truncate up to terms linear in the number operator $b^\dagger b$, that is

$$\exp \left\{ i\pi b^\dagger b \right\} \simeq 1 - 2b^\dagger b$$  (2.38)

This approximation renders all reservoir traces linear in exponentials of bosonic operators. The tracing can now be carried out straightforwardly (see Appendix A.2). The final solution takes the form

$$\bar{\sigma}_{11}(t) = \frac{1}{2} + \text{Re} \left[ \sigma_{12}(0) \right] \tanh \left( \frac{1}{2} \beta\omega \right).$$  (2.39)
\[
\bar{\sigma}_{12}(t) = \exp\left\{ i \frac{\lambda^2}{w^2 - 4J^2} \Phi(\omega, J, t) + 2iJt \right\}
\]
\[
\left\{ \frac{\left( \frac{1}{2} - \sigma_{11}(0) \right)(1-e^{-\beta \omega})}{1+e^{-\beta \omega(t)}} \exp \left[ \frac{\lambda^2 \Theta(\omega, J, t)}{w^2 - 4J^2} \tan \left( \frac{\beta \omega(t)}{2} \right) \right] + \right.
\]
\[
\frac{\text{Im}[\sigma_{12}(0)](1-e^{-\beta \omega})}{1-e^{-\beta \omega(t)}} \exp \left[ \frac{\lambda^2 \Theta(\omega, J, t)}{w^2 - 4J^2} \coth \left( \frac{\beta \omega + i \Delta \omega}{2} \right) \right] \right\}
\]

(2.40)

\[
\Phi(\omega, J, t) = -\Delta \omega t + \sin (\Delta \omega t) - 2\omega \left[ \frac{\sin (\omega_+ t)}{\omega_+} - \frac{\sin (\omega_- t)}{\omega_-} \right]
\]

(2.41)

\[
\Theta(\omega, J, t) = -\frac{\omega_+^2 + \omega_-^2 + \omega_+ \omega_-}{\omega_+ \omega_-} - \cos (\Delta \omega t) + 2\omega \left[ \frac{\cos (\omega_+ t)}{\omega_+} + \frac{\cos (\omega_- t)}{\omega_-} \right]
\]

(2.42)

where

\[
\omega_+ = \omega + 2J
\]

(2.43)

\[
\omega_- = \omega - 2J
\]

(2.44)

\[
\Delta \omega = \omega_+ - \omega_- \quad \text{(2.45)}
\]

\[
\bar{\omega}(t) = \omega + \frac{\Delta \omega}{\beta} t
\]

(2.46)

\[
\lambda = \frac{1}{2} \hbar
\]

(2.47)

At \( t = 0 \) these expressions are reduced to

\[
\bar{\sigma}(0) = \begin{pmatrix}
\frac{1}{2} + \text{Re}[\sigma_{12}(0)] \tanh \left( \frac{1}{2} \beta \omega \right) & \left[ \frac{1}{2} - \sigma_{11}(0) \right] \tanh \left( \frac{1}{2} \beta \omega \right) + i \text{Im}[\sigma_{12}(0)] \\
\left[ \frac{1}{2} - \sigma_{11}(0) \right] \tanh \left( \frac{1}{2} \beta \omega \right) - i \text{Im}[\sigma_{12}(0)] & \frac{1}{2} - \text{Re}[\sigma_{12}(0)] \tanh \left( \frac{1}{2} \beta \omega \right)
\end{pmatrix}
\]

(2.48)

which establishes a relationship between the initial conditions in the two bases, and is equivalent to Eq. (2.35). To understand the implications of the truncation, we expand the FG Hamiltonian for the excited state in the phonon basis. Denoting the excited state by \(|+\rangle\), the basis states of the problem are the tensor product of the electronic and the phonon parts, that is \(|+\rangle \otimes \{|n\rangle\} = \{|+, 0\rangle, |+, 1\rangle, |+, 2\rangle, \ldots\}\). The Hamiltonian in this basis is given by
The Hamiltonian of the lower exciton state $|\rangle$, can similarly be expanded in the $|\rangle \otimes \{|n\rangle\}$ basis. The total Hamiltonian in the FG basis is the direct sum of these two contributions: $D = A \oplus B$. Upon the approximation of (2.38) we arrive at the following expression for $A$,

$$
A \approx \begin{pmatrix}
\epsilon - J & \frac{1}{2} \hbar \\
\frac{1}{2} \hbar & \omega + J + \epsilon & \frac{\sqrt{2}}{2} \hbar \\
\frac{\sqrt{2}}{2} \hbar & 2\omega - J + \epsilon & \frac{\sqrt{3}}{2} \hbar \\
\frac{\sqrt{3}}{2} \hbar & 3\omega + J + \epsilon & \frac{\sqrt{4}}{2} \hbar \\
\frac{\sqrt{4}}{2} \hbar & 4\omega - J + \epsilon & \epsilon ... \\
\vdots & \vdots & \vdots 
\end{pmatrix}.
$$

(2.50)

The diagonal elements thus quickly diverge owing to the truncation of the parity operator. The validity of the theory is therefore limited to scenarios where no more than a few phonon modes are populated. As the occupation of the phonon modes is determined by a Boltzmann factor, the theory is valid at low temperatures where higher phonon modes are unoccupied. Moreover, the electronic coupling needs to be small in comparison to the bath frequency that is $J \ll \omega$, making the theory suitable for high frequency vibrational modes. The theory will turn out to be valid close to the Förster limit, but unlike the Förster formula, the evolution is not assumed to be purely incoherent. If the initial state is chosen such that $\text{Im}[\sigma_{12}(0)] = 0$, the FG dynamics is simplified to

$$
\bar{\sigma}_{11}(t) = \frac{1}{2} + \text{Re} [\sigma_{12}(0)] \tanh \left( \frac{1}{2} \beta \omega \right)
$$

(2.51)
\[ \bar{\sigma}_{12}(t) = \exp \left\{ i \frac{\lambda^2}{\omega^2 - 4J^2} \Phi(\omega, J, t) + 2iJt \right\} \]
\[ \exp \left\{ \frac{[1 - \sigma_{11}(0)](1 - e^{\beta \tilde{\omega}(t)})}{1 + e^{-\beta \tilde{\omega}(t)}} \exp \left[ \frac{\lambda^2 \Theta(\omega, J, t)}{\omega^2 - 4J^2} \tanh \left( \frac{\beta \tilde{\omega}(t)}{2} \right) \right] \right\} \]  
(2.52)

Eq. (2.52) thus predicts that the coherences oscillate at a frequency (or several frequencies) determined by the first exponential, and decay at a rate determined by the second exponential. The nature of the oscillations are both electronic and vibrational.

A generalization of this result to multiple bath modes is as follows,

\[ \bar{\sigma}_{11}(t) = \frac{1}{2} + \Re \left[ \sigma_{12}(0) \right] \Pi_k \tanh \left( \frac{1}{2} \beta \omega_k \right) \]  
(2.53)

\[ \bar{\sigma}_{12}(t) = \exp \left\{ \sum_k i \frac{\lambda^2}{\omega^2 - 4J^2} \Phi(\omega_k, J, t) + 2iJt \right\} \]
\[ \left[ \frac{1}{2} - \sigma_{11}(0) \right] \Pi_q \frac{1 - e^{-\beta \omega_q}}{1 + e^{-\beta \omega_q}(t)} \exp \left[ \sum_k \frac{\lambda^2 \Theta(\omega_k, J, t)}{\omega^2_k - 4J^2} \tanh \left( \frac{\beta \tilde{\omega}_k(t)}{2} \right) \right] \]  
(2.54)

In the next section we compute these expressions for a discrete vibrational bath, and compare the decoherence time for different initial conditions.

**Approximated solution in the site basis**

The solutions presented in the previous section can equivalently be expressed in the site basis. The basis transformation needs to be applied before the trace over the bath modes is evaluated. The details of this calculation are presented in Appendix B. The final solution for a general initial state and a single bath mode are as follows: The evolution of the population is determined by

\[ \sigma_{11}(t) = \frac{1}{2} + \Re \left[ \sigma_{12}(0) \right] \left\{ e^{2iJt} \exp \left[ i \frac{h^2}{4\omega^2 \omega - \Phi_a(\omega, J, t)} \right] \right\} \]
\[ \times \frac{1 - e^{-\beta t}}{1 - e^{-\beta \omega(t)}} \exp \left[ \frac{h^2}{4\omega^2 \omega - \Theta_a(\omega, J, t) \coth \left( \frac{1}{2} \beta \tilde{\omega}(t) \right)} \right] \]
\[ + \Im \left[ \sigma_{12}(0) \right] \left\{ e^{2iJt} \exp \left[ i \frac{h^2}{4\omega^2 \omega - \Phi_a(\omega, J, t)} \right] \right\} \]
\[ \times \frac{1 - e^{-\beta t}}{1 + e^{-\beta \omega(t)}} \exp \left[ \frac{h^2}{4\omega^2 \omega - \Theta_a(\omega, J, t) \tanh \left( \frac{1}{2} \beta \tilde{\omega}(t) \right)} \right] \]  
(2.55)
The real part of the coherence is given by

\[
\text{Re}\left[\sigma_{12}(t)\right] = \frac{1}{2}\text{Re}\left[\sigma_{12}(0)\right]\left\{ \exp \left[ h^2 \coth \left( \frac{1}{2} \beta \omega \right) \left( \frac{\cos \left( \omega_+ t \right) - 1}{\omega_+^2} \right) \right] + \exp \left[ h^2 \coth \left( \frac{1}{2} \beta \omega \right) \left( \frac{\cos \left( \omega_- t \right) - 1}{\omega_-^2} \right) \right] \right\} 
\]

\[+ \frac{1}{4} \tanh \left( \frac{1}{2} \beta \omega \right) \left\{ \exp \left[ h^2 \tanh \left( \frac{1}{2} \beta \omega \right) \left( \frac{\cos \left( \omega_+ t \right) - 1}{\omega_+^2} \right) \right] - \exp \left[ h^2 \tanh \left( \frac{1}{2} \beta \omega \right) \left( \frac{\cos \left( \omega_- t \right) - 1}{\omega_-^2} \right) \right] \right\} \]

and the imaginary part is

\[
\text{Im}\left[\sigma_{12}(t)\right] = \left[ \frac{1}{2} - \sigma_{11}(0) \right] \text{Im}\left\{ e^{2iJt} \exp \left[ i \frac{h^2}{4 \omega_+ \omega_-} \Phi_s(\omega, J, t) \right] \right\}
\]

\[\times \frac{1 - e^{-\beta \omega}}{1 + e^{-\beta \omega(t)}} \exp \left[ h^2 \frac{\omega_+ - \omega_-}{4 \omega_+ \omega_-} \Theta_s(\omega, J, t) \tanh \left( \frac{1}{2} \beta \tilde{\omega}(t) \right) \right] \right\} + \]

\[
\text{Im}\left[\sigma_{12}(0)\right] \text{Re}\left\{ e^{2iJt} \exp \left[ i \frac{h^2}{4 \omega_+ \omega_-} \Phi_s(\omega, J, t) \right] \right\} \left\{ \frac{1 - e^{-\beta \omega}}{1 + e^{-\beta \omega(t)}} \exp \left[ h^2 \frac{\omega_+ - \omega_-}{4 \omega_+ \omega_-} \Theta_s(\omega, J, t) \tanh \left( \frac{1}{2} \beta \tilde{\omega}(t) \right) \right] \right\}
\]

where we have defined the following functions

\[
\Phi_s(\omega, J, t) = -\Delta \omega t + \sin (\Delta \omega t) - (\omega_+ + \omega_-) \left[ \frac{\sin (\omega_+ t)}{\omega_+} - \frac{\sin (\omega_- t)}{\omega_-} \right]
\]

\[
\Phi_a(\omega, J, t) = -\Delta \omega t - \sin (\Delta \omega t) + (\omega_+ - \omega_-) \left[ \frac{\sin (\omega_+ t)}{\omega_+} + \frac{\sin (\omega_- t)}{\omega_-} \right]
\]

\[
\Theta_s(\omega, J, t) = -\frac{\omega_+^2 + \omega_-^2}{\omega_+ \omega_-} - [1 + \cos (\Delta \omega t)] + (\omega_+ + \omega_-) \left[ \frac{\cos (\omega_+ t)}{\omega_+} + \frac{\cos (\omega_- t)}{\omega_-} \right]
\]

\[
\Theta_a(\omega, J, t) = -\frac{\omega_+^2 + \omega_-^2}{\omega_+ \omega_-} + [1 + \cos (\Delta \omega t)] - (\omega_+ - \omega_-) \left[ \frac{\cos (\omega_+ t)}{\omega_+} - \frac{\cos (\omega_- t)}{\omega_-} \right]
\]

\[
\tilde{\omega}(t) = \omega + \frac{i \Delta \omega}{\beta}
\]

\[
\omega_{\pm} = \omega \pm 2J
\]

\[
\Delta \omega = \omega_+ - \omega_-
\]

Note that in the limit of vanishing electronic coupling, we recover the dynamics of a single molecule, as governed by Eq. (2.11) and Eq. (2.12). In this limit the site basis is also the FG basis, and the decay of coherence occurs at a rate independent of the electronic coupling. The above equations can readily be generalized to multiple modes.
2.3.3 Numerical Results

Population and coherence dynamics

In this section we numerically compute the evolution of the reduced density matrix in the site and the FG basis as governed by the equations derived in the previous section. We consider an arbitrary discrete vibrational bath of the form \( \lambda_k(\omega_k) = 8\omega_k e^{-0.05\omega_k} \) where the lowest bath frequency is 20 cm\(^{-1}\), and the reorganization energy of the bath is 2438 cm\(^{-1}\). The electronic coupling sets the lowest energy scale of the system and is chosen to be 5 cm\(^{-1}\). Figure 2.1 shows a plot of the density matrix in the FG and the site basis for two different initial states at a temperature of 10 K. The left panel corresponds to the initial state \( |e\rangle_A \otimes |g\rangle_B \), that is, one in which molecule A is excited and molecule B is in the ground state. The right panel is the dynamics of the coherent superposition state \( \sqrt{0.8} |e\rangle_A \otimes |g\rangle_B + \sqrt{0.2} |g\rangle_A \otimes |e\rangle_B \). Coherences are observed to vanish in the steady-state in both basis.

Note that diagonal and off-diagonal parts are interconnected: evolution creates a finite coherence over a time period of 10 fs, even though initially the system contains no coherence at all. This can be seen in Fig. 2.1 (e) and (f). An initial imbalance of population in the site basis is sufficient to generate a finite coherence in the site or the FG basis. The imaginary part of the coherence, in both bases, arises due to this initial population imbalance.

We have not invoked on a Markov approximation and the dynamical generation of coherence is likely to be a consequence of the non-Markovian dynamics. Non-Markovianity is an indicator of reversible transfer of ‘information’ between the system and the bath (loss of phase coherence in the present case). The Markov assumption rests on the premise that due to the numeracy of the bath modes the information flow is a one-way process; that is, once the information is lost to the bath, it will not be restored to the system. This assumption is, however, problematic for a discrete vibrational bath, or for a bath whose
Figure 2.1: Left column: reduced density matrix for the initial state $|e\rangle_A \otimes |g\rangle_B$. Coherences decay on the same time scale in both basis. Populations reach the steady-state on a slower time scale than the decoherence time. Right column: reduced density matrix for the initial state $\sqrt{0.8}|e\rangle_A \otimes |g\rangle_B + \sqrt{0.2}|g\rangle_A \otimes |e\rangle_B$. 

[Graphs showing population, real and imaginary parts of coherence, and time evolution for both basis and initial states.]
energy is of the same order as the electronic coupling. Within a Markovian framework coherences can only be lost (in the relevant diagonal basis), as the system is dynamically driven to a maximally mixed state. However, we observe a dynamic generation of coherence over a time scale of 10 fs, in both the FG and the site basis.

Focusing on the site basis, we now investigate the dynamics as the electronic coupling is varied. The lowest bath frequency is set to 30 cm$^{-1}$, resulting in a total reorganization energy of 1221 cm$^{-1}$. Figure 2.2 is a plot of the density matrix in the site basis for different values of the electronic coupling for the initial state $\sqrt{0.8}|e\rangle_A \otimes |g\rangle_B + \sqrt{0.2}|g\rangle_A \otimes |e\rangle_B$. Larger electronic coupling results in faster transfer as expected. The oscillations in the populations occur at a frequency of $2J$ and can only be observed if the population transfer is sufficiently slow.

The change in the decoherence time however, is very small and subtle for the range of parameters considered. These trends are reminiscent of Förster energy transfer: Förster resonance energy transfer concerns itself with EET in the limit of weak electronic coupling, assuming that the energy transfer is incoherent and off-diagonal elements can be neglected. Our theory is valid in the weak coupling limit, but include non-Markovian effects and obtains an estimate for the decoherence time. The decoherence time is faster than the population transfer time as expected, and the two time scales deviate further as the electronic coupling is reduced. It is curious that the variation of the decoherence time as the electronic coupling is varied is so subtle and indicates that over the range of interest the bath dominates the decoherence. Since the electronic coupling must remain the smallest energy scale in the system, it cannot be made arbitrary large for fixed bath parameters.

Next we investigate the influence of temperature on the dynamics of the system with the original bath parameters. Figure 3.5 is a plot of the reduced density matrix in the site basis. Higher temperatures result in faster transfer and rapid decoherence. Care must be taken as the temperature cannot be raised arbitrarily within the current model since
Figure 2.2: Reduced density matrix in the site basis for the initial state \( \sqrt{0.8}|e\rangle_A \otimes |g\rangle_B + \sqrt{0.2}|g\rangle_A \otimes |e\rangle_B \) for different values of the electronic coupling. a) Larger electronic coupling results in faster energy transfer, b) the corresponding change in the decoherence time however is negligible over the range of the parameters considered. The reorganization energy of the bath is 1221 cm\(^{-1}\), and the lowest bath frequency is 30 cm\(^{-1}\).
the error in the calculation is increased at higher temperatures. Despite this limitation we observe the anticipated trend over a moderate temperature range.

\[ \sigma_{11}(t) \]

\[ \sigma_{12}(t) \]

\begin{align*}
0 & \quad 10 & \quad 20 & \quad 30 \\
0 & \quad 10 & \quad 15 & \quad 20 \\
0.8 & \quad 0.5 & \quad 0.4 & \quad 0.2 & \quad 0
\end{align*}

(a)

(b)

\begin{align*}
0 & \quad 10 & \quad 15 & \quad 20 \\
0 & \quad 0.2 & \quad 0.4 \\
T = 5 \text{ K} & \quad T = 40 \text{ K} & \quad T = 80 \text{ K}
\end{align*}

Figure 2.3: Reduced density matrix in the site basis for the initial state \( \sqrt{0.8} |e\rangle_A \otimes |g\rangle_B + \sqrt{0.2} |g\rangle_A \otimes |e\rangle_B \) for different temperatures.

2.3.4 Entanglement between sites

Entanglement is a measure of non-local correlations between quantum objects and a tool of immense importance in quantum information science where non-local correlations are a resource for quantum information processing [82]. Entanglement can also serve as a useful tool for quantification of quantum correlations between a given degree of freedom of molecules. However, it cannot be emphasized more that entanglement is only one requirement for quantum information processing, and molecular systems of interest in EET are far too complex and uncontrollable for quantum information purposes in the conventional sense.
Moreover, there is an important difference between entanglement in this context and in the quantum information sense of entanglement among qubits that merits further elaboration. Existence of long-range electronic coupling implies that non-local correlations between molecules are to be expected. This is in contrast to qubits (ions, photons, superconducting qubits, etc) where the interactions are induced externally and are fragile as a consequence. The non-trivial feature of the dynamics in the present context is the oscillatory nature of coherence (and thus entanglement). A persistent entanglement in the steady-state for instance implies that the system has relaxed towards states with finite delocalization, a common feature of many excitonic systems with strong electronic coupling. The tools of quantum information science must therefore be applied in this field with caution, and the distinction between trivial and non-trivial quantum features must be made clear.

Within the restricted model that the system contains one excitation only, there is a one-to-one correlation between coherence in the site basis and entanglement between the sites [83]. The decoherence time in the site basis is thus equivalent to the time scale over which entanglement dies out. Our prototype system for instance has a disentanglement time of $\sim 10$ fs. Note that if the system relaxes towards states with finite delocalization, a case that will be considered in chapters 5 and 6, the sites remain entangled in the steady-state. This entanglement persists on the time scale of the exciton life time and has important implications for EET. In this context the decoherence time in a diagonal basis (such as the FG basis) is a better indicator of the time scale of short-lived quantum correlations.

2.4 Comparison to other treatments

Jang formulated a theory of excitation energy transfer based on a polaron-transformed master equation [84]. Evolution of coherences were not discussed in Ref. [84], but as far
as the population transfer is concerned several features of the theory can be compared to the present model. Jang observes that for coherent initial conditions the evolution of site population has a curious dependence on the phase of the initial state. Namely the two states $|\psi_1\rangle = |e\rangle_A \otimes |g\rangle_B + |g\rangle_A \otimes |e\rangle_B$ and $|\psi_2\rangle = |e\rangle_A \otimes |g\rangle_B - |g\rangle_A \otimes |e\rangle_B$ have distinct population dynamics provided that the sites have different energies. Our treatment is limited to resonant molecules and predicts a sensitivity to the imaginary part of the initial coherence only, a case that was not discussed by Jang. Kimura and Kakitani have formulated a theory of energy transfer that extrapolates between the two limits but is limited to incoherent initial conditions [85]. This is an extension of the Kenkre and Knox theory of energy transfer that will be discussed in detail in the next two chapters [86, 87]. Since the starting point of our calculation has not been a master equation, many of the assumptions introduced in standard treatments of EET (such as the Kenkre and Knox theory) do not explicitly appear in our theory. For instance the bath correlation function is often assumed to have an exponential decay profile, with a time constant that determines the bath memory. Short bath memory recovers the Markov limit and long memory is a signature of non-Markovianity. Our theory is non-Markovian, and the bath memory is determined by the reorganization energy and the frequency spectrum of the bath. Despite the relatively large bath reorganization energy, due to the discrete nature of the bath, non-Markovinity can still be observed in the dynamics.

A further distinguishing feature of our model is that coherences can be created dynamically during the course of evolution. Such behavior can only be observed in ‘non-secular’ formulations of EET. The secular approximation decouples the evolution of populations and coherences and is, for instance, invoked in the original form of the Redfield theory [72, 71].
2.5 Conclusion and further work

In this chapter we considered the dynamics of a molecular dimer as described by the spin-boson model and aimed to obtain a solution for the evolution of the reduced density matrix of the system. The standard perturbative treatments utilized in solving this problem regard either the bath or the electronic coupling as a perturbation, obtaining a solution for the dynamics in a given limit. In this chapter we aimed to take a fresh look at the problem and obtain the dynamics by exponentiating the Hamiltonian as exactly as possible. The Fulton-Gouterman (FG) diagonalization recipe was used to achieve this goal. The transformation diagonalizes the electronic part of the Hamiltonian by projecting the Hamiltonian into subspaces of even and odd parity, where the parity is with respect to the number of phonons in a given mode. The resulting Hamiltonian is diagonal in the electronic basis but tridiagonal in the phonon basis. Unfortunately the transformation renders the exact evaluation of the trace over the bath modes impossible. An approximation thus must be introduced to compute the reduced density matrix. The approximation is an effective weak (electronic) coupling approximation, and restricts the dynamics to low temperatures and small electronic couplings (in comparison to the bath frequencies).

We obtain analytic solutions for the evolution of the reduced density matrix in this limit and compute the dynamics for a discrete vibrational bath in the site as well as the FG basis. Populations reach a steady-state over a time scale of $\sim 30$ fs, decoherence time however, is observed to be significantly shorter ($\sim 10$ fs), as might be expected in the weak coupling limit. The two time scales deviate further as the electronic coupling is reduced, as larger electronic coupling results in faster energy transfer but influences the decoherence time minimally.

The limitation with regards to temperature implies that the theory is of little relevance in photosynthetic complexes \textit{in vivo}. It may however be applied to other systems exhibiting EET. If broadening of the bath modes can be adequately incorporated in the
theory, the model can be applied to describe the interaction between the electronic and the high frequency vibrational modes of organic molecules (such as naphthalene or anthracene) in the gas phase. There is a weak electronic coupling between these molecules that promotes the transfer of energy. The torsional modes of the molecules can be modelled as an anti correlated bath, in the manner presented in the present treatment.
Chapter 3

Phonon-mediated path-interference in electronic energy transfer

3.1 Introduction

A characteristic feature of some light-harvesting complexes is that the electronic coupling between the pigments is small in comparison to the reorganization energy of the vibrational modes that are coupled to the electronic degrees of freedom. Under such circumstances the phonon bath is understood to mediate the transfer of electronic energy and localize electronic excitation to individual pigments. Moreover, in this regime, the electronic energy transfer (EET) is often described as an incoherent transfer process for which Förster theory provides an adequate description of the dynamics of probabilities for the excitation to reside at any of the pigments [88]. However, subtle quantum phenomena such as quantum interference between transfer pathways, that cannot be captured within the Förster formalism, might persist in this limit. In this chapter we pose the question: can ‘non-classical’ phenomena in the incoherent regime of energy transfer be thought of as a correction to the classical transfer rates, arising from the interference of classical pathways? We use the term ‘non-classical’ to refer to corrections to the transfer rates
due to path-interference. This is to emphasize the fact that although these corrections have no classical analogue as far as the manipulation of probabilities are concerned, the term ‘quantum corrections’ might be misleading, as the entire framework in which the transfer rates are computed is quantum mechanical.

The dynamics and spectroscopy of natural and synthetic multichromophore systems is dominated by the interplay between electronic and vibrational degrees of freedom. Decoherence of electronic excitations is normally caused by low-frequency solvent modes described by a continuous spectral density. Interaction with high-energy vibrational modes is generally described via a spectral density composed of a set of discrete harmonic oscillators with energies larger than the thermal energy. The precise role played by each set of modes in EET, and their influence in coherent dynamics is an intriguing question which has been the subject of recent attention [42, 89, 90]. Of particular interest is the role played by localized vibrational modes whose frequency match the energy transitions in the system, as observed in several pigment dimers [42] and multichromophore assemblies [91]. Here we visit this problem by investigating the influence of each set of modes on the interference correction.

The problem of path interference in energy transfer has been addressed by a number of authors in various contexts [92]. For instance, electron transfer through intervening bonds or high energy intermediate sites has been a subject of extensive research in the chemical physics community [93, 94, 95, 96, 5, 97, 98]. These formalisms are often perturbative (as well as Markovian) and demand the energy of the intermediate site to be large, such that the perturbation remains small [93]. More recent treatments have considered non-Markovian corrections to the transfer rate and can be applied to both near-resonant and off-resonant intermediate sites [99, 100, 101]. Energy transfer in donor-bridge-acceptor systems have also been considered in a recent work by Jang via a polaronic master equation [102].

In this chapter we consider a prototype system consisting of a donor-acceptor pair
and a mediator site, and present analytic solutions for the non-Markovian corrections to the transfer rate due to path-interference. The vibrational and electronic parameters of phycoerythrin 545 (PE545), a light harvesting antenna in which quantum mechanical coherence is believed to play an important role in excitation energy transfer [39], are used in computation of the interference correction for the prototype three-site system. We observe that within a localized transfer model, and for physically realistic parameters, path-interference makes a finite (\( \sim 10\% \)) correction to the transfer rate, and is dependent on the vibrational spectra, the electronic couplings, as well as the distribution of the site energies in the system.

The material presented in this chapter follows closely the results of the article [103]. The details of the calculations presented in this chapter can be found in Appendix D.

3.2 Theoretical Methodology

3.2.1 Kenkre and Knox revisited

Kenkre and Knox theory of non-Markovian energy transfer states that in phonon-assisted EET each mode of the phonon bath contributes an oscillatory term to a time-dependent transfer rate, and by keeping track of these contributions one can solve for the time-dependence of the population transfer rate [86, 87]. In the steady-state, the non-Markovian master equation is reduced to the Pauli master equation. In this section we begin by deriving the Kenkre and Knox result via time-dependent perturbation theory. We demonstrate that non-markovian transfer rate is a first-order term in a perturbative expansion in which the higher order terms can be interpreted as either the probabilities associated with indirect pathways, or ‘coherences’ arising from quantum mechanical path-interference. We furthermore check the consistency of our formalism by demonstrating that path-interference is negligible if the reorganization energy of the bath is sufficiently large.
We begin by recalling that in time-dependent perturbation theory the system Hamiltonian is partitioned into a zero-order term and a time-dependent perturbation. We use the complete basis \( \{ |n\rangle \} \) to denote the eigenstates of the unperturbed Hamiltonian, that is

\[
H = H_0 + V(t),
\]

\[
H_0 |n\rangle = E_n |n\rangle.
\]

If the system starts in the state \( |i\rangle \) and evolves to the state \( |\alpha(t)\rangle \), one can write the expansion,

\[
|\alpha(t)\rangle = U_I(t) |i\rangle = \sum_f c_{if}(t) |f\rangle,
\]

where \( U_I(t) \) is the unitary evolution operator in the interaction picture. We then write the Dyson expansion for the amplitude \( c_{if}(t) \)

\[
c_{if}(t) = \langle f | U_I(t) | i \rangle = c_{if}^{(0)}(t) + c_{if}^{(1)}(t) + c_{if}^{(2)}(t) + ...
\]

The terms of the Dyson series are determined by the matrix element of the perturbation \( V(t) \). The leading terms of the expansion are given by [24]

\[
c_{if}^{(0)}(t) = \delta_{if},
\]

\[
c_{if}^{(1)}(t) = -i \int_0^t e^{i\Omega_{fi}t'} V_{fi}(t') dt',
\]

\[
c_{if}^{(2)}(t) = (-i)^2 \sum_m \int_0^t dt' \int_0^{t'} dt'' e^{i\Omega_{fm}t'} V_{fm}(t') e^{i\Omega_{im}t''} V_{mi}(t'').
\]

The transition probability from the state \( |i\rangle \) to the state \( |f\rangle \) is given by

\[
P_{if}(t) = |c_{if}^{(1)}(t) + c_{if}^{(2)}(t) + ...|^2.
\]

One can apply the above general formalism to EET by assuming that \( |i\rangle \) represents the state of an excited donor molecule and \( |f\rangle \) the state of an acceptor after the excitation transfer. The probability of excitation transfer at time \( t \) is then obtained from Eq. (3.8).
If the perturbation is assumed to be time-independent, the rate of change of population at $|f\rangle$ to the first order in the perturbation is given by

$$k_{if}(t) \simeq \frac{d}{dt}|c_{if}^{(1)}|^2 = 2\frac{|V_{fi}|^2}{\Omega_{fi}} \sin(\Omega_{fi}t).$$

(3.9)

The temporal variations of this rate can be expressed in terms of the memory kernel $G_{if}(t)$, defined by the equation

$$k_{if}(t) = \int_0^t G_{if}(\tau)d\tau.$$  

(3.10)

Thus, the memory kernel associated with the amplitude $c_{if}^{(1)}(t)$ is given by

$$G_{if}^{(1)}(t) = 2|V_{fi}|^2 \cos(\omega_{fi}t).$$

(3.11)

To describe phonon-assisted energy transfer we next assume that the electronic state $|i\rangle$ ($|f\rangle$) is coupled to a ladder of phonon modes $\{|k\rangle\}$ ($\{|q\rangle\}$), and that the occupation probabilities of the phonon modes are determined by a Boltzmann factor. Upon this assumption Eq. (3.11) becomes

$$G_{if}^{(1)}(t) = 2\sum_{kq} \frac{e^{-\beta \epsilon_k}}{Z} |\langle f,q|V|i,k\rangle|^2 \cos [(\omega_{kj} + \Omega_{if})t],$$

(3.12)

where $\beta$ is the inverse temperature and $Z$ is the partition function. The energy difference between the initial and final states has been divided into the change in the electronic energy $\Omega_{if}$, and the change in the phonon energy $\omega_{kj}$. Eq. (3.12) is the ‘memory possessing transition probability’ of Kenkre and Knox (Eq. (2.5) in [87]).

### 3.2.2 Manipulation of probabilities: sequential versus super-exchange

Before going any further, it is insightful to consider the manipulation of probabilities as governed by Eq. (3.8). Figure 3.1 is a schematic illustration of the three sites and the
energy transfer pathways. Classically, the transfer probability from the state $|i\rangle$ to the state $|f\rangle$ can be written as

$$P_{if}^{SQ}(t) = P_{if}(t) + P_{im}(t)P_{mf}(t)$$

(3.13)

where all probabilities are quantum mechanical, but are manipulated classically. This describes a sequential transfer process where the probabilities of the successive transfer steps are uncorrelated. In phonon-assisted energy transfer, sequential transfer occurs in the fast thermalization limit where the vibrational states of the intermediate site are relaxed to a thermally equilibrated state before the excitation is transferred to the acceptor site. That is, the memory of the $|i\rangle \rightarrow |m\rangle$ transfer is lost before the $|m\rangle \rightarrow |f\rangle$ transfer occurs. The probabilities $P_{im}(t)$ and $P_{mf}(t)$ describe first order processes and are given by $P_{im}(t) = |c_{im}^{(1)}(t)|^2$ and $P_{mf}(t) = |c_{mf}^{(1)}(t)|^2$.

In the slow thermalization limit however, the indirect transfer is a coherent process and the corresponding probability is given by

$$P_{if}^{SX}(t) = |c_{if}^{(1)}(t) + c_{if}^{(2)}(t)|^2.$$  

(3.14)

Such coherent indirect transfer is often refereed as a superexchange process [104]. It is evident that the interference term in Eq. (3.14) has no classical equivalent. Moreover, unlike the sequential case the probability associated with the indirect path cannot be expressed as the product of two uncorrelated probabilities, that is $|c_{if}^{(2)}(t)|^2 \neq |c_{im}^{(1)}(t)|^2|c_{mf}^{(1)}(t)|^2$.

In summary, a sequential process demands classical manipulation of uncorrelated probabilities whereas a superexchange process involves quantum mechanical manipulation of the pathway amplitudes. Fast thermalization in the sequential limit destroys the coherent second order amplitude. There is therefore no interference in the sequential limit. A superexchange process leads to: 1) a coherent second order contribution to the transfer rate and thus correlations between probabilities of sequential events, 2) corrections due to interference of pathways. In the regime of weak electronic coupling, the direct transfer rate is much larger than the indirect coherent contribution. We therefore
only concern ourselves with the direct transfer rate and the interference correction in the superexchange limit.

### 3.2.3 Linear exciton-phonon Hamiltonian

The successive orders of the Dyson series in Eq. (3.4) can be evaluated for a given perturbation. In this section we evaluate the first three terms of the expansion for the linear exciton-phonon Hamiltonian. The Hamiltonian is given by

\[
H = \sum_{n,k} a_n^\dagger a_n \left[ \epsilon_n + \phi_{nk} \omega_k (b_k^\dagger + b_k) \right] - \sum_{mn} J_{mn} a_m^\dagger a_n + \sum_k \omega_k b_k^\dagger b_k
\]  

(3.15)

where \( J_{mn} \) is the electronic coupling between the sites \( m \) and \( n \), \( \{ a_n^\dagger, a_n \} \) are the molecular raising and lowering operators for site \( n \), \( \epsilon_n \) is the electronic transition energy at site \( n \), \( \{ b_k^\dagger, b_k \} \) are the bosonic creation and annihilation operators for mode \( k \) of the bath, \( \phi_{nk} \) is a dimensionless displacement quantifying the exciton-phonon coupling between site \( n \) and mode \( k \), and \( \omega_k \) are the bath frequencies. To incorporate bath-induced localization we next apply a small-polaron transformation on the Hamiltonian and identify the off-diagonal element in the polaron basis as the relevant perturbation [24], that is

\[
\tilde{H} = \sum_n a_n^\dagger a_n \tilde{\epsilon}_n + \sum_k \omega_k \tilde{b}_k^\dagger \tilde{b}_k - \sum_{n \neq m} J_{nm} [a_n^\dagger F_n^\dagger F_m a_m]
\]  

(3.16)

\[
V = -\sum_{n \neq m} J_{nm} [a_n^\dagger F_n F_m a_m]
\]  

(3.17)
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where

\[ F_n = e^{-\sum_k \phi_{nk} (b_k^\dagger - b_k)}, \]  

(3.18)

\[ \tilde{\epsilon}_n = \epsilon_n - \sum_k \frac{\hbar_k^2}{\omega_k}, \]  

(3.19)

The transfer rates computed henceforth are thus between the dressed sites. It is noteworthy that although polaron formation modifies the transfer rates, the basis in which the populations are computed is still the site basis. Next we note that Eq. (3.8) can equivalently be written as the expansion of a generalized memory kernel, that is

\[ G_{if}(t) = G_{ij}^{(1)}(t) + G_{ij}^{(12)}(t) + G_{ij}^{(2)}(t) + \ldots, \]  

(3.20)

where

\[ G_{ij}^{(1)}(t) = \partial_t^2 |c_{ij}^{(1)}(t)|^2, \]  

(3.21)

\[ G_{ij}^{(12)}(t) = 2\partial_t^2 \text{Re} [c_{ij}^{(1)}(t)c_{ij}^{(2)}(t)^*], \]  

(3.22)

\[ G_{ij}^{(2)}(t) = \partial_t^2 |c_{ij}^{(2)}(t)|^2. \]  

(3.23)

In these expressions \( G_{ij}^{(1)}(t) \) is the Kenkre and Knox memory associated with a direct transfer pathway, \( G_{ij}^{(2)}(t) \) is the correction due to the coherent indirect pathway with one intermediate site, \( G_{ij}^{(12)}(t) \) is a correction arising from the interference of these two pathways. This contribution is henceforth referred to as the first-order interference. More generally this expansion involves terms of the form \( G_{ij}^{(p)}(t) \) which are associated with coherent pathways with \( p - 1 \) intermediate sites, as well as terms of the form \( G_{ij}^{(pq)}(t) \) which arise from the interference of two pathways, one with \( p - 1 \) and the other with \( q - 1 \) intermediate sites. For a finite-size system, there are a finite number of pathways whose associated memory can, in principle, be explicitly evaluated.

In this chapter we are interested in quantifying the first-order interference \( G_{ij}^{(12)}(t) \) and identifying the conditions under which it influences the transfer rate. We therefore specialize to the simplest case of three sites. We furthermore demonstrate that as the number of intermediate sites associated with a given pathway is increased, the amplitude
of that pathway is exponentially reduced. This shows that in the incoherent limit where the electronic couplings are small, the expansion is always convergent and the generalized memory is dominated by contributions from pathways with fewer intermediate sites.

### 3.2.4 Pathway associated memory kernels

By applying the perturbation of Eq. (3.17) to Eq. (3.6) and Eq. (3.7), and considering a continuous spectral density, we arrive at the following results for the first-order memory,

\[
G^{(1)}_{ij}(t) = 2|J_{ij}|^2 \text{Re} \left\{ e^{i\Omega_{ij} t} I^{(2)}(t, 0) \right\},
\]

where the two-time bath correlation function \( I^{(2)}(t_1, t_2) \) is defined at the end of this section. The first-order interference is the summation of four contributions and is given by

\[
G^{(12)}_{ij}(t) = J_{ij} J_{fm} J_{mi} \sum_{\alpha=1}^{4} f^{(12)}_{\alpha}(t),
\]

where

\[
f^{(12)}_{1}(t) = 4 \text{Re} \left\{ i e^{-i\Omega_{ij} t} \sum_m \int_0^\infty dt_1 e^{-i\Omega_{im} t_1} I^{(3)}(-t, 0, t_1) \right\},
\]

\[
f^{(12)}_{2}(t) = 2 \text{Re} \left\{ i e^{i\Omega_{fm} t} \int_0^\infty dt_1 \int_0^\infty dt_2 \left[ i\Omega_{fm} + \partial_i \right] I^{(3)}(-t_1, t_2, -t) e^{i\Omega_{it_1} t} e^{i\Omega_{mt_2}} \right\},
\]

\[
f^{(12)}_{3}(t) = 2 \text{Re} \left\{ i e^{i\Omega_{fm} t} \int_0^\infty dt_1 \int_0^\infty dt_2 \left[ i\Omega_{fm} + \partial_i \right] I^{(3)}(-t_1, t_2, t) e^{i\Omega_{it_1} t} e^{-i\Omega_{mt_2}} \right\},
\]

\[
f^{(12)}_{4}(t) = -2 \text{Re} \left\{ i e^{i\Omega_{it} t} \int_0^\infty dt_2 \int_0^\infty dt_1 \left[ i\Omega_{it} + \partial_i \right] I^{(3)}(t, t_1, t_2) e^{-i\Omega_{mt_1} t} e^{i\Omega_{mt_2}} \right\},
\]

and \( m \) is the index associated with the intermediate site. \( I^{(2)}(t_1, t_2) \) and \( I^{(3)}(t_1, t_2, t_3) \) are the two-time and three-time bath correlation functions and are given by

\[
I^{(2)}(t_1, t_2) = \exp \left\{ -2 \int_0^\infty d\omega \frac{J(\omega)}{\omega^2} [1 + 2n(\omega)] \right\}
\]

\[
\times \exp \left\{ 2 \int_0^\infty d\omega \frac{J(\omega)}{\omega^2} n(\omega) e^{i\omega(t_1 - t_2)} \right\}
\]

\[
\times \exp \left\{ 2 \int_0^\infty d\omega \frac{J(\omega)}{\omega^2} [n(\omega) + 1] e^{-i\omega(t_1 - t_2)} \right\}
\]

\[
I^{(3)}(t_1, t_2, t_3) = \exp \left\{ -2 \int_0^\infty d\omega \frac{J(\omega)}{\omega^2} [1 + 2n(\omega)] \right\}
\]

\[
\times \exp \left\{ 2 \int_0^\infty d\omega \frac{J(\omega)}{\omega^2} n(\omega) e^{i\omega(t_1 - t_2)} \right\}
\]

\[
\times \exp \left\{ 2 \int_0^\infty d\omega \frac{J(\omega)}{\omega^2} [n(\omega) + 1] e^{-i\omega(t_1 - t_2)} \right\}\]
and
\[ I^{(3)}(t_1, t_2, t_3) = I^{(2)}(t_1, t_2)^{1/2} I^{(2)}(t_1, t_3)^{1/2} I^{(2)}(t_2, t_3)^{1/2} \quad (3.31) \]

where \( J(\omega) \) is the spectral density of the bath and \( n(\omega) = [\exp (\beta \omega) - 1]^{-1} \) is the thermal occupation number at frequency \( \omega \). Higher order terms can be evaluated in the same manner and have not been considered in the present chapter.

Note that the factor \( I^{(2)}(t, 0) = \langle F_i^\dagger(t) F_n(t) F_n^\dagger F_i \rangle \) is a vibrational overlap, or Frank-Condon term, which quantifies the thermally averaged squared overlap of the initial harmonic vibrational level of the donor state, with the vibrational excited state of the acceptor state [25, 24]. The vibrational overlap integral is an essential ingredient in phonon-assisted transport problems, and appears explicitly in other formulations of EET [105, 106, 107].

The two-point correlation function of the type defined in Eq. (3.30) has been historically investigated by Kubo [108], and forms the basis for calculation of spectral line-broadening in linear spectroscopy [109, 110]. It can be demonstrated that for short times \((\omega_c t < 1)\), the function has a Gaussian decay profile, that is \( I^{(2)}(\tau) \sim \exp \left[ -\tau^2/(2\sigma^2) \right] \) where the characteristic decay time is given by \( \sigma^{-2} = \int_0^\infty \omega J(\omega) \coth (\beta \omega/2) \). For long times \((t \gg \beta)\) however the decay is exponential, that is \( I^{(2)}(\tau) \sim \exp [-\tau/\tau_d] \) [111].

For the purpose of the present chapter we suffice to note that under the assumption of independent and identical bath modes, an \( n \)-point correlation function can always be factorized as the product of \( n \) two-point correlation functions, as shown in Eq. (3.31). If the two-point correlation functions are assumed to decay exponentially, it can readily be demonstrated that the function \( \int_0^\infty dt_2 \cdots \int_0^\infty dt_n I^{(n)}(t_1, \ldots, t_n) \) decays on the same time scale as \( I^{(2)}(t_1, 0) \), but has a much smaller amplitude. This point will be of importance in the next section where we numerically compute the first two terms in the expansion of the memory kernel and observe that although the higher order terms are exponentially smaller, all orders of the memory kernel decay on the same time scale.

The contribution of the coherent indirect pathway is not discussed on the grounds
that it is the highest order term in the expansion and we estimate it to be two orders of magnitude smaller than the direct term.

3.3 Results and discussion

3.3.1 First-order interference in PE545

In this section we numerically solve for the time-dependence of the memory kernels obtained in the previous section. Inspired by the observation of coherence in EET in light-harvesting antennae, we consider the electronic and vibrational parameters of PE545 protein in our investigations of path-interference in a prototype three-site model. The electronic and vibrational parameters of PE545 are documented in Refs [112, 91]. Later on however, we shall vary the system and the bath parameters at will to explore the different regimes under which interference makes a significant contribution to energy transfer.

The structural arrangement of the light-absorbing molecules in PE545 (isolated from *Rhodomonas* sp. strain CS24) is shown in Fig. 3.2. The vibrational spectrum of PE545 can be modeled as two low-frequency Brownian oscillator spectral densities, and a total of fourteen discrete modes at higher frequencies [91]. Inspired by this system, we aim to investigate the form of the interference correction for each of these contributions to the spectral densities. We consider a prototype three-site model and compute: 2) The interference correction due to a localized high-frequency mode, whose energy is of the order of the donor-acceptor energy difference, 1) The interference correction for thermally populated low-frequency modes, described by a continuous spectral density with a characteristics cutoff frequency.
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Figure 3.2: Chromophores from the structural model of PE545 (*Rhodomonas* sp. strain CS24). We investigate the influence of PEB 158 C (intermediate site) to the transfer rate from DBV 19 A to DBV 19 B.

**Single mode spectral density**

We first consider a Lorentzian spectral density centered at $718 \text{ cm}^{-1}$, with a narrow width of $50 \text{ cm}^{-1}$ and a total reorganization energy of $E_R = 110 \text{ cm}^{-1}$. For this spectral density we compute the first two orders of the memory kernel between the two pathways: DBV A $\rightarrow$ DBV B and DBV A $\rightarrow$ PEB 158 C $\rightarrow$ DBV B as indicated in Fig. 3.2. The left panel on Fig. 3.3 depicts the spectral density and the corresponding memory terms. The relevant intermediate transition frequencies are denoted on the spectral density. The oscillations in the first-order memory, as well the interference term, have a vibrational origin and occur at the frequency of the single bath mode.

**Brownian Oscillator spectral density**

We now consider a Brownian oscillator spectral density of the form

$$J(\omega) = \frac{2E_R}{\pi} \frac{\omega \omega_c}{\omega^2 + \omega_c^2}$$  \hspace{1cm} (3.32)

with a total reorganization energy of $E_R = 110 \text{ cm}^{-1}$, and a cutoff frequency of $\omega_c = 100 \text{ cm}^{-1}$. The spectral density and the corresponding memory terms are depicted on
the right panel in Fig. 3.3. The oscillations in $G_{ij}^{(12)}(t)$ occur at the frequencies of the intermediate transitions ($\omega_{im}$ and $\omega_{mf}$) and will be explored further in this section. By comparing the form of the interference correction for each choice of the spectral density, one can conclude that depending on the form of the spectral density, and its relation to the intermediate transition frequencies, the oscillations in the interference correction may have an electronic or a vibrational character. Moreover, regardless of the form of the spectral density, the interference correction to the transfer rate in the steady-state is given by

$$k_{ij}^{(12)} \simeq \int_0^\infty dt \ G_{ij}^{(12)}(t).$$  \hspace{1cm} (3.33)

Thus, if the interference correction exhibits fast oscillations on the time-scale of the bath memory, it contributes a vanishingly small correction to the transfer rate in the steady-state. Such fast oscillations can occur due to: 1) high frequency intermediate sites, 2) high frequency discrete bath modes. There is always a correction on a short time-scale ($\sim 100$ fs) which demands a non-Markovian treatment of the bath and cannot be captured within a Markovian (or course-grained) formulation.

### 3.3.2 Path-interference correction: short time versus steady state

To investigate the influence of the intermediate energy state on the nature of the interference correction, we next consider three different intermediate states, as depicted in Fig. 3.4. For each scenario we obtain the interference correction. The first-order memory is independent of the intermediate site and is plotted in Fig. 3.3d. The interference corrections for specific states are plotted on Fig. 3.4b. If the intermediate site is energetically far from the donor, it constitutes a virtual bridging state. A virtual state contributes to the donor-acceptor transition rate, but can only be populated for a short time $\Delta t$, satisfying the Heisenberg uncertainty relation $\Delta t \ \Delta E \sim 1$, where $\Delta E$ is the
Figure 3.3: Left panel: a) Lorentzian spectral density of width 50 cm$^{-1}$, and reorganization energy $E_R = 110$ cm$^{-1}$. c) Direct transfer kernel and, e) interference kernel for the Lorentzian spectral density. Right panel: b) Brownian oscillator spectral density of cutoff frequency $\omega_c = 100$ cm$^{-1}$, and reorganization energy $E_R = 110$ cm$^{-1}$. d) Direct transfer kernel and, f) interference kernel for the Brownian oscillator bath. The donor-acceptor energy gap is $\omega_{if} = 35$ cm$^{-1}$, the intermediate site has an energy of $\omega_{mi} = 703$ cm$^{-1}$. The relevant electronic couplings are $J_{if} = -4.08$ cm$^{-1}$, $J_{im} = -31.85$ cm$^{-1}$, $J_{mf} = -2.88$ cm$^{-1}$. 
Figure 3.4: a) The energetics of different intermediate states. The relevant frequencies are $\omega_{if} = 35\text{ cm}^{-1}$, $\omega_{m0i} = 1500\text{ cm}^{-1}$, and $\omega_{m1i} = \omega_{fm2} = 703\text{ cm}^{-1}$. b) First-order interference for different intermediate states. c) Steady-state correction to the transfer rate as a function of the energy of the intermediate site. Note that static disorder in the site energy is $\pm 200\text{ cm}^{-1}$. 
energy difference between the donor state and the intermediate site. The state $|m_0\rangle$ in Fig. 3.4a. is such a virtual state. For this state the interference term exhibits oscillations at the intermediate transition frequency. The interference correction is significant for short times, but vanishing in the steady-state.

The steady-state correction to the transfer rate due to path-interference as a function of the energy of the intermediate site, is plotted in Fig. 3.4c. The states that lie between the donor and acceptor contribute minimally to the transfer rate. States with energy gap of $\sim 300 \text{ cm}^{-1}$ either above the donor or below the acceptor give the largest contributions.

In this example all electronic couplings are negative. If the sign of an odd number of coupling matrix elements is changed, the sign of the interference contribution is also changed. The classical probabilities however depend on the squared modulus of the couplings, and are thus phase-invariant.

### 3.3.3 Classical limit

If the interference corrections have a truly quantum origin, they must vanish in a suitable classical limit. In this section we argue that by changing the bath reorganization energy we can observe this quantum to classical transition. Figure 3.5 shows the two orders of the memory kernel for the intermediate state $|m_1\rangle$ as the reorganization energy of the bath is raised. All orders of the memory become smaller as the reorganization energy is increased. To investigate whether the interference contribution is diminishing faster than the direct transfer rate, we define the function $R(E_R)$ to be the relative correction to the donor-acceptor steady-state transfer rate due to the first-order interference. That is

$$R(E_R) = \frac{\int_0^\infty dt \ G_{ij}^{(12)}(t)}{\int_0^\infty dt \ [G_{ij}^{(1)}(t)+G_{ij}^{(2)}(t)]} \times 100$$

$$\simeq \frac{\int_0^\infty dt \ G_{ij}^{(12)}(t)}{\int_0^\infty dt \ G_{ij}^{(1)}(t)} \times 100$$

(3.34)
where in the second line the correction due to the indirect pathway has been neglected on the grounds that it is two orders of magnitude smaller than the first-order term. Figure 3.5d. is a plot of this correction ratio versus the reorganization energy of the bath for the intermediate state $|m_1\rangle$. Due to the small-polaron transformation, the bath cutoff cannot be made arbitrarily small. For the state $|m_1\rangle$ the magnitude of this correction is 5.7% for a bath energy of 110 cm$^{-1}$, and is reduced to less than 4% for a bath energy of 1000 cm$^{-1}$. Thus in the limit of weak electronic coupling raising the bath energy reduces the interference contribution slowly, and interference vanishes in the limit of infinite bath energy.

Figure 3.5: a) Brownian oscillator spectral density for different reorganization energies. b) First-order memory, c) first-order interference for different bath reorganization energies for the intermediate state $|m_1\rangle$. d) The correction due to the first-order interference relative to the first-order memory as a function of the bath reorganization energy.
3.3.4 Higher order pathways

In this section we demonstrate that, provided that the electronic couplings are sufficiently small, each term in the expansion of the memory kernel is smaller than its previous, such that the most important pathways are always the ones with fewer intermediate sites. The amplitude of a generalized memory associated with a path with \( p - 1 \) intermediate sites is determined by

\[
G_{ij}^{(p)} \sim J_{i,m_1}^2 \ldots J_{m_{p-1},f}^2 I^{(2p)}(t_1, \ldots, t_{2p})
\]

(3.35)

where the magnitude of the \( p \)-point correlation function \( I^{(p)}(t_1, \ldots, t_p) \), is dominated by the following exponential pre-factor

\[
I^{(p)}(t_1, \ldots, t_p) \sim \exp \left\{ - p \int_{0}^{\infty} d\omega \frac{J(\omega)}{\omega^2} [1 + 2n(\omega)] \right\}.
\]

(3.36)

We now assume, for the sake of simplicity, that all the couplings are of the same order. That is,

\[
G_{ij}^{(p)} \sim J^2 I^{(2p)}(t_1, \ldots, t_{2p}).
\]

(3.37)

The ratio of two successive terms is thus determined by

\[
\frac{G_{ij}^{(p+1)}}{G_{ij}^{(p)}} \sim J^2 \exp \left\{ - 2 \int_{0}^{\infty} d\omega \frac{J(\omega)}{\omega^2} [1 + 2n(\omega)] \right\}.
\]

(3.38)

The exponential pre-factor therefore guarantees that terms with higher order temporal correlations are significantly smaller than the ones with lower order correlations. For large electronic couplings however, the \( J^2 \) term may exceed the exponential pre-factor. We observe that for realistic parameters that satisfy the condition \( J < E_R \) (as demanded by the small-polaron transformation) the ratio is always dominated by the exponential pre-factor. We therefore conclude that in the localized regime of energy transfer where the electronic couplings are small, the coherent contribution of a given pathway to the transfer process is exponentially diminished as the number of intermediate ‘relay’ sites
in that pathway is increased. The same conclusion can be applied to the interference corrections: The contribution of an interference term may exceed that of a classical pathway if it involves a lower-order temporal correlation function.

A crucial question arising at this juncture is, what happens to the interference corrections as the size of the system is increased? For a system of size $n$, there are $\binom{n-2}{p}$ ways that pathways with $p$ intermediate sites can arise. It is therefore somewhat trivial that the integrated contribution due to higher order pathways is more significant for larger systems. Our preliminary analysis shows that if all pathways with a given number of intermediate sites carry approximately the same weight, the sum total of all path interference contributions does not, in general, vanish as the system size is increased. However, the assumption that the transfer time is much shorter than the thermalization time-scale, becomes more difficult to satisfy as the number of intermediate sites is increased. Arbitrarily high order coherent pathways can therefore only exist at close to zero temperature. Thermal equilibration destroys the higher order coherent contributions, and at any finite temperature coherent pathways with more than a few intermediate sites can be neglected.

### 3.3.5 Comparison to other treatments

In bridge-assisted EET, the excitation can be thermalized at the mediator site before hopping to the acceptor. This describes a sequential process, with no interference corrections. A super-exchange process on the other hand describes a coherent second order process where the time scale of thermalization is slower than the EET time scale. These two limiting cases have been historically treated distinctively, because the perturbative expansions applied for a superexchange interaction are divergent for a sequential process. A unified treatment that extrapolates between the two limits was first formulated by Sumi and Kakitani [99, 100]. Our treatment assumes that there is a coherent second order contribution and that the excitation is not thermalized at the mediator site.

Scholes and Ghiggino [113] and Lin [114] have studied the higher order perturbative
terms of the transfer rate expansion for the superexchange case. In the Markov (steady-state) limit, we found our results to be in agreement with their findings. Our treatment however, captures subtle short time features of the interference correction which are washed out in the coarse graining approximation of a time-independent Markovian formulation.

In a formulation similar to ours, Kimura [101] applied time-dependent third-order perturbation theory to compute the modification to the transfer rate due to a mediator state. The difference between the two formulations lies in our treatment of the bath, and the application of the small polaron transformation which takes explicit account of bath-induced localization. Kimura obtains similar results for the dependence of the steady-state interference correction on the energy of the mediator site.

### 3.4 Conclusion

It has already been noted in the literature that a bridging molecule can substantially modify the energy transfer rate from a donor to an acceptor site. Existing theoretical models however, often assume a Markovian vibrational bath, and due to the short time-scale of non-Markovianity in many systems of interest, the influence of an intermediate ‘relay’ state on a memory-possessing transition rate has largely been overlooked. In this chapter we have generalized the Kenkre and Knox theory of non-Markovian energy transfer to account for this influence. Our results indicate that within a localized transfer representation, a bridging molecule can modify the transfer rate between a donor and an acceptor, provided that it is not too energetically far from the donor and the acceptor. For small electronic couplings this modification is by and large dominated by the interference between the direct and the indirect classical pathways.

Many of the subtle features of phonon-mediated path-interference demand a careful averaging of the $n$-point temporal correlation function, and cannot be reproduced with a
Markovian approach. For instance, path-interference may lead to oscillatory corrections to the transfer rate if the energy of the intermediate site is sufficiently far from the donor-acceptor transition. Such oscillations require consideration of a finite non-Markovianity window and cannot occur within a Markovian formulation. For off-resonant intermediate states, the interference correction to the transfer rate is only important over short time scales (∼100 fs), and is vanishingly small in the steady-state. Near-resonant intermediate states however, can make a measurable (∼10 %) correction to the transfer rate in the steady-state. The distinct short time and steady-state dynamics of off-resonant and near-resonant intermediate states are examples of some of the subtle features of phonon-assisted path-interference that require a non-Markovian treatment of the bath. We furthermore speculate that the interference correction may contribute to the anomalous enhanced transfer rates observed in systems with multiple acceptors [115].

Our calculation does not include the influence of static disorder in the site energies. In the system considered the magnitude of static disorder at room temperature is 200 cm⁻¹ and a better estimation of the contribution of path interference should incorporate an averaging over diagonal energy fluctuations. The static disorder is likely to reduce the interference correction as the states close to resonance with the donor and acceptor contribute maximally to the interference correction. If static disorder lowers (or raises) the energy of a near-resonant intermediate site, it can change the sign of the interference correction. At room temperature contributions of these states are likely to cancel out after this averaging. A small static disorder is therefore an important factor in ensuring that interference corrections do not cancel out.

We conclude by noting that even close to the Förster limit the correction arising from interference of higher order pathways can make a measurable correction to the steady-state transfer rate. This observation is of current experimental relevance since two-dimentional electronic spectroscopy has revealed that molecules in photosynthetic antenna complexes are not as weakly coupled as is assumed in the Förster theory. Such
corrections may therefore be of importance in systems exhibiting EET where the electronic coupling is small enough (in comparison to the bath reorganization energy) to consider the excitations as localized, but large enough to render the assumption of Markovian bath correlations and instantaneous relaxation of vibrational modes questionable. In other words, if the bath retains its memory over an indirect pathway, the probabilities of sequential events remain correlated. Depending on the spectra of the vibrational bath, such coherent second order contributions can make a detectable correction to the steady-state transfer rate.
Chapter 4

Energy transfer on a multi-protein scale: A hybrid quantum-classical approach

4.1 Introduction

Until now two-dimensional electronic spectroscopy (2D ES) experiments have been used to study exclusively single light-harvesting proteins. The conclusions regarding the existence of long-lasting coherence are thus limited to the single protein scale, and the dynamics of energy transfer on a multi-protein level, or the existence of inter-protein coherence are, at present, matters of theoretical speculation. If quantum phenomena are indeed the driving force behind efficient excitation transfer, one might expect to find signatures of quantum behaviour on a larger scale, as an excitation must journey through several units of closely packed protein molecules before sensitizing the reaction centre.

Moreover, to explore the consequences of coherent behavior on larger scales (ideally on the scale of the energy funnel in the light-harvesting complex), the different operating conditions of the experiments and the natural systems must be carefully considered. In
2D ES experiments femtosecond pulses are used to create coherent superpositions of the excitonic eigenstates, and the phase coherence of this state is observed to persist for hundreds of femtoseconds. Under natural conditions however, the excitation is created by broadband sunlight, and the corresponding initial state may be described as an incoherent mixture of the excitonic eigenstates. This poses the crucial question that if coherent initial states are unlikely to be created by sunlight, how can quantum phenomena, which are revealed in the experiments as phase coherence, be manifested under natural conditions?

One implication of persistent phase coherence is that the excitonic eigenstates can maintain a finite delocalization in the steady state. In other words, as the eigenstate decoherence time is much shorter than the localization time scale, and in light of the experimentally-observed long (eigenstate) decoherence times, it is plausible to argue that in the thermodynamic limit the system relaxes towards states with finite delocalization, and that this delocalization can persist on the time scale of long-range energy transfer (\(\sim 100\text{ps}\)).

The second important question in long-range energy transfer is whether one needs to include all chromophores in the dynamics in order to obtain a reasonable estimate of the transfer time. If coherent phenomena are limited to the single protein scale, one might expect the excitation to flow towards the lowest energy sites on a single protein, and then hop from one protein to another without visiting the sites at higher energies. Within this Förster-like approximation, each protein may be modelled by its lowest energy dimer, and inter-protein energy transfer may be viewed as a random walk between the low energy dimers of neighboring proteins. If coherent phenomena are relevant on a multi-protein level (or if the transitions are strongly thermally activated), this approximation is unlikely to be valid, as the path to the reaction centre may include the higher energy sites.

In chapter 3 energy transfer pathways within a single unit of PE545 was investigated, and it was demonstrated that path-interference may make a small correction to the energy transfer time-scale if second order coherent pathways persist at ambient tem-
peratures. In this chapter we look at energy transfer on a larger scale, taking the PE545
tetramer as the prototype of a large antenna complex. Energy transfer is viewed as an
incoherent hopping process and is simulated via a Monte Carlo approach. We find that if
the pairwise transfer rates are accurately computed, the incoherent hopping mechanism
provides a reasonable estimate of the long-range transfer time (transfer time between
two chromophores in the tetramer that are farthest-apart). We adopt different hopping
models, based on various formulations of the exciton transfer problem [116, 117], and
find a transfer mechanism in which energy hops between delocalized eigenstates to yield
the fastest dynamics. Our results indicate that close packing of proteins can delocalize
an excitation between chromophores on adjacent units. This delocalization may be used
advantageously in long-range exciton transport, suggesting that exciton delocalization is
an important manifestation of quantum phenomena on a multi-protein scale.

4.2 Theoretical Methodology

Kenkre and Knox theory of excitation transfer was reviewed in chapter 2 and the details
of it derivation were presented in Appendix D. The same mathematical framework is
utilized in this chapter to compute the transfer rates. We thus begin by reviewing the
Kenkre and Knox theory and highlighting the fact that the theory may be applied to
EET in different regimes.

We recall that the time-dependence of excitation transfer from an initial state \(|i\rangle\) to a
final state \(|n\rangle\) under the influence of a non-Markovian bath, can be written as the integral
of the memory kernel \(G_{in}(t)\), associated with the transfer process, that is

\[
G_{in}(t) = 2\text{Re}\left[e^{i\Omega_{in}t}\langle V_{in}(t)V_{ni}(0)\rangle\right],
\]

(4.1)

where \(\Omega_{in}\) is the frequency difference between the initial and final states \((\hbar = 1)\), \(V_{in}\)
is the matrix element of the perturbation driving the transition, and the angle brackets
indicate an averaging over the thermally equilibrated bath modes. The rate of energy
transfer is subsequently obtained as the time integral of $G_{in}(t)$,

$$k_{in}(t) = \int_{0}^{t} G_{in}(\tau)d\tau.$$  \hspace{1cm} (4.2)

This is the Kenkre and Knox theory of non-Markovian energy transfer [86, 87], which is reduced to the Fermi Golden rule in the limit of Markovian bath correlations. In the Markov limit the bath correlations are instantaneous, and are described by delta functions. The Markov limit may thus be obtained by making the following substitution

$$G_{in}(t) \rightarrow \delta(t) \int_{0}^{\infty} G_{in}(s)ds$$  \hspace{1cm} (4.3)

The transfer rate in this limit is therefore given by

$$k_{in} = \int_{0}^{\infty} G_{in}(\tau)d\tau$$

$$= 2\text{Re}\left\{ \int_{0}^{\infty} \delta(\tau)d\tau \int_{0}^{\infty} e^{i\Omega_{in} s} \langle V_{in}(s)V_{ni}(0) \rangle ds \right\}$$

$$= 2\text{Re}\left\{ \int_{0}^{\infty} e^{i\Omega_{in} s} \langle V_{in}(s)V_{ni}(0) \rangle ds \right\}$$  \hspace{1cm} (4.4)

This result is reassuring as it indicates that in the steady-state the Kenkre and Knox transfer rate is reduced to the Markovian transfer rate.

The above formulation gives rise to a subtlety that for a given Hamiltonian distinct memory kernels may be constructed, depending on the term that is identified as the perturbation driving the transition. This raises a question regarding the regimes of applicability of each formalism, as distinct constructions of the memory kernel predict different transition rates. We return to this point later on when we compare the two different constructions of the memory kernel for the spin-boson Hamiltonian.

In this chapter we are interested in excitation transfer between chromophores of the PE545 antenna proteins, as modeled by the linear exciton-phonon Hamiltonian. The linear exciton-phonon Hamiltonian describing the interaction of $N$ coupled two-level molecules and with a phonon bath was discussed in the previous chapter and is given by
where $J_{mn}$ is the electronic coupling between the sites $m$ and $n$, $\{a_n^\dagger, a_n\}$ are the molecular raising and lowering operators for site $n$, $\epsilon_n$ is the electronic transition energy at site $n$, $\{b_k^\dagger, b_k\}$ are the bosonic creation and annihilation operators for mode $k$ of the bath, $\phi_{nk} = h_{nk}/\omega_k$ (known as the Huang-Rhys factor) is a dimensionless displacement quantifying the exciton-phonon coupling between site $n$ and mode $k$, $h_{nk}$ is the exciton-phonon coupling in energy units, and $\omega_k$ are the bath frequencies. Eq. (4.1) may be applied to the linear exciton-phonon Hamiltonian in two inequivalent ways. The first approach is the formulation of Grover and Silbey (henceforth referred to as the GS formulation) in which the shift in the nuclear coordinates in Eq. (4.5) is removed via a small-polaron transformation [24]. The transformed Hamiltonian is found to be

$$\bar{H} = \sum_n \bar{\epsilon}_n a_n^\dagger a_n + \sum_k \omega_k b_k^\dagger b_k - \sum_{n \neq m} J_{nm} F_n^\dagger F_m a_m,$$  

(4.6)

where $F_n$ is the vibrational shift operator and $\bar{\epsilon}_n$ are the shifted energies,

$$F_n = e^{-\sum_k \phi_{nk} (b_k^\dagger - b_k)},$$  

(4.7)

$$\bar{\epsilon}_n = \epsilon_n - \sum_k \frac{h_{nk}^2}{\omega_k}.$$  

(4.8)

Note that the quantity $\sum_k \frac{h_{nk}^2}{\omega_k}$ is the reorganization energy of the bath. The off-diagonal term in Eq. (4.6) may now be identified as the perturbation driving the transfer. The memory function associated with this perturbation can be written as,

$$G_{site}^{in} (t) = 2 |J_{in}|^2 \text{Re} \left\{ e^{i\Omega_{in} t} \langle F_i^\dagger(t)F_n(t)F_n^\dagger F_i \rangle \right\},$$  

(4.9)

where $\Omega_{in}$ is the frequency difference between the dressed sites, $i$ and $n$. Notice that the perturbation is a simple product of contributions from the bath and the electronic part. The thermal expectation value is therefore taken with respect to the bath parameters
only. After tracing over the bath modes, and assuming that the phonon modes are at thermal equilibrium, we arrive at the well-known result [24],

\[
\langle F_i^\dagger(t) F_n(t) F_n^\dagger F_i \rangle = \exp \left\{ - \sum_k (\phi_{ik} - \phi_{nk})^2 (1 + 2n_k) \right\} \exp \left\{ \sum_k (\phi_{ik} - \phi_{nk})^2 \left[ n_k e^{i\omega_k t} + (n_k + 1) e^{-i\omega_k t} \right] \right\}
\]

where \( n_k \) is the thermal occupation number of mode \( k \),

\[
n_k = \frac{1}{e^{\beta \omega_k} - 1}.
\]

This formalism was used in chapter 3 to investigate the path-interference correction to the transfer rate in a single unit of PE545. The theory assumes that the excitons are confined to single molecules and that the electronic excitations remain dressed by the phonon bath at all times. In other words the vibrational bath localizes the excitation on a time scale much faster that the transfer time.

An alternative construction of memory kernel from Eq. (4.5) involves transforming the full Hamiltonian by the operator that diagonalizes the electronic part. Assuming that \( T \) is the operator that brings the electronic part of the Hamiltonian to the diagonal form, one can write

\[
T^\dagger \left[ \sum_{nm} J_{nm} a_n^\dagger a_m + \sum_{nk} \epsilon_n a_n^\dagger a_n \right] T = \sum_{\alpha} E_\alpha A_\alpha^\dagger A_\alpha,
\]

where \( E_\alpha \) are the diagonalized energies and \( \{ A_\alpha, A_\alpha^\dagger \} \) are the new set of molecular operators in the excitonic basis. The bath part of the Hamiltonian is unaffected by this transformation. The exciton-phonon part is transformed as follows,

\[
T^\dagger \left[ \sum_{n,k} \phi_{nk} \omega_k (b_k^\dagger + b_k) a_n^\dagger a_n \right] T = \sum_{\alpha\beta k} g_{\alpha\beta k} A_\beta^\dagger A_\alpha (b_k + b_k^\dagger)
\]

where

\[
g_{\alpha\beta k} = \sum_i T_{i\alpha} T_{i\beta} \omega_k \phi_{ik},
\]

The Hamiltonian in the eigenstate representation is therefore given by

\[
\bar{H} = \sum_{\alpha} E_\alpha A_\alpha^\dagger A_\alpha + \sum_{\alpha\beta k} g_{\alpha\beta k} A_\beta^\dagger A_\alpha (b_k + b_k^\dagger) + \sum_k \omega_k b_k^\dagger b_k.
\]
We now identify the off-diagonal bath coupling as the perturbation and write the Hamiltonian as

\[ \tilde{H} = \tilde{H}_0 + \tilde{V}, \]  

\[ \tilde{H}_0 = \sum_\alpha E_\alpha A_\alpha^\dagger A_\alpha + \sum_{\alpha,k} g_{\alpha\alpha k} A_\alpha^\dagger A_\alpha (b_k + b_k^\dagger) + \sum_k \omega_k b_k^\dagger b_k, \]  

\[ \tilde{V} = \sum_{\alpha \neq \beta, k} g_{\alpha\beta k} A_\beta^\dagger A_\alpha (b_k + b_k^\dagger). \]  

Lastly, we eliminate the shift in the nuclear coordinates of the diagonal part of the Hamiltonian, and write the final expression as a diagonal zero-order term and an off-diagonal perturbation,

\[ \tilde{H} = \tilde{H}_0 + \tilde{V}, \]

\[ \tilde{H}_0 = \sum_\alpha E_\alpha A_\alpha^\dagger A_\alpha + \sum_k \omega_k b_k^\dagger b_k, \]

\[ \tilde{V} = \sum_{\alpha \neq \beta, k} A_\beta^\dagger A_\alpha M_{\alpha\beta k}, \]

where

\[ M_{\beta\alpha k} = g_{\alpha\beta k} \left( b_k^\dagger + b_k - \frac{2g_{\alpha\alpha k}}{\omega_k} \right) \exp \left\{ \sum_q \frac{g_{\alpha\alpha q} - g_{\beta\beta q}}{\omega_q} (b_q^\dagger - b_q) \right\}, \]

\[ \tilde{E}_\alpha = E_\alpha - \sum_k \frac{g_{\alpha\alpha k}^2}{\omega_k}. \]

The quantity \( \tilde{E}_\alpha^R = \sum_k \frac{g_{\alpha\alpha k}^2}{\omega_k} \) is the effective bath reorganization energy associated with the eigenstate \(|\alpha\rangle\). This is an important quantity and will be revisited later on when considering the regimes of applicability of the PB formulation. Identifying Eq. (4.21) as the Kenkre and Knox perturbation, one can immediately write the associated memory kernel, and arrive at the result of Pereverzev and Bittner [116]

\[ G_{\alpha\beta}(t) = 2\text{Re} \left\{ e^{i\tilde{\Omega}_{\alpha\beta}t} \sum_{kq} \langle M_{\alpha\beta k}(t) M_{\beta\alpha q}(0) \rangle \right\}, \]

where \( \tilde{\Omega}_{\alpha\beta} \) is the frequency difference between the dressed excitonic eigenstates. Averaging over the bath modes at thermal equilibrium is a straightforward but tedious exercise.
The final answer takes the form [116],

\[
\langle M_{\alpha\beta k}(\tau)M_{\beta\alpha q}(0) \rangle = (4.25)
\]

\[
g_{\alpha\beta}(\tau)f_{\alpha\beta}(\tau)g_{\alpha\beta k}g_{\beta\alpha q} \left\{ \Delta_{\alpha\beta k}(n_k + 1)e^{-i\omega_k \tau} - \Delta_{\alpha\beta k}n_k e^{i\omega_k \tau} + \Omega_{\alpha\beta k} \right\} 
\]

\[
\left[ \Delta_{\alpha\beta q}(n_q + 1)e^{-i\omega_q \tau} - \Delta_{\alpha\beta q}n_q e^{i\omega_q \tau} + \Omega_{\alpha\beta q} \right] + \delta_{kq}(n_k + 1)e^{-i\omega_k \tau} + \delta_{kq}n_k e^{i\omega_k \tau} \right\}
\]

where

\[
\Delta_{\alpha\beta k} = \frac{g_{\alpha\alpha k} - g_{\beta\beta k}}{\omega_k} \quad (4.26)
\]

\[
\Omega_{\alpha\beta k} = \frac{g_{\alpha\alpha k} + g_{\beta\beta k}}{\omega_k} \quad (4.27)
\]

\[
q_{\alpha\beta}(\tau) = \exp \left\{ -i \sum_k \Delta_{\alpha\beta k}^2 \sin (\omega_k \tau) \right\} \quad (4.28)
\]

\[
f_{\alpha\beta}(\tau) = \exp \left\{ -2 \sum_k (n_k + \frac{1}{2})\Delta_{\alpha\beta k}^2 [1 - \cos (\omega_k \tau)] \right\}. \quad (4.29)
\]

Henceforth this formulation is referred to as the PB (Pereverzev and Bittner) theory. Unlike Eq. (4.6) the perturbation of Eq. (4.22) is not a simple product of contributions from the system and the bath, and the system parameters also appear in the thermal averaging. The interpretation of this formulation is as follows: if the vibrational bath is sufficiently weak, the excitonic eigenstates retain their delocalized character. The bath influence will consequently be limited to inducing transitions between the dressed eigenstates. This formalism can thus be valid if: 1) The reorganization energy of the bath as ‘seen’ by the eigenstates is smaller than the typical value of the electronic coupling $J$, so that the eigenstates can maintain their delocalized character. 2) The off-diagonal bath coupling which induces transitions between the eigenstates is smaller than the diagonal bath coupling, such that the perturbation of Eq. (4.18) remains small.

To formalize the first condition we recall that the effective bath reorganization energy associated with the eigenstates $|\alpha\rangle$ is given by

\[
\tilde{E}_R^\alpha = \sum_k \frac{g_{\alpha\alpha k}^2}{\omega_k}. \quad (4.30)
\]
Chapter 4. Energy transfer on a multi-protein scale

By substituting Eq. (4.14) into Eq. (4.30) and assuming that the bath modes at different sites are identical and independent, we arrive at the following equation for the re-normalized bath energy

\[ E_R^\alpha = E_R \sum_i T_{i\alpha}^4, \quad (4.31) \]

where \( E_R = \sum_k \frac{h^2}{\omega_k} \) is the bare reorganization energy of the bath and \( \sum_i T_{i\alpha}^4 \) is the inverse participation ratio (IPR) of the eigenstate \( |\alpha\rangle \) (for the electronic eigenstates all entries of the matrix \( T \) are real). IPR is an inverse measure of the delocalization length of the eigenstates [118]. For maximally delocalized states IPR = 1/N, and for localized states IPR = 1. If increasing the system size enhances exciton delocalization, the effective bath reorganization energy would be a size-dependent quantity, and would be reduced as the system size is increased.

The second condition demands \( \sum_k |g_{\alpha k}|^2 > \sum_k |g_{\alpha\beta k}|^2 \) and is reduced to \( \sum_i |T_{i\alpha}|^4 > \sum_i |T_{i\alpha}|^2 |T_{i\beta}|^2 \) if the bath modes are identical and independent for all sites. The right-hand-side of the inequality is the squared overlap between the exciton states \( |\alpha\rangle \) and \( |\beta\rangle \). For localized states \( \sum_i |T_{i\alpha}|^2 |T_{i\beta}|^2 = 0 \) and the inequality is satisfied. For maximally delocalized states \( \sum_i |T_{i\alpha}|^2 |T_{i\beta}|^2 = 1 \) and we obtain an equality. Thus in contrast to the first condition, the second condition favours localization. A balance of disorder and delocalization is thus necessary in order for both conditions to hold.

In the PE545 tetramer, the bare reorganization energy of the bath is larger than the electronic coupling. The GS diagonalization is thus a viable procedure. Aggregation, however, delocalizes the excitation between sites on neighboring proteins, thereby lowering the effective bath reorganization energy. This re-normalized bath energy is now of the same order as the electronic coupling. The first condition of the PB procedure is thus satisfied. There is also sufficient energetic disorder for the second condition to hold. It is therefore by no means obvious that which diagonalization procedure is best suited for the system. Motivated by these observations, we present a numerical comparison of the dynamics of energy transfer as obtained by each formulation. We find that the approaches...
do not converge in the limit of small electronic coupling, as even a small delocalization can generate correlations which are absent in a localized transfer model.

### 4.3 PE545 Molecular cluster

In this chapter we study the inter-protein energy transfer dynamics at ambient temperature among PE545 proteins that serve as the primary light-harvesting antenna complexes for the unicellular cryptophyte algae *Rhodomonas CS24*. PE545 contains eight light-absorbing bilin molecules covalently bound to the protein scaffold [119]. Its structure and absorption spectrum is shown in Fig. 4.1 [61]. The lowest energy chromophores are a pair of dihydrobiliverdin (DBV) bilins. There are additionally two pairs of phycoerythrobilin (PEB) chromophores with a single covalent bond to the protein and a dimer of doubly bound PEB chromophores, labelled PEB’. The structure of PE545 and reason behind its experimental interest was discussed in chapter 1.

In order to study the energy transfer dynamics among PE545 units, we build a model system composed of four densely packed PE545 units. We first adopt the high-resolution crystal structure of PE545 (PDB ID 1XG0) [61]. Then, we use a rigid-body protein-protein docking algorithm in order to build a tetramer of PE545 units. In particular, we use the docking server ZDOCK to obtain a reasonable structure of the tetramer [120, 121]. ZDOCK algorithm starts by building a large number of possible orientations between two proteins (in this case two PE545 monomers). Then, the predicted structures are ranked according to a scoring function based on shape complementarity, desolvation energy, and electrostatics. In this work we always choose the first structure from this ranking. We start by predicting a suitable arrangement between two PE545 units. Then, we predict the orientation between this dimer and a new PE545 unit. This procedure is repeated until we find the structure of the PE545 tetramer, shown in Fig. 4.2. We note that in order to predict the true binding mode of a protein-protein complex, it would be necessary
to post-process a considerable number of ZDOCK predicted structures using a flexible protein-protein method. Here, however, we aim at building a reasonable, representative arrangement between the four units among the many others that could occur in the lumen, so the rigid-body docking approach is sufficient for our purposes.

Figure 4.1: a) Chromophores from the structural model of PE545. b) Absorption spectrum of PE545. The colour of the bars correspond to the coloring of chromophores in a).

4.3.1 PE545 Hamiltonian

Electronic couplings between all chromophores in the assembly were computed using quantum chemical calculations, whereas values for the diagonal site energies were taken from a fitting to steady-state spectra and transient absorption (model E from Ref. [91]). The geometries of the chromophores were taken from the PE545 tetramer structure and hydrogens were added and optimized at the HF/6-31G(d) level of theory.

We considered the fully protonated state of the two central pyrrole rings for all chromophores, consistent with previous observations [61], and substituted the cysteine residues bonded to the chromophores by the -S-CH₃ groups. Electronic couplings were
then obtained at the CIS/6-31G level of theory incorporating environment screening effects through the Polarizable Continuum Model (PCM) [122, 123, 124]. PCM cavities were built from radii obtained by applying the United Atom Topological Model to the atomic radii of the UFF force field [125]. All quantum chemical calculations were performed using a local version of Gaussian 09 adapted to perform calculations of electronic couplings between excited states on molecules [126].

The protein medium and surrounding water solvent was collectively modeled as a dielectric continuum with a relative static dielectric constant of 15 and optical dielectric constant of 2 [127]. The Hamiltonian of an isolated PE545 is listed in Table 4.1. The computed electronic couplings and diagonal energies of the tetramer are provided in appendix E.

In addition, static disorder in the chromophore transition energies caused by slow fluctuations in the protein environment was modelled by assuming uncorrelated shifts in the site energies randomly taken from a Gaussian distribution with a width (FWHM) of $\Gamma_\sigma = 400 \text{ cm}^{-1}$ [91]. Off-diagonal disorder was neglected.

Table 4.1: Diagonal elements: transition energies (cm$^{-1}$), model E from Ref. [91]. Off-diagonal elements, upper half: electronic coupling (cm$^{-1}$) between chromophore pairs. Off-diagonal elements, lower half: centre to centre separation between bilins (Å).
4.3.2 PE545 discrete vibrational modes

High-frequency intramolecular vibrational modes of the bilin chromophores were described by a set of 14 discrete oscillators [91]. In addition, the coupling of excitations to low-frequency collective modes of the pigment-protein complex was described phenomenologically by an additional discrete mode (frequency 8 cm$^{-1}$, Huang-Rhys factor 13.75) obtained by fitting to room temperature and 77 K fluorescence spectra. The fitting was performed using the emission spectra expression, Eq. 3 from Ref. [128], and adopting the electronic couplings, site energies, and static disorder described in the previous section. Note however, that here the lineshape is taken to be the sum of the above mentioned 15 discrete oscillators.

4.4 Kinetic Monte Carlo algorithm

The disorder-generating algorithm stated in the previous section was used to generate 2000 realizations of the diagonal energies. For each realization two matrices quantifying the direct transfer rate between all pairs of chromophores in the site and the eigenstate basis were computed. To obtain an estimate of the time scale of long-range energy transfer, two chromophores were chosen as the initial and final sites to host the excitation. The initial site is the higher energy DBV chromophore on the second protein (p2 DBV 19 A) and the final site is the lower energy DBV chromophore on the fourth protein (p4 DBV 19 B). These two chromophores are the pair farthest-apart in the entire assembly, separated by a distance of 83.5 Å (4.2a). The computed transfer rates were subsequently used to generate a cumulative probability distribution (CPD) function. The CPD function associated with a transition $i \rightarrow n$ is defined to be

$$\text{CPD}_i(n) = \frac{\sum_{p=1}^{n} k_{ip}}{\sum_{m} k_{im}}.$$  \hspace{1cm} (4.32)

where $k_{im}$ is the $i \rightarrow m$ transfer rate. The Monte Carlo hopping algorithm can be summarized as follows: 1. For each realization of the Hamiltonian compute the pairwise
transfer rates and use that to calculate the CPD function for each site. 2. Start at site $i$. Choose a random number $r$ and hop to site $m$, where $m = \text{CPD}_i^{-1}(r)$. 3. Compute the waiting time $t_w$ at site $i$ as $t_w = -\frac{\ln(r')}{\sum_m k_{im}}$, where $r'$ is a newly-generated random number. 4. Choose a new random number and continue the hop, while keeping track of the total accumulated waiting time. 5. Stop if the final site has been reached, or if the total time exceeds a preset value $t_{max}$. In the latter case record the hopping sequence as a failure.

To gain an understanding of the role played by the PEB bilins, two transfer scenarios were considered. In the first scenario each protein was approximated by the low energy DBV molecules. The idea behind this approximation is that according to the Förster theory the ratio of the downhill versus the uphill transfer as governed by the detailed balance is given by $\exp\{\beta\omega_{in}\}$, where $\omega_{in}$ is the transition energy. At room temperature and for a transition frequency of 1100 cm$^{-1}$, this corresponds to a ratio of 266:1. We thus neglect all uphill transfer, and assume that if the excitation is initially on a low energy DBV, it can hop to other DBVs only. In the second scenario energy transfer in the full assembly was studied. Each scenario was investigated via both the site and the eigenstate model. The maximum time to complete the journey was set to $t_{max} = 10$ ns, which is an order of magnitude larger than the excitation lifetime in PE545 [61]. For each realization the time taken to complete the journey, the number of hops between the sites (or eigenstates), as well as the percentage of trajectories that fail to reach the destination chromophore, were recorded.
Figure 4.2: a) PE545 molecular tetramer. The initial excitation was assumed to be on $p_2$ DBV 19A. The time scale for the excitation to reach $p_4$ DBV 19B was investigated. b) Only the lowest energy chromophores (DBVs) are shown. c) Arrangement of the DBV and the doubly bound PEB’ bilins. d) Arrangement of the DBV and the singly bound PEB bilins. The chromophore labellings are listed in Table 1.
4.5 Results and discussion

Figure 4.3 is a plot of the delocalization length of the excitonic eigenstates averaged over 2000 realizations of the Hamiltonian. Delocalization length is defined to be

\[ L_n = \left\{ \sum_i^{N} |c_i^n|^4 \right\}^{-1} \]  

(4.33)

where \( c_i^n \) are the normalized amplitudes of the eigenstate \( |\psi_n\rangle \) with respect to the site \( |i\rangle \),

\[ |\psi_n\rangle = \sum_i^n c_i^n |i\rangle, \]  

(4.34)

\[ \sum_i^{N} |c_i^n|^2 = 1. \]  

(4.35)

Chromophores with maximum delocalization are found to be those in the middle of the assembly and the ones with small delocalization are at the edge of the assembly. For comparison the exciton delocalization length of an isolated PE545 unit is also plotted (Fig. 4.3b). The tetramer eigenstates are significantly more delocalized. This suggests that close packing of proteins inside the thylakoid lumen can result in substantial delocalization among chromophores on neighboring units.
Figure 4.3: a) Average delocalization length of the eigenstates in the PE545 tetramer computed over 2000 realizations of the Hamiltonian. The labelings of the chromophores (site index) are listed in Table 1. The five chromophores with the largest delocalization are labeled on the graph. b) Delocalization length of chromophores in an isolated PE545 unit.
Table 4.2: Chromophore labeling. The protein index $n$, can take the values 1 to 4.

<table>
<thead>
<tr>
<th>site index</th>
<th>bilin type</th>
</tr>
</thead>
<tbody>
<tr>
<td>1+8(n-1)</td>
<td>$p_n$ DBV 19 A</td>
</tr>
<tr>
<td>2+8(n-1)</td>
<td>$p_n$ DBV 19 B</td>
</tr>
<tr>
<td>3+8(n-1)</td>
<td>$p_n$ PEB 158C 501</td>
</tr>
<tr>
<td>4+8(n-1)</td>
<td>$p_n$ PEB 158D 504</td>
</tr>
<tr>
<td>5+8(n-1)</td>
<td>$p_n$ PEB 5061C 500 (PEB’)</td>
</tr>
<tr>
<td>6+8(n-1)</td>
<td>$p_n$ PEB 5061D 503 (PEB’)</td>
</tr>
<tr>
<td>7+8(n-1)</td>
<td>$p_n$ PEB 82C 502</td>
</tr>
<tr>
<td>8+8(n-1)</td>
<td>$p_n$ PEB 82D 505</td>
</tr>
</tbody>
</table>

In order to understand the origin of any differences between the two formulations of exciton transfer, we first present a comparison of the memory kernel between arbitrarily chosen sites as obtained from each model. We then proceed to discuss the results of the Monte Carlo simulation.

Memory kernel quantifies the temporal variations of the transfer rate. This variation can either arise from the bath non-Markovianity, or from coherent electronic oscillations. In the former scenario (regime of interest in the present article) the time taken for the memory kernel to establish its steady-state value is known as the bath memory. Non-Markovianity must be accounted for if bath memory is longer than, or comparable to, the time scale of the physical process that one wishes to study. In physical terms non-Markovianity implies the possibility of reversible information flow between the system and the bath, in contrast to Markovian dynamics where the flow of information is from the system to the bath only [129]. For the system under investigation the memory time is found to be $\sim 20$ fs. Since the bath memory is short in comparison to the time scale of energy transfer, the time dependence of the transfer rate may be neglected, and the rate may be approximated by its steady state value, that is $k \approx \int_0^\infty G(t)dt$. This course-
graining approximation of the non-Markovian transfer rate is in fact equivalent to the Markov approximation as was demonstrated in section 4.2.

Figure 4.4a is a plot of the memory kernel in the eigenstate and the site model, calculated between the sites $i = 9$ ($p_2$ DBV 19A) and $i = 26$ ($p_4$ DBV 19B) for the tetramer where all chromophores are included in the simulation. These are the farthest pair in the assembly, separated by a distance of 83.5 Å, with a small electronic coupling of 0.2 cm$^{-1}$. The steady state value of the transfer time is shorter by two orders of magnitude in the eigenstate model, 9.5 ns, compared to 5 μs in the site model. The negative values of the memory kernel in these plots have a vibrational origin, and indicate that the instantaneous rate of transfer may decrease as a function of time. Increasing the bath reorganization energy would eliminate any oscillations or negative values of the memory kernel, as one recovers the Markov limit for large reorganization energies. In these plots memory decays over the same time scale in both models. The enhancement in rate is therefore due to the larger value of the memory kernel at $t = 0$, which, in turn, is due to exciton delocalization, as well as a subtle interplay between the system and the bath. We elaborate on the role of these factors in the following paragraph.

To demonstrate how exciton delocalization can enhance energy transfer, consider a transfer scenario in which the donor (acceptor) state $|\phi_i\rangle$ ($|\phi_j\rangle$), is delocalized over $n$ ($m$) sites, labelled $\{i_1, \ldots, i_n\}$ ($\{j_1, \ldots, j_m\}$). We furthermore assume that each eigenstate is at least 60% localized on a particular chromophore, so that one can unambiguously assign each eigenstate to a unique site index (this is the case in the PE545 tetramer). We label the site with maximum amplitude in each set as $i_1$ and $j_1$ respectively. If the sites $i_1$ and $j_1$ are weakly coupled, but there are strongly coupled pairs in the two sets, the contribution of these pairs to the transfer process can boost the overall transfer dynamics between the two excitonic states [5]. Under these conditions, the effective coupling between two excitonic states is larger than the coupling between $i_1$ and $j_1$. Moreover, the difference between the two theories is maximal if many intermediate sites reside between the initial
and final chromophores. In the site representation energy transfer is a two-body event, mediated by the direct coupling between $i_1$ and $j_1$. The existence of many intermediate sites often implies that the direct coupling and the corresponding transfer rate are small. In the eigenstate representation however, energy transfer is a collective phenomenon, which accounts the influence of the intermediate sites. This co-operative nature of the transfer process is the key factor behind the fast dynamics in the eigenstate formulation. In other words, delocalization enhances energy transfer in much the same way that has been documented in the generalized Förster theory as adopted to aggregated molecular assemblies [130, 5, 10, 9]. This argument suggests that the difference between the two models would be reduced if the initial and final states were nearest neighbours. Figure 4.4b shows the corresponding plots for sites $i = 1$ and $i = 27$, with a coupling of 72.5 cm$^{-1}$. The average transfer time between this pair is 1.5 ps in the eigenstate basis, compared to 27 ps in the site basis, a significantly closer result than the previous pair.

The second factor influencing the disagreement between the two theories is with regards to the influence of the vibrational bath. In the site model the bath determines the rate at which the memory kernel decays, but has no effect on its initial amplitude. In the eigenstate model however, both the electronic and the bath part influence the initial value of the memory kernel. Figure 4.4c depicts the memory kernel between the sites $i = 1$ and $i = 27$, with the system-bath coupling reduced by a factor of two. In the site model this manifests itself only in the damping rate of the memory function, whereas in the eigenstate model the initial amplitude is also reduced by an order of magnitude. The average transfer time between the sites is now 281 fs in the eigenstate model, compared to 870 fs in the site model. The theories therefore appear to converge for nearest-neighbour sites, for smaller bath couplings. In this limit the two distinguishing features of a delocalized model, namely long-range correlations and a reduced effective reorganization energy, have minimal influence and a local transfer model provides an adequate description. Beyond nearest-neighbour sites, collective effects persist, and the theories do not,
in general, converge. We therefore conclude that in large systems with sufficient exciton
delocalization and energetic disorder, the eigenstate formulation provides a more reliable
picture of the long-range dynamics.

Figure 4.4: Memory function versus time a) between $i = 9$ and $i = 26$ in the eigenstate
and the site model. b) Corresponding plots between $i = 1$ and $i = 27$. c) Memory
function between $i = 1$ and $i = 27$ with the bath couplings reduced by a factor of two.
Figure 4.5a and b show the CPD functions for the DBV chromophores, in the eigenstate and the site model respectively. Without the PEB chromophores, the transfer probability from a given DBV is completely dominated by its nearest DBV neighbour. As the DBVs within a protein unit are positioned at the opposite ends of the molecule, the nearest DBV neighbour is more likely to lie on an adjacent protein. This gives rise to strong energy traps between DBVs on adjacent proteins, and is manifested in the rapid rise of the CPD function. Once the PEB chromophores are introduced in the assembly, the CPD function is changed significantly. The PEB’ dimer is positioned in the middle of the DBV dimer, while the PEB bilins are positioned in an open arrangement on the outside of the protein. This arrangement of chromophores funnels the energy out of the DBV traps, and is manifested in Fig. 4.5c and d by the gradual rise of the CPD function. This demonstrates the inadequacy of a Förster mechanism in which energy is assumed to flow irreversibly towards the low energy sites. Unless energy transfer is strongly thermally activated, excitation is likely to be trapped at a local minima.

Figure 4.6 shows the distribution of the transfer times and Table 4.3 summarizes the statistics of the transfer process in the four sets of data. With only the DBV chromophores present, the site model generates a large number of failed trajectories. In the eigenstates model, owing to faster pairwise transfer, the success rate is significantly larger. Strong trapping pairs in the eigenstate model give rise to large numbers of hops, as the energy is bounced back and forth many times in the ‘trap’ before it can escape. With the PEB chromophores included in the dynamics, the total transfer time is reduced by an order of magnitude in the eigenstate model. In both models the failure rate is also substantially decreased. This demonstrates the importance of high energy sites and static disorder in boosting the efficiency of long-range EET. Static disorder in the site energies can bring the higher energy sites in resonance with the low energy ones, mediating faster uphill transfer. The open arrangement of the PEB bilins creates an extended network of connections which prevents the formation of local traps and enables the excitation to
explore different regions of the aggregate.

In summary, we find that three independent processes are important for efficient long-range energy transfer: 1) Exciton delocalization, which induces long-range correlations in the aggregate, giving the transfer process a collective character. 2) High energy intermediate sites that bring chromophores from neighboring proteins within close proximity and prevent the formation of local energy traps. 3) Static disorder that brings the higher energy sites in resonance with the low energy ones. A transfer model that includes the PEB chromophores in the dynamics, takes into account the static disorder, and regards long-range transfer as a biased-random walk between delocalized eigenstates, utilizes the above factors maximally and predicts the fastest dynamics.

Time-resolved florescence anisotropy experiments have revealed three timescales for the transfer of excitation from PE545 to the membrane associated chlorophylls at room temperature: 17 ps, 58 ps and 113 ps [131], in comparison to the fastest transfer time of 247 ps obtained from this simulation. If our model were to be extended to the scale of a energy funnel, many more proteins would have to be included in the simulation as the funnel typically involves ∼ 200 molecules, and the energy is transferred across a total distance of ∼ 20-100 nm [60]. Furthermore, the reaction centre has a finite trapping rate which would further increase the transfer time. This suggests that on the scale of a natural energy funnel this simulation is likely to predict a slower transfer than the experimental findings. Further refinements in computation of the pairwise rates are therefore required if the experimental value of transfer time is to be reproduced.

One possible factor that was not included in the theory and may alter the transfer rates is the vibronic progression of the excitonic eigenstates [42]. The system has been partitioned such that the high frequency vibrational modes are part of the bath, such that they can be modelled by a series of delta functions in the spectral density. This limits the influence of these modes to line-broadening of the spectra. If the partitioning is done such that the high frequency modes are part of the system instead, a different
picture emerges and the relaxation pathways are altered [42]. The resulting correction to the transfer rates is particularly significant if the energy of the vibrational modes matches the difference between two exciton states [132].

Figure 4.5: a) and c) Cumulative Probability Distribution (CPD) as defined by Eq. (4.32) in the eigenstate picture for site $i$ with respect to sites $n$, for a) only the DBV bilins, c) all chromophores. b) and d) The corresponding plots in the site picture, b) DBV bilins only, d) all chromophores.
Figure 4.6: Histograms representing the distribution of the transfer times over 2000 realizations of the Hamiltonian. a) Eigenstate transfer model with only the DBV bilins present. b) Site transfer model with only the DBV bilins present. c) Eigenstate model with all chromophores included. d) Site picture with all chromophores present.
## 4.5.1 Conclusion

We have presented a computational study of long-range energy transfer in a cluster consisting of four units of PE545 proteins. Energy transfer is viewed as 1) transitions among the dressed excitonic eigensates mediated by the vibrational bath, 2) a random walk between the dressed localized sites induced by mutual electronic interactions. We found that aggregation brings chromophores from adjacent proteins within close proximity of each other, thereby delocalizing the excitation between sites on neighboring units. This delocalization leads to a collective dynamics that can substantially boost long-range energy transfer. We have furthermore demonstrated that the arrangement of PEB chromophores in the PE545 tetramer, together with static disorder, prevents excitation trapping at the low energy dimers. These two factors help to create a large interconnected network, allowing the excitation to collectively explore different regions of the assembly and eventually sensitize the reaction centre.

We emphasize that in this simulation the initial and final sites are chosen arbitrarily, as we merely intend to acquire an insight regarding the dynamics of multi-protein energy
transfer, and do not aim to replicate a realistic transfer process, in which the excitation is funneled towards an external reaction centre. Moreover, our results do not answer the question of quantum effects on an inter-protein scale unequivocally, as the model adopted to simulate the transfer process is a semi-classical random walk. What the current work does establish however, is the importance of exciton delocalization in long-range energy transfer: despite the small electronic couplings and the relatively small delocalization length of the excitonic eigenstates, a theory that includes delocalization predicts a much faster dynamics on an inter-protein level, suggesting that persistent exciton delocalization is a necessary ingredient for fast long-range energy transport.
Chapter 5

Thermodynamics of rare trajectories in phonon-mediated electronic energy transfer

5.1 Introduction

One characteristic feature of photosynthetic systems is the constant interaction of the chromophores with the protein environment. These interactions are in fact advantageous as they lead to broadening of the spectral line-shapes. The resulting spectral overlap facilitates the transfer of electronic excitation between molecules of different energies as stated in the Förster theory. However, the influence of the protein environment beyond spectral broadening, is still largely an open question. For instance, it was recently demonstrated that solvent-induced screening effects can significantly modify the electronic coupling between molecules in a typical light-harvesting complex [133].

In theoretical treatments of electronic energy transfer (EET) the protein environment is often described via an empirical spectral density whose modes are assumed to remain at thermal equilibrium throughout the EET process. However, like all biological systems,
the protein is inherently a non-equilibrium environment: thermal fluctuations or absorption of photons can perturb the occupancy of the phonon modes, driving the environment out of thermal equilibrium. The electronic degrees of freedom of the system are coupled to the environmental modes and are influenced by such perturbations. In this chapter we investigate how the dynamics of the electronic degrees of freedom are influenced by out of equilibrium fluctuations of the environment.

The difficulty in addressing this question is due to the different nature of the two influences: the fluctuations of the environment are of a classical character and are described via the tools of non-equilibrium thermodynamics. The electronic degrees of freedom are, however, quantized and their interaction with the environment is described via the theory of open quantum systems [134]. There has been a historical distinction between the two approaches, rendering the study of their mutual influence a non-trivial one.

An important connection between the two descriptions was provided by Garrahan and Lesanovsky in a recent contribution [135]. The link between the two descriptions was provided through the well-known mathematical theory of large deviation principle (LDP) [136]. LDP will be reviewed in some detail in the next section. For the time being it suffices to say that LDP is the mathematical foundation of statistical mechanics, and concerns itself with exponential decay of probabilities of extreme or tail events as the number of observations grows large.

In statistical mechanics LDP provides a framework to deduce thermodynamic quantities from sub-ensembles of particles in the configuration space. In quantum mechanics however, it serves as a tool for statistical analysis of rare (i.e.: out of equilibrium) trajectories of a quantum system that interacts with a classical environment (bath). A trajectory in this context is defined to be a period of unitary evolution of the quantum system interrupted by bath-induced measurements at stochastic intervals [137, 138]. LDP thus provides an intriguing one-to-one correspondence between thermodynamic functions defined in the configuration space, such as entropy and free energy, and their quantum
analogues defined in the trajectory space. Moreover, in thermodynamics singularities in an order parameter indicate a phase transition, suggesting that analogous dynamical transitions could occur in the trajectory space of a quantum system. The significance of transitions in the statistics of quantum processes, or the means by which they may be observed, are not always clear and tend to be problem-specific. Their existence have so far been predicted in photon counting in quantum optical systems [135, 139, 140, 141]. Moreover, the technique has been applied to analyze the statistics of a variety of other systems including electrons transported through a nanoscopic structure [142, 143], or the number of spikes produced by a neuronal system [144].

In this chapter we apply LDP to analyze the statistics of a specific master equation: one that describes bath-induced incoherent hopping of an electronic excitation between delocalized excitons in the limit of weak system-bath coupling. EET as described within this framework is of considerable practical importance and occurs in a wide variety of systems, including natural and artificial photosynthetic complexes [145, 74], and conjugated polymers [146, 147, 21]. As far as the ensemble averages and the equilibrium dynamics are concerned, EET in this regime is a well-investigated phenomena. However, the more subtle non-equilibrium effects considered in this study have not been investigated previously.

In this chapter we consider a prototype multichromophoric system exhibiting EET facilitated by weak environmental interactions. We assume that rare trajectories can be accessed through a coupling field $s$. The coupling field serves as a mathematical tool to tune the system out of equilibrium. The electronic and vibrational parameters of the Fenna-Matthews-Olson (FMO) photosynthetic complex are used in computation of the numerical results, as the Lindblad master equation considered in this article has been found to make a reasonable prediction of the steady-state of the complex.

The FMO complex is found in green sulfur bacteria and acts as a molecular wire connecting a large light-harvesting antenna, the chlorosome, to the reaction centre of the
Chapter 5. Statistics of rare trajectories in EET

photosynthetic complex [1]. Observation of persistent electronic coherence in the complex [34, 148] has led to extensive investigation of the EET dynamics and role of quantum coherence in the complex [149, 150, 151, 152, 153]. For the purposes of the present discussion the FMO merely serves as a viable platform to compute the statistics of rare trajectories. The treatment can equivalently be applied to any non-equilibrium system exhibiting EET whose dynamics can be described by the Lindblad master equation.

In the next section we lay the foundation of this analysis by stating the mathematics of LDP as applied to a counting process. Note that LDP is a generalization of the central limit theorem, but enables a problem-specific description of fluctuations that goes beyond a first-order Gaussian approximation. The interested reader is referred to an excellent review article by Hugo Touchette on the application of LDP in physics [136].

5.2 Theoretical Methodology

5.2.1 Large deviation principle as applied to a counting process

A counting process can be decomposed into a number of trajectories where in each trajectory the process occurs at different stochastic intervals [154]. In the context of quantum jumps, the counting process is the number of jumps observed after a given time \( t \). Let us denote the probability of observing \( K \) jumps after a time \( t \) by \( P_t(K) \), where \( \sum_{K=0}^{\infty} P_t(K) = 1 \), and \( \{0 \leq P_t(K) \leq 1\} \). For a counting process that satisfies the large deviation theory, \( P_t(K) \) acquires a large deviation form for large \( t \). That is

\[
P_t(K) \approx e^{-t\varphi(k)}
\]

(5.1)

where the function \( \varphi(k) \) is known as the rate function [136], and \( k = K/t \) is the jump rate. For a simple (unimodal) counting process, \( \varphi(k) \) has a local minima corresponding to the most probable jump rate after a long observation time (Fig. 5.1). For fixed \( t \), the probability of observing \( K \) jumps decays exponentially as \( K \) deviates from the most
probable outcome. This exponential decay of probabilities is known as the large deviation
principle (LDP). The central limit theorem (CLT) approximates $\varphi(k)$ as quadratic about
the mean, leading to a Gaussian distribution of probabilities. For fixed $t$, the prediction of
CLT is only valid up to a given accuracy in a central region of the counting probabilities
(sufficiently close to the mean). LDP, on the other hand, enables an accurate description
of rare events that are arbitrarily far from the mean. LDP is reduced to the CLT for
small fluctuations, as differentiable functions are quadratic about a local minima. To

Figure 5.1: a) Quadratic rate function $\varphi(k)$, results in a normal probability distribu-
tion $P(K/t)$. b) Non-quadratic (and in this case asymmetric) rate function results in
an asymmetric probability distribution. Close to the minima however, the probability
distribution can be well approximated by a Gaussian function.

summarize, LDP is a series of mathematical postulates that: 1) establishes whether a
given counting process has a large deviation form, i.e.: exhibits exponential decay of
probabilities for long observation times, 2) allows the computation of the rate function
for such a process. In the remainder of this section we state, without proof, how LDP
enables the computation of the statistical parameters of a counting process.

The generating function of a probability distribution is defined to be

$$Z_t(s) = \sum_{K=0}^{\infty} P_t(K) e^{-sK}$$

(5.2)
If the counting process has a large deviation form, the generating function can be written as

$$Z_t(s) \simeq e^{t\theta(s)}$$

where the function $\theta(s)$ is known as the cumulant generating function. The cumulant generating function and the rate function are related via a Legendre transform,

$$\theta(s) = -\min_k [\varphi(k) + ks]$$

The average and the standard deviation of the number of jumps at thermal equilibrium can be deduced from the cumulant generating function, and are given by

$$\langle k \rangle = -\theta'(0)$$
$$\langle k^2 \rangle - \langle k \rangle^2 = \theta''(0).$$

Similarly, higher derivatives of $\theta(s)$ are higher order statistical cumulants. A knowledge of $\varphi(k), \theta(s)$, or $P_t(K)$ enables the computation of the statistical moments of the counting process.

The applicability of LDP to non-equilibrium processes becomes evident when the behaviour of the cumulant generating function away from $s = 0$ is considered. To illustrate this let us construct an associated stochastic process defined by the probabilities

$$q_t(K, s) = \frac{1}{Z_t(s)} P_t(K) e^{-sK}$$

For $s = 0$ we recover the original counting process. For $s < 0$ ($s > 0$) the exponential factor amplifies (lowers) the probabilities of rare events. The coupling field $s$, provides a systematic means by which rare events can be accessed: unlikely events of the counting process $\{P_t(k)\}$, correspond to typical events of the associated process $\{q_t(k, s)\}$. Rare events can thus be accessed without generating a large number of typical events and relying on the statistics of the original counting process.

To illustrate this consider an unbiased binary sequence of length $N$, $\ell = \{00101\ldots\}$. We define the counting process to be the statistics of occurrence of ones in this sequence.
For sufficiently long chains, a balanced chain that contains as many ones as zeros is the most likely sequence, and a rare event corresponds to a significantly unbalanced sequence. Generation of rare events by relying on the statistics of the original counting process becomes costly as the length of the chain is increased. Such rare events could contain interesting physics, necessitating the need for a more efficient way of their simulation.

In the context of non-equilibrium thermodynamics, the coupling field \( s \) is interpreted as a means by which the system is perturbed out of equilibrium. The influence of non-equilibrium perturbations are thus deviations from the thermodynamic probabilities. A rare event corresponds to a particular trajectory of the system that has been significantly perturbed out of equilibrium.

Note that in statistical mechanics the counting process is the occupation number of a given state, \( Z(s) \) is the partition function, \( \varphi(k) \) is the entropy and \( \theta(s) \) is the free energy. The variable \( s \) is (minus) the chemical potential \( s \equiv -\mu \) [155]. Free energy serves as an order parameter: singularities in free energy predict first-order thermodynamic phase transitions. We demonstrate in the next section that for a quantum system, singularities in \( \theta(s) \) predict analogous dynamical transitions in the trajectory space.

The major limitation of this approach with respect to EET is that the large deviation formalism relays on statistical patterns that emerge after a long observation time. The formalism is independent of the initial conditions and can describe fluctuations around the thermodynamic equilibrium in the steady-state, i.e.: it conveys no information with regards to short-time dynamics, or how different trajectories have approached equilibrium. This point will be discussed in more detail in the next section.

5.2.2 Large deviation principle in electronic energy transfer

In this section we apply LDP to investigate the trajectories of a particular open quantum system, modelled by the Markovian Lindblad master equation. The system of interest consists of a number of sites coupled via electronic couplings and weakly interacting...
with their environment. The resulting excitons are delocalized and the influence of the environment is to induce jumps between them at stochastic intervals (much like the models considered in chapter 4).

The idea behind the application of LDP to this system is as follows: in the steady-state the average population of the exciton states is constant. At a microscopic level, however, transfer of excitation still occurs in a dynamical manner. For instance for a system of two sites, steady-state implies that \( k_{1 \rightarrow 2} P_1 = k_{2 \rightarrow 1} P_2 \), where \( k_{i \rightarrow j} \) is the transfer rate from the state \( i \) to the state \( j \), and \( P_i \) is the steady-state population of the state \( i \). Moreover, the ratio of the transfer rates satisfies detailed balance: \( k_{1 \rightarrow 2} = k_{2 \rightarrow 1} e^{-\beta \omega_{12}} \), where \( \omega_{12} \) is the energy difference between the two states. \( k_{1 \rightarrow 2} P_1 \) is also the average number of jumps per second between the two states: upward and downward jumps occur with equal frequency in the steady-state. If the environment is perturbed out of equilibrium, detailed balance no longer holds and the frequency of jumps deviates from the thermally equilibrated rate. The nature of this deviation is the subject of investigation in the present study.

The question therefore is: How do the statistics of jumps vary as the system is driven out of equilibrium?

The cumulant generating function of this process may be deduced from the equations of motion as follows: The Lindblad equation as applied to EET, in the limit of weak system-bath coupling and with secular approximation is given by [134]

\[
\dot{\sigma}(t) = -i[H_s, \sigma(t)] + \sum_{\omega,m} \gamma(\omega) \left[ A_m(\omega) \sigma(t) A_m^\dagger(\omega) - \frac{1}{2} \{A_m^\dagger, A_m(\omega), \sigma(t)\} \right]. \tag{5.8}
\]

This equation describes relaxation and dephasing in the eigenstates \( \{ |\alpha\rangle \} \) of the unperturbed system Hamiltonian \( H_s \). \( H_s \) is the diagonalized Hamiltonian in the electronic basis. The Lindblad operators are given by \( A_m(\omega) = \sum_{\omega=\epsilon_\alpha-\epsilon_\alpha'} c_m^*(\alpha) c_{m}(\alpha') |\alpha\rangle \langle \alpha'| \) where \( \{\omega\} \) is the energy difference associated with single excitation eigenstates, and \( c_m^*(\alpha) c_m(\alpha') \) is the exciton overlap at site \( m \). The factor \( \gamma(\omega) \) determines the rate of energy transfer between two excitons and is related to the spectral density of the bath \( J(\omega) \), via the expression \( \gamma(\omega) = 2\pi J(|\omega|) n(\omega) \), where \( n(\omega) = (e^{\beta \omega} - 1)^{-1} \) is the thermal occupation.
number. It is assumed that each molecule interacts with an identical and independent phonon bath. This master equation describes the incoherent jumps between the exciton states as induced by the phonon bath. In the quantum jump approach the Hamiltonian evolution of the subsystem is interrupted by jumps at stochastic intervals. A sequence of stochastic jumps constitutes a trajectory of the system, and an averaging over a large number of trajectories recovers the reduced density matrix \( \sigma(t) \) \[138\].

If \( K \) jumps are observed after a time \( t \), the (unnormalized) reduced density matrix of the system prior to detection is given by the projection of the total density matrix into the subspace of \( K \) events \[156, 157\]. We denote this projected density matrix by \( \sigma^K(t) \). Conversely, the total density matrix can be written as an expansion of all projected density matrices, that is \( \sigma(t) = \sum_{K=0}^{\infty} \sigma^K(t) \). The probability of observing \( K \) events after a time \( t \) is given by \( P_t(K) = \text{Tr}[\sigma^K(t)] \). At this point for the sake of clarity we restrict the analysis to the statistics of jumps between two exciton states separated in energy by \( \omega_1 \). Note that the total system may still contain an arbitrary number of excitons. Upon this constraint, it can be shown that the Laplace transform of the projected density operator, defined by the expression \( \sigma_s(t) = \sum_{K=0}^{\infty} \sigma^K e^{-sK} \) obeys the equation

\[
\dot{\sigma}_s(t) = W_s[\sigma_s],
\]

(5.9)

Note that \( \sigma_s(t) \) has the same structure as the variable \( q_t(K, s) \) in Eq. (5.7). Typical trajectories of \( \sigma_s(t) \) thus correspond to rare trajectories of the original master equation. The ensemble of trajectories generated by Eq. (5.9) is known as the \( s \)-ensemble \[135\]. The index \( s \) indicates how far from thermal equilibrium the system has been perturbed. Physical time evolution is retrieved at \( s = 0 \), whereas \( s \neq 0 \) contains information with regards to rare trajectories of the system.

The Markovian nature of the Lindblad equation enables us to compute the statistical
moments of the number of jumps in the steady-state via LDP. LDP states that for a Markov process, the largest real eigenvalue of the superoperator $W_s$ is the cumulant generating function of the statistics [136]. Following the notation of the previous section, we denote this generator by $\theta(s)$. In the next section we compute the cumulant generating function and the associated statistical moments for a system of two, three and four sites.

### 5.2.3 Results and Discussion

#### Two and three site models

Adopting the electronic and vibrational parameters of the FMO complex, we first consider two sites (chromophores) and study the statistics of jumps between the two exciton states. We subsequently include further sites in the dynamics and study the statistics of jumps between particular pairs of eigenstates.

The vibrational bath is described through the spectral density

$$J(\omega) = \frac{2E_r}{\pi} \frac{\omega \omega_c}{\omega^2 + \omega_c^2}$$

where $E_r = 35$ cm$^{-1}$ is the reorganization energy and $\omega_c = 150$ cm$^{-1}$ is the cutoff frequency of the bath [150, 74]. We compute the matrix $W_s$ and solve for the cumulant generating function $\theta(s)$. Figure 5.2 (a) and 1(b) illustrate the exciton states where two and three sites are included in the dynamics respectively. The exciton states are labelled via a greek letter and a number, where the greek letter represents the position of the exciton state in the energy ladder, and the number indicates the site that carries the maximum amplitude. For instance $|\alpha : 1\rangle$ represents the lowest eigenstate, and indicates that this eigenstate is predominately localized on site 1. Due to significant exciton localization in the FMO protein, each exciton can be unambiguously assigned to a unique site index. The site indices are the standard indices assigned to the chromophores in the FMO protein. We first consider the statistics of jumps between a pair of eigenstates in the two site and the three site models, where the two site model includes sites 1 and 2, and the
Figure 5.2: a) Excitation states with only two sites present and the corresponding schematics of the interacting sites. The circle containing both sites indicates that they are strongly interacting. b) Excitation states in the three site model. The three site model consists of a strongly interacting pair, weakly interacting with a third site. For each case the statistics of jumps between the excitons associated with sites 1 and 2 are computed. c) $\theta(s)$ for the two site model, d) and the three site model. e) $Q(s)$ for the two site, f) and the three site model. The site energies and electronic couplings are listed in Appendix F and were taken from [74].
three site model includes sites 1, 2 and 3. Figure 5.2 (c) and (d) illustrate the cumulant generating function versus the activation parameter $s$ for different temperatures. The plots suggest that the two cases have similar statistics in the active phase, but begin to diverge close to $s = 0$. Figure 5.2 (e) illustrates the Mandel parameter for the case of two sites. Mandel parameter is an indicator of the nature of first-order statistical correlations in the system and is defined to be

$$Q(s) = \frac{\langle k^2 \rangle - \langle k \rangle^2}{\langle k \rangle} - 1 = -\frac{\theta''(s)}{\theta'(s)} - 1.$$  (5.11)

$Q = 0$ implies Poissonian statistics where probabilities of subsequent events are uncorrelated. $Q > 0$ ($Q < 0$) indicates super-Poissonian (sub-Poissonian) statistics where subsequent jumps exhibit first-order correlations.

For the case of two sites, the Mandel parameter is negative for all activations. This indicates sub-Poissonian correlations (anti-bunching) where a waiting period for re-excitation is required before the system can relax back to the lower state. As the activation parameter is increased, the Mandel parameter approaches zero (Poissonian limit). In this limit there are so few jumps that correlations vanish asymptotically. Note that anti-bunching is observed even though the transitions are thermally activated, and the steady-state dynamics obey a classical rate equation. This can indeed be confirmed by eliminating all dephasing terms and considering the evolution matrix

$$W_{\text{class}}(s) = \begin{bmatrix} -\kappa & \Gamma e^{-s} \\ \kappa & -\Gamma \end{bmatrix}$$

where $\kappa$ and $\Gamma$ are the relevant equilibrium transfer rates, and $\Gamma = \kappa e^{-\beta \omega}$ as required by detailed balance. By diagonalizing $W_{\text{class}}(s)$, we arrive at the following expression for $Q(s)$

$$Q(s) = \frac{-2\kappa\Gamma}{(\kappa + \Gamma)^2 - 4\kappa\Gamma(1 - e^{-s})} e^{-s} < 0 \quad \forall s$$  (5.12)

One obtains the same expression if the full Lindblad equation with the dephasing terms are instead considered. The formalism thus captures the fluctuations of a quantum system.
due to its coupling to a fluctuating bath. For the system under consideration the nature of these fluctuations are entirely classical.

The corresponding plot for a system of three sites is shown in Fig. 5.2 (f). The trajectories exhibit a dynamical cross-over in their statistics, i.e.: the correlations change from sub-Poissonian \((Q(s) < 0)\) to super-Poissonian \((Q(s) > 0)\) as the activation parameter is varied. The cross-over point is temperature dependent and is closer to \(s = 0\) at higher temperatures. Typical trajectories \((s = 0)\) are bunched, and the Mandel parameter has a peak close to \(s = 0\).

One can continue to add more sites to the model and investigate the statistics of a particular jump, or the collective statistics of a number of jumps. For instance the collective statistics of all jumps to the lowest eigenstate can be investigated. In general, beyond a few sites there are many possible jumps and there is no obvious advantageous collective counting strategy.

Four interacting sites exhibit the combination of the features of the two site and the three site models, as illustrated in Fig. 5.3. Figure 5.3 (b) exhibits the new feature that typical trajectories \((s = 0)\) show different statistics at different temperatures: anti-bunching at higher temperatures and bunching at lower temperatures. In Fig. 5.3 (c) the trajectories remain anti-bunched over the computed temperature range, similar to the results of the two site model.

We consider all possible pairwise jumps of the four site model and conclude that for sufficiently high activations all trajectories become bunched and approach a temperature independent but transition dependent value of the Mandel parameter. For sufficiently low activations, on the other hand, all trajectories approach the Poissonian limit. Trajectories that undergo a statistical cross-over, approach the Poissonian limit from the positive values of \(Q(s)\), but those that do not remain in the \(Q(s) < 0\) portion. Approach to the Poissonian limit from the \(Q(s) > 0\) side, is therefore a sufficient indicator of the existence of statistical cross-overs. These conclusions are also observed to be valid for
larger systems.

Figure 5.3: a) Exciton states for the four site model, and the corresponding schematics of the interacting sites. The four site model consists of two groups of strongly interacting dimers. b) and c) Mandel parameter versus the activation parameter for selected downward jumps in the four site model.

Finally, statistics of a selected number of jumps from the seven site system of the FMO protein are illustrated in Fig. 5.4. We observe that strongly interacting dimers are more likely to show statistical cross-overs, whereas the weakly interacting sites tend to exhibit the simple anti-bunching statistics of the two site model, or a combination of statistical cross-overs at low temperatures and anti-bunching at higher temperatures.
Figure 5.4: a) to d) Mandel parameter for selected downward transitions. e) Exciton states of the seven site system and the corresponding schematics of the interacting sites. The seven site system consists of three strongly interacting dimers, coupled weakly to a seventh site.
5.3 Conclusion

Markovian master equations are an established way of computing the time evolution of many systems exhibiting transport properties. These equations are commonly used to compute the ensemble averages, but in fact contain more information pertaining to higher order statistical moments that cannot be gleaned unless an unravelling formalism is first implemented. Such an unravelling formalism has been applied in the present article to analyze the statistics of Markovian excitation transport.

The steady-state statistics of a system undergoing EET exhibits surprisingly rich statistics, characterized by dynamical cross-overs and temperature and size dependent first-order correlations. Although the transitions between the exciton states are purely thermally activated, they do not, in general, exhibit Poissonian statistics. The features that are often associated with quantum correlations such as bunching and anti-bunching can be observed in the steady-state statistics of the jumps between the eigenstates, even at thermal equilibrium.

Away from thermal equilibrium systems of two and three sites exhibit qualitatively different correlations: while in the former the jumps are always sub-Poissonian, in the latter they can undergo statistical cross-overs as the system is perturbed out of equilibrium. Transitions in larger systems show a combination of these two characteristic behaviours. In general, at sufficiently low activations all trajectories approach the Poissonian limit, and for sufficiently high activations they approach a temperature independent, but transition dependent sub-Poissonian asymptote of the Mandel parameter.

The importance of the Markovian assumption in the present treatment poses a difficulty for many systems exhibiting EET whose environmental interactions are strongly non-Markovian. The formalism can, however, be applied to model certain types of non-Markovianity by extending the Hilbert space of the system Hamiltonian to contain the environmental modes that show the strong non-Markovian features [89, 132].
Chapter 6

Conclusions

There is a large body of theoretical work concerning the quantum mechanics of energy transfer in photosynthetic complexes and the role of the environment in determining the operating regime of electronic energy transfer. In particular, there is a considerable volume of research on the FMO protein of the green sulfur bacteria. The extent of the corresponding body of work on cryptophytes is substantially smaller, and is largely limited to various master equation treatments. While the FMO protein and the phycobiliproteins of cryptophyte algae operate at different regimes, both have shown long-lasting exciton coherence in 2D ES experiments. These observations motivated us to study the dynamics of the PE545 light-harvesting protein found in cryptophyte algae, and explore the consequences of quantum phenomena, such as path-interference and wavefunction delocalization, for energy transport.

One of the difficulties in modelling the PE545 antenna is that although the electronic couplings are weak, they are not sufficiently weak for the dynamics to be adequately described via the Förster theory. In chapter 3 and 4 we present a comparison of the different theoretical approaches to the modelling of the PE545 protein and discuss some of the subtle features of energy transfer that cannot be captured within incoherent Förster-like dynamics. One such feature is path-interference which can make a small, but measurable,
correction to the steady-state transfer rate close to the Förster limit. Such corrections are of relevance in systems wherein the vibrational bath is strong enough to localize the excitations, but weak enough to preserve the coherence of pathways with multiple sites.

A further important observation is with regards to the magnitude of the contribution of the higher order coherent pathways. Thermalization favours incoherent transfer, and coherent pathways with more than one or two intermediate sites are destroyed at ambient temperatures. Quantum mechanical sampling of different pathways to find the most efficient route to the reaction centre, as was speculated in some of the original articles on this subject, demands a fully quantum evolution across the entire complex, and is incompatible with the level of noise in such systems. Quantum corrections instead have a more subtle influence and arise if the action of the bath is analogous to a ‘weak measurement’ that does not localize the excitation on an intermediate site, thus preserving the coherence of pathways with multiple sites. Moreover, the sensitive dependence of the constructive or the destructive nature of the interference correction on the energy of the intermediate site, suggests that in systems with substantial static disorder in the site energies the contributions of different pathways are likely to cancel. These contributions are therefore important in systems of a few interacting molecules with small static disorder, and are unlikely to make a dramatic difference to the EET efficiencies at ambient temperatures for larger systems.

Experimental verification of the magnitude of interference correction as a function of the energy of the intermediate site is an important next step in establishing the validity of the theory. Foreseeable applications of such effects are in artificial photosynthetic circuits and molecular wires that aim to control the rate of energy delivery to a target molecule. The rate of energy transfer to the target site can be altered by changing the energy of an intermediate site, in such a way that the sign of the interference correction is changed.

The second observation that elucidated the inadequacy of a Förster-like transfer pro-
cess was the realization that such a formulation cannot reproduce the high quantum yield of excitation transport in the algae where many proteins participate in a given transfer path. This was demonstrated in chapter 4 where EET within an aggregate of PE545 antenna proteins was investigated. The important conclusion drawn from this work is the significance of exciton delocalization in enhancing the inter-protein transfer rates. Delocalized excitons utilize long-range correlations, resulting in much faster dynamics than localized hopping. This faster transfer rate also implies a longer exciton diffusion length. This is perhaps the most important lesson as far as replication of natural light-harvesting strategies in artificial devices are concerned: increasing the exciton diffusion length is one of the primary challenges in the design of solid-state photovoltaics. Using materials that promote exciton delocalization can therefore result in faster exciton transport and a longer diffusion length.

In chapter 5 we focused on the dynamical nature of the steady-state in excitonic systems, and investigated the influence of non-equilibrium fluctuations of the environment on the steady-state statistics of the quantum system. Markovian master equations are an established way of computing the time evolution of many systems exhibiting excitation or charge transport. These equations are commonly used to compute the ensemble averages, but in fact contain more information pertaining to higher order statistical moments that cannot be gleaned unless an unravelling formalism is first implemented. Such an unravelling formalism was applied in chapter 5 to analyze the statistics of Markovian excitation transport.

It was found that the steady-state statistics of a system undergoing EET exhibits surprisingly rich statistics, characterized by dynamical cross-overs and temperature and size dependent first-order correlations. Although the transitions between the exciton states are purely thermally activated, they do not, in general, exhibit Poissonian statistics. The features that are often associated with quantum correlations such as bunching and anti-bunching can be observed in the steady-state statistics of the jumps between the
eigenstates, even at thermal equilibrium. The findings of this chapter are of fundamental importance as such transitions have never been observed in undriven systems, and for thermally activated transitions.

The conclusions of this thesis are largely complementary to those of the existing body of theoretical work. In particular, delocalization-induced enhancement in energy transfer in light-harvesting antennas has been known in the literature. This work, however, highlights the importance of delocalization in non-trivial settings: Even in systems with large localization, that operate in the incoherent limit of energy transfer, a small delocalization can substantially enhance the long-range transfer. The conclusions with regards to interference corrections are also complimentary to those of the existing theoretical treatments, but go beyond the current models by investigating the short time and steady-state corrections, as well as the influence of solvent and inter-molecular vibrational modes.

To summarize, in this thesis we have demonstrated the importance of looking beyond ensemble averages to understand the intricate dynamics of systems exhibiting EET. Path interference and persistent delocalization are shown to be two manifestations of quantum effects in light-harvesting antennas. Although interference can enhance or suppress energy transfer to specific sites, its relatively small magnitude suggests that it is most likely a consequence of system-environment interactions, rather than an optimization strategy that offers the antenna a competitive edge. This however does not rule out its potential significance in the design of artificial photosynthetic circuits that aim to direct energy to specific target sites by controlling certain parameters of the system.

Persistent exciton delocalization on the other hand, is found to enhance the rate of energy transfer in light-harvesting complexes by an order of magnitude. The influence is of particular relevance in cryptophytes where the mobility of the phycobiliproteins in the lumen changes their relative separation, and can bring adjacent proteins within closely proximity, thus promoting exciton delocalization.
Appendix A

Reduced density matrix in the FG basis

A.1 Exact expression

In this appendix we present the details of the computation of the reduced density matrix in the FG basis. The time evolution of the reduced density matrix in the FG basis is determined by

\[
\bar{\sigma}(t) = \text{Tr}_b\{\bar{\rho}(t)\}
\]
\[
= \text{Tr}_b\{e^{-iDt}\bar{\rho}(0)e^{iDt}\}
\]
\[
= \text{Tr}_b\{e^{-iDt}\bar{\sigma}(t)\rho_b e^{iDt}\}
\]

where \( D \) is the FG-transformed Hamiltonian,\n
\[
D = \begin{pmatrix}
A & 0 \\
0 & B
\end{pmatrix}
\]

\[
A = H_b + \frac{1}{2}\Delta - J(-1)^{b^*_b b_k} + \epsilon,
\]
\[
B = H_b - \frac{1}{2}\Delta + J(-1)^{b^*_b b_k} + \epsilon.
\]
Care must be taken in the evaluation of Eq. (A.3) as $[D, \rho_b] \neq 0$. By writing $D$ in the matrix form, we arrive at the following expressions for the evolution of the elements of $\bar{\sigma}(t)$,

\begin{align}
\bar{\sigma}_{11}(t) & = \text{Tr}_b\{\bar{\sigma}_{11}(0)\rho_b\} \\
\bar{\sigma}_{21}(t) & = \text{Tr}_b\{e^{-iBt}\bar{\sigma}_{21}(0)\rho_b e^{iBt}\}
\end{align}

We wish to rewrite these equations such that the initial conditions are expressed in the site basis. We therefore note that

\begin{align}
\bar{\rho}(0) & = U\rho(0)U^\dagger \\
& = \rho_b U\sigma(0)U^\dagger \\
& = \rho_b \bar{\sigma}(0)
\end{align}

where

$$U = \frac{1}{\sqrt{2}} \begin{pmatrix} 1 & R \\ -R & 1 \end{pmatrix},$$

and we have used the fact that $[U, \rho_b] = 0$. The reduced density matrices at $t = 0$ are therefore related via the following expression

$$\bar{\sigma}(0) = U\sigma(0)U^\dagger$$

By writing $U$ in the matrix form, we arrive at the following expressions for the relation between the two basis at $t = 0$

\begin{align}
\bar{\sigma}_{11}(0) & = \frac{1}{2}[\sigma_{11}(0) + R\sigma_{21}(0) + R\sigma_{12}(0) + \sigma_{22}(0)] \\
\bar{\sigma}_{12}(0) & = \frac{1}{2}[\sigma_{11}(0) - \sigma_{21}(0) + \sigma_{12}(0) + R\sigma_{22}(0)]
\end{align}

Substituting Eq. (A.14) and Eq. (A.15) into Eq. (A.7) and Eq. (A.8), we arrive at the following expression for the evolution of the density matrix in the FG basis with the
Appendix A. Reduced density matrix in the FG basis

initial conditions expressed in the site basis,

\[ \bar{\sigma}_{11}(t) = \frac{1}{2} + \Re[\sigma_{12}(0)] \text{Tr}_b \left\{ R \rho_b \right\} \] (A.16)

\[ \bar{\sigma}_{12}(t) = \left[ \frac{1}{2} - \sigma_{11}(0) \right] \text{Tr}_b \left\{ e^{-iA t} \rho_b R e^{iB t} \right\} + i \Im[\sigma_{12}(0)] \text{Tr}_b \left\{ e^{-iA t} \rho_b e^{iB t} \right\} \] (A.17)

The trace \( \text{Tr}_b \{ R \rho_b \} \) can be evaluated in the Fock basis as follows

\[ \text{Tr}_b \left\{ R \rho_b \right\} = \text{Tr}_{\text{even}} \left\{ e^{i \pi b^\dagger b} \rho_b \right\} + \text{Tr}_{\text{odd}} \left\{ e^{i \pi b^\dagger b} \rho_b \right\} \] (A.18)

\[ = \sum_{n=0}^{\infty} \langle 2n | e^{i \pi b^\dagger b} \rho_b | 2n \rangle + \sum_{n=0}^{\infty} \langle 2n + 1 | e^{i \pi b^\dagger b} \rho_b | 2n + 1 \rangle \] (A.19)

\[ = \sum_{n=0}^{\infty} \langle 2n | \rho_b | 2n \rangle - \sum_{n=0}^{\infty} \langle 2n + 1 | \rho_b | 2n + 1 \rangle \] (A.20)

Since the bath density matrix is diagonal we obtain

\[ \text{Tr}_b \left\{ R \rho_b \right\} = \frac{1}{Z} \sum_{n=0}^{\infty} \left[ e^{-2n\beta \omega} - e^{-(2n+1)\beta \omega} \right] \] (A.21)

\[ = \frac{1 - e^{-\beta \omega}}{Z} \sum_{n=0}^{\infty} e^{-2n\beta \omega} \] (A.22)

where the partition function \( Z \) is given by

\[ Z = \frac{1}{1 - e^{-\beta \omega}} \] (A.23)

The summation in Eq. (A.22) is a geometric series and can be evaluated straightforwardly. We arrive at the following expression

\[ \text{Tr}_b \left\{ R \rho_b \right\} = \tanh \left( \frac{1}{2} \beta \omega \right) \] (A.24)

which gives the following exact expression for the population

\[ \bar{\sigma}_{11}(t) = \frac{1}{2} + \Re[\sigma_{12}(0)] \tanh \left( \frac{1}{2} \beta \omega \right) \] (A.25)

A.2 Approximated expression

In order to evaluate the traces in Eq. (A.17) we make the following approximation,

\[ \exp \left( i \pi b^\dagger b \right) \approx 1 - 2b^\dagger b \] (A.26)
Upon this approximation $A$ and $B$ are simplified to

$$A \simeq -J + (\omega + 2J)b^\dagger b + \frac{\hbar}{2}(b^\dagger + b)$$  \hspace{1cm} (A.27)$$

$$B \simeq J + (\omega - 2J)b^\dagger b - \frac{\hbar}{2}(b^\dagger + b)$$  \hspace{1cm} (A.28)$$

We are interested in the evolution of the following two traces,

$$I_1 = \text{Tr}_b \left\{ e^{-iAt} \rho_b e^{iBt} \right\}$$  \hspace{1cm} (A.29)$$

$$I_2 = \text{Tr}_b \left\{ e^{-iAt} \rho_b \text{Re}^{iBt} \right\}$$  \hspace{1cm} (A.30)$$

The problem therefore simplifies to the evaluation of the following general trace

$$\text{Tr}_b \left\{ e^{i\Omega b^\dagger b} e^{itB} e^{-itA} \right\} \simeq$$  \hspace{1cm} (A.31)$$

$$\text{Tr}_b \left\{ e^{2iJt} e^{i\Omega b^\dagger b} \exp \left\{ it \left[ \omega_+ b^\dagger b - \lambda (b^\dagger + b) \right] \right\} \exp \left\{ -it \left[ \omega_+ b^\dagger b + \lambda (b^\dagger + b) \right] \right\} \right\}$$

where we have defined the new variables

$$\omega_\pm = \omega \pm 2J$$  \hspace{1cm} (A.32)$$

$$\lambda = \frac{1}{2}\hbar$$  \hspace{1cm} (A.33)$$

$$\Omega \in \{-\beta \omega, -\beta \omega + i\pi\}$$  \hspace{1cm} (A.34)$$

We simplify this expression further and arrive at

$$\text{Tr}_b \left\{ e^{i\Omega b^\dagger b} e^{itB} e^{-itA} \right\} \simeq$$  \hspace{1cm} (A.35)$$

$$\exp \left( \frac{i\Delta \omega t}{2} \right) \exp \left\{ \frac{i\lambda^2}{\omega_+ \omega_-} \left[ -\Delta \omega t + \sin(\Delta \omega t) - 2\omega \left( \frac{\sin(\omega_+ t)}{\omega_+} - \frac{\sin(\omega_- t)}{\omega_-} \right) \right] \right\}$$

$$\times \text{Tr}_b \left\{ \exp \left( (\Omega - i\Delta \omega) b^\dagger b \right) D(-\lambda \zeta) \right\}$$

where the displacement operator $D$ is given by

$$D(-\lambda \zeta) = \exp \left\{ -\lambda \left[ \zeta b^\dagger - \zeta^* b \right] \right\}$$  \hspace{1cm} (A.36)$$

and the frequency difference is defined to be

$$\Delta \omega = \omega_+ - \omega_-$$  \hspace{1cm} (A.37)$$
The trace of the displacement operator can be evaluated by noting the following,

\[ \langle n | D(-\lambda \zeta) | n \rangle = \langle n | \exp \left\{ -\lambda \left[ \zeta b^\dagger - \zeta^* b \right] \right\} | n \rangle \]

\[ = \exp \left\{ -\frac{\lambda^2 |\zeta|^2}{2} \right\} \langle n | \exp \left( -\lambda \zeta b^\dagger \right) \exp \left( \lambda \zeta^* b \right) | n \rangle \]

\[ = \exp \left\{ -\frac{\lambda^2 |\zeta|^2}{2} \right\} L_n(\lambda^2 |\zeta|^2) \]  

(A.38)

where \( L_n(x) \) is the Laguerre polynomial [25]. The generating function of the Laguerre polynomials is given by [158]

\[ \sum_{n=0}^{\infty} z^n L_n(x) = \frac{1}{1 - z} \exp \left\{ \frac{-xz}{1 - z} \right\} \]  

(A.39)

This identity can be used to evaluate the trace as follows

\[ \text{Tr}_b \left\{ \exp \left[ (\Omega - i\Delta \omega t) b^\dagger b \right] D(-\lambda \zeta) \right\} = \sum_{n=0}^{\infty} \langle n | \exp \left[ (\Omega - i\Delta \omega t) b^\dagger b \right] D(-\lambda \zeta) | n \rangle \]

\[ = \sum_{n=0}^{\infty} z^n \exp \left\{ -\frac{\lambda^2 |\zeta|^2}{2} \right\} L_n(\lambda^2 |\zeta|^2) \]  

(A.40)

Where \( z \) is defined to be

\[ z = \exp \left\{ \Omega - i\Delta \omega t \right\} \]  

(A.41)

We simplify and arrive at

\[ \text{Tr}_b \left\{ \exp \left[ (\Omega - i\Delta \omega t) b^\dagger b \right] D(-\lambda \zeta) \right\} = \frac{1}{1 - z} \exp \left\{ -\lambda^2 |\zeta|^2 \left[ \frac{z}{1 - z} + \frac{1}{2} \right] \right\} \]  

(A.42)

The off-diagonal element of the reduced density matrix can now be computed straightforwardly and is given by

\[ \bar{\sigma}_{12}(t) = \left[ \frac{1}{2} - \sigma_{11}(0) \right] \frac{1}{Z} \text{Tr}_b \left\{ e^{\Omega \hat{h} b^\dagger b + iA t} e^{-i A t} \right\} \Omega = -\beta \omega + i\pi \]

\[ + i \text{Im}[\sigma_{12}(0)] \frac{1}{Z} \text{Tr}_b \left\{ e^{\Omega \hat{h} b^\dagger b + iA t} e^{-i A t} \right\} \Omega = -\beta \omega \]  

(A.43)

Upon substitution of Eq. (A.42) into Eq. (A.35) and the resulting expression in Eq. (A.43) we arrive at the following expression for the evolution of coherence in the FG
basis (Eq. (2.40) in chapter 2)

\[
\bar{\sigma}_{12}(t) = \exp \left\{ i \frac{\lambda^2}{\omega^2 - 4J^2} \Phi(\omega, J, t) + 2iJt \right\} \\
\left\{ \frac{\sigma_{11}(0)[1-e^{-\beta\omega}]}{1+e^{-\beta\omega(t)}} \exp \left[ \frac{\lambda^2 \Theta(\omega, J, t)}{\omega^2 - 4J^2} \tanh \left( \frac{\beta \omega(t)}{2} \right) \right] + \\
\frac{i \Im[\sigma_{12}(0)][1-e^{-\beta\omega}]}{1-e^{-\beta\omega(t)}} \exp \left[ \frac{\lambda^2 \Theta(\omega, J, t)}{\omega^2 - 4J^2} \coth \left( \frac{\beta \omega + i \Delta \omega t}{2} \right) \right] \right\} 
\] (A.44)
Appendix B

Reduced density matrix in the site basis

B.1 Exact expression

In this appendix we compute the reduced density matrix of the system of two interacting molecules in the site basis. The reduced density matrix is determined by

\[ \sigma(t) = \text{Tr}_b\{\rho(t)\} \]
\[ = \text{Tr}_b\{e^{-iHt}\rho(0)e^{iHt}\} \]

The Hamiltonian is diagonalized via the operator \( U \), we therefore have

\[ e^{-itD} = U e^{-itH} U^\dagger \]
\[ e^{-itH} = U^\dagger e^{-itD} U \]

Upon substitution we arrive at

\[ \sigma(t) = \text{Tr}_b\{U^\dagger e^{-itD} U \rho(0) U^\dagger e^{itD} U\} \]
\[ = \text{Tr}_b\{U^\dagger e^{-itD} \bar{\rho}(0) e^{itD} U\} \]
where \( \bar{\rho}(0) \) is the initial density matrix in the FG basis, and is given by

\[
\bar{\rho}(0) = U \rho(0) U^\dagger \tag{B.7}
\]

\[
= U \sigma(0) \rho_b U^\dagger \tag{B.8}
\]

\[
= \rho_b \bar{\sigma}(0) \tag{B.9}
\]

In other words, since \([\rho_b, U] = 0\), initial separability of the density matrix in the site basis implies separability in the FG basis. Moreover, we can deduce the following simple transformation between the initial conditions in the two bases by writing the operator \( U \) in the matrix form

\[
\bar{\sigma}_{11}(0) = \frac{1}{2} + \text{Re}[\sigma_{12}(0)] R \tag{B.10}
\]

\[
\bar{\sigma}_{12}(0) = [1 - 2\sigma_{11}(0)] R - 2i \text{Im}[\sigma_{12}(0)] \tag{B.11}
\]

The transformations suggest that instead of exponentiating the Hamiltonian of Eq. (B.6), we can evaluate the following expression,

\[
\sigma(t) = \text{Tr}_b \{ U^\dagger \bar{\rho}(t) U \} \tag{B.12}
\]

We write \( U \) in the matrix form and multiply through to arrive at the following expression,

\[
\sigma_{11}(t) = \frac{1}{2} - \frac{1}{2} \text{Re} \left\{ \text{Tr}_b [ R \bar{\rho}_{12}(t) ] \right\} \tag{B.13}
\]

\[
\sigma_{12}(t) = \frac{1}{4} \text{Tr}_b \left\{ R [ \bar{\rho}_{11}(t) - \bar{\rho}_{22}(t) ] \right\} + \frac{1}{2} i \text{Im} \left\{ \text{Tr}_b [ \bar{\rho}_{12}(t) ] \right\} \tag{B.14}
\]

We next obtain expressions for time dependence of the density matrix in the FG basis, that is

\[
\bar{\rho}(t) = e^{-itD} \bar{\rho}(0) e^{itD} \tag{B.15}
\]

By writing \( e^{-itD} \) in the matrix form, we arrive at the following expressions for elements of \( \bar{\rho}(t) \)

\[
\bar{\rho}_{11}(t) = e^{-iAt} \rho_b \bar{\sigma}_{11}(0) e^{iAt} \tag{B.16}
\]

\[
\bar{\rho}_{12}(t) = e^{-iAt} \rho_b \bar{\sigma}_{12}(0) e^{iBt} \tag{B.17}
\]
Finally by substituting Eq. (B.10) and Eq. (B.11) into Eq. (B.16) and Eq. (B.17), and substituting the resulting expressions into Eq. (B.13) and Eq. (B.14), we arrive at the following exact expressions for the evolution of the reduced density matrix in the site basis,

\[
\sigma_{11}(t) = \frac{1}{2} + \left[ \sigma_{11}(0) - \frac{1}{2} \right] \text{Re} \left[ \text{Tr}_b \left\{ \rho_b e^{i\tilde{B}t} e^{iAt} \right\} \right] + \text{Im}[\sigma_{12}(0)] \text{Im} \left[ \text{Tr}_b \left\{ \rho_b Re^{i\tilde{B}t} e^{-iAt} \right\} \right]
\]

(B.18)

\[
\sigma_{12}(t) = \frac{1}{4} \text{Tr}_b \left[ \rho_b Re^{i\tilde{A}t} e^{-iAt} - \rho_b Re^{i\tilde{B}t} e^{-iBt} \right] + \frac{1}{2} \text{Re}[\sigma_{12}(0)] \text{Tr}_b \left[ \rho_b e^{i\tilde{A}t} e^{-iAt} + \rho_b e^{i\tilde{B}t} e^{-iBt} \right]
\]

\[
+ i \left[ \frac{1}{2} - \sigma_{11}(0) \right] \text{Im} \left[ \text{Tr}_b \left\{ \rho_b Re^{i\tilde{B}t} e^{-iAt} \right\} \right] + i \text{Im}[\sigma_{12}(0)] \text{Re} \left[ \text{Tr}_b \left\{ \rho_b e^{i\tilde{B}t} e^{-iAt} \right\} \right]
\]

(B.19)

where

\[
e^{-iBt} = Re^{iBt} \tag{B.20}
\]

### B.2 Approximated expression

The parts pertaining to the Hamiltonian are given by

\[
A = \omega b^\dagger b + \frac{h}{2} (b^\dagger + b) - J e^{i\pi b^\dagger b} \tag{B.21}
\]

\[
\tilde{A} = \omega b^\dagger b - \frac{h}{2} (b^\dagger + b) - J e^{i\pi b^\dagger b} \tag{B.22}
\]

\[
B = \omega b^\dagger b - \frac{h}{2} (b^\dagger + b) + J e^{i\pi b^\dagger b} \tag{B.23}
\]

\[
\tilde{B} = \omega b^\dagger b + \frac{h}{2} (b^\dagger + b) + J e^{i\pi b^\dagger b} \tag{B.24}
\]

We now introduce the following approximation,

\[
\exp \left[ i\pi b^\dagger b \right] \simeq 1 - 2b^\dagger b \tag{B.25}
\]
Appendix B. Reduced density matrix in the site basis

Upon this approximation the Hamiltonian contributions become

\[ A \simeq -J + (\omega + 2J)b^\dagger b + \frac{h}{2}(b^\dagger + b) \]  \hspace{1cm} (B.26)

\[ \tilde{A} \simeq -J + (\omega + 2J)b^\dagger b - \frac{h}{2}(b^\dagger + b) \]  \hspace{1cm} (B.27)

\[ B \simeq J + (\omega - 2J)b^\dagger b - \frac{h}{2}(b^\dagger + b) \]  \hspace{1cm} (B.28)

\[ \tilde{B} \simeq J + (\omega - 2J)b^\dagger b + \frac{h}{2}(b^\dagger + b) \]  \hspace{1cm} (B.29)

The exponentials of these variables are given by

\[ \exp \left[ iAt \right] \simeq \exp \left[ -iJt \right] \exp \left\{ i\Lambda(\omega_+, \lambda)t \right\} \]  \hspace{1cm} (B.30)

\[ \exp \left[ i\tilde{A}t \right] \simeq \exp \left[ -iJt \right] \exp \left\{ -i\Lambda(\omega_+, -\lambda)t \right\} \]  \hspace{1cm} (B.31)

\[ \exp \left[ iBt \right] \simeq \exp \left[ iJt \right] \exp \left\{ i\Lambda(\omega_-, -\lambda)t \right\} \]  \hspace{1cm} (B.32)

\[ \exp \left[ i\tilde{B}t \right] \simeq \exp \left[ iJt \right] \exp \left\{ i\Lambda(\omega_-, \lambda)t \right\} \]  \hspace{1cm} (B.33)

where we have defined the new set of variables

\[ \Lambda(\omega_\pm, \lambda) = \omega_\pm b^\dagger b + \lambda(b^\dagger + b) \]  \hspace{1cm} (B.34)

\[ \omega_\pm = \omega \pm 2J \]  \hspace{1cm} (B.35)

\[ \lambda = \frac{1}{2}h \]  \hspace{1cm} (B.36)

Computation of the density matrix is thus reduced to evaluation of the traces in Eq. (B.18) and Eq. (B.19) after substitution of the approximated expressions in Eq. (B.30) to (B.33). Evaluation of such traces is discussed in Appendix C. We arrive at the following final expressions for the evolution of the density matrix in the site basis. The diagonal part is given by

\[
\sigma_{11}(t) = \frac{1}{2} + \left[ \sigma_{11}(0) - \frac{1}{2} \right] \text{Re} \left\{ e^{2iJt} \exp \left\{ i\frac{h^2}{4\omega_+\omega_-} \Phi_a(\omega, J, t) \right\} \right. \\
\times \left. \frac{1-e^{-\beta t}}{1-e^{-\beta \omega(t)}} \exp \left\{ \frac{h^2}{4\omega_+\omega_-} \Theta_a(\omega, J, t) \coth \left[ \frac{\beta}{2} \omega(t) \right] \right\} \right] \\
+ \text{Im} \{ \sigma_{12}(0) \} \text{Im} \left\{ e^{2iJt} \exp \left\{ i\frac{h^2}{4\omega_+\omega_-} \Phi_a(\omega, J, t) \right\} \frac{1-e^{-\beta t}}{1+e^{-\beta \omega(t)}} \exp \left\{ \frac{h^2}{4\omega_+\omega_-} \Theta_a(\omega, J, t) \tanh \left[ \frac{\beta}{2} \omega(t) \right] \right\} \right]
\]
For the off-diagonal part we obtain

\[
\text{Re}\{\sigma_{12}(t)\} = \frac{1}{2}\text{Re}\{\sigma_{12}(0)\}\left\{ \exp\left[ \hbar^2 \coth\left( \frac{1}{2} \beta \omega \right) \left( \frac{\cos (\omega t) - 1}{\omega^2} \right) \right] + \exp\left[ \hbar^2 \coth\left( \frac{1}{2} \beta \omega \right) \left( \frac{\cos (\omega t) - 1}{\omega^2} \right) \right] \right\}
+ \frac{1}{4} \tanh\left( \frac{1}{2} \beta \omega \right) \left\{ \exp\left[ \hbar^2 \tanh\left( \frac{1}{2} \beta \omega \right) \left( \frac{\cos (\omega t) - 1}{\omega^2} \right) \right] - \exp\left[ \hbar^2 \tanh\left( \frac{1}{2} \beta \omega \right) \left( \frac{\cos (\omega t) - 1}{\omega^2} \right) \right] \right\}
\]

(B.38)

where

\[
\Phi_s(\omega, J, t) = -\Delta \omega t + \sin (\Delta \omega t) - (\omega_+ + \omega_-) \left[ \frac{\sin (\omega_+ t)}{\omega_+} - \frac{\sin (\omega_- t)}{\omega_-} \right]
\]

(B.40)

\[
\Phi_a(\omega, J, t) = -\Delta \omega t - \sin (\Delta \omega t) + (\omega_+ - \omega_-) \left[ \frac{\sin (\omega_+ t)}{\omega_+} + \frac{\sin (\omega_- t)}{\omega_-} \right]
\]

(B.41)

\[
\Theta_s(\omega, J, t) = -\frac{\omega_+^2 + \omega_-^2}{\omega_+ \omega_-} - [1 + \cos (\Delta \omega t)] + (\omega_+ + \omega_-) \left[ \frac{\cos (\omega_+ t)}{\omega_+} + \frac{\cos (\omega_- t)}{\omega_-} \right]
\]

(B.42)

\[
\Theta_a(\omega, J, t) = -\frac{\omega_+^2 + \omega_-^2}{\omega_+ \omega_-} + [1 + \cos (\Delta \omega t)] - (\omega_+ - \omega_-) \left[ \frac{\cos (\omega_+ t)}{\omega_+} - \frac{\cos (\omega_- t)}{\omega_-} \right]
\]

(B.43)

\[
\tilde{\omega}(t) = \omega + i \frac{\Delta \omega}{\beta}
\]

(B.44)

\[
\omega_\pm = \omega \pm 2J
\]

(B.45)

\[
\Delta \omega = \omega_+ - \omega_-
\]

(B.46)
Appendix C

Evaluation of traces

C.1 Useful operations

In this section we first quote a number of useful operator identities before moving on to the evaluation of the operator traces encountered in chapter 2. We start with a well-known formula for non-commuting operators $A, B$ (Eq. (3.1.14) in Ref. [159]):

$$e^{\xi A} B e^{-\xi A} = B + \xi [A, B] + \frac{\xi^2}{2!} [A, [A, B]] + \frac{\xi^3}{3!} [A, [A, [A, B]]] + ... \quad (C.1)$$

where $\xi$ is a constant. Moreover, if $[A, B] = C$, where $C$ is a constant, we have the identity (Eq. (3.1.20) in Ref. [159])

$$e^{A+B} = e^A e^B e^{-\frac{1}{2} [A,B]} = e^{\frac{1}{2} [A,B]} e^B e^A. \quad (C.2)$$

A further useful formula is (Eq. (3.3.5) in Ref. [159]):

$$e^{xb\dagger b} F (b\dagger, b) e^{-xb\dagger b} = F (b\dagger e^x, be^{-x}) \quad (C.3)$$

where $\{b, b\dagger\}$ are the bosonic annihilation and creation operators, $x$ is a constant and $F$ is an arbitrary function. A further useful expansion is (Eq. (3.3.24) [159]):

$$e^{\lambda b\dagger b} = \sum_{n=0}^{\infty} \frac{(e^\lambda - 1)^n}{n!} (b\dagger)^n b^n \quad (C.4)$$
We also know the action of the displacement operator on the displaced-harmonic oscillator (with $p = \pm 1$):

\[
\exp \{ \alpha \left[ \omega b^\dagger b + p\lambda (b^\dagger + b) \right] \} = \exp \left( -\frac{\alpha \lambda^2}{\omega} \right) D^\dagger \left( \frac{\lambda}{\omega} \right) \exp \left( \alpha \omega b^\dagger b \right) D \left( \frac{\lambda}{\omega} \right) \tag{C.5}
\]

Properties of the displacement operator can be listed as follows

\[
D(\alpha) = \exp \left( \alpha b^\dagger - \alpha^* b \right) \tag{C.6}
\]

\[
D^\dagger (\alpha) = D^{-1} (\alpha) = D (-\alpha) \tag{C.7}
\]

\[
D(\alpha) D(\beta) = \exp \left[ \frac{1}{2} (\alpha \beta^* - \beta^* \alpha) \right] D(\alpha + \beta) = \exp [i \beta \text{Im}(\alpha)] = D(\alpha + \beta) \tag{C.8}
\]

\[
D(\alpha e^{i\theta}) D(\beta e^{i\phi}) = \exp \left[ \frac{1}{2} \alpha \beta \left( e^{i(\theta - \phi)} - e^{-i(\theta - \phi)} \right) \right] D\left( \alpha e^{i\theta} + \beta e^{i\phi} \right) = \exp \left[ i \alpha \beta \sin(\theta - \phi) \right] D\left( \alpha e^{i\theta} + \beta e^{i\phi} \right) \tag{C.9}
\]

\[
D\left[ A\left( \alpha e^{i\theta} + \beta e^{i\phi} \right) \right] D(\gamma) = \exp \left[ i \gamma \text{Im} \left\{ A \left( \alpha e^{i\theta} + \beta e^{i\phi} \right) \right\} \right] D\left[ A\left( \alpha e^{i\theta} + \beta e^{i\phi} \right) + \gamma \right] = \exp \left[ i \gamma A \left( \alpha \sin(\theta) + \beta \sin(\phi) \right) \right] D\left[ A\left( \alpha e^{i\theta} + \beta e^{i\phi} \right) + \gamma \right] \tag{C.10}
\]

where $\alpha, \beta, \gamma, A$ are real constants,

\section*{C.2 Evaluation of the trace}

We wish to evaluate the expression

\[
X = \text{Tr}_b \left[ \exp \left( \Omega b^\dagger b \right) \exp \{ it \left[ \omega_- + p\lambda (b^\dagger + b) \right] \} \exp \{ -it \left[ \omega_+ + q\lambda (b^\dagger + b) \right] \} \right] \tag{C.11}
\]
for the parameters

\[ p, q = \pm 1 \quad (C.12) \]

\[ p^2, q^2 = 1 \quad (C.13) \]

\[ \Delta \omega = \omega_+ - \omega_- \quad (C.14) \]

Using Eq. (C.5) we obtain

\[
\exp \{ it [\omega_- + p \lambda (b^\dagger + b)] \} = \exp \left( -it \frac{\lambda^2}{\omega_-} \right) D^\dagger \left( p \frac{\lambda}{\omega_-} \right) \exp (it\omega_- b^\dagger b) D \left( p \frac{\lambda}{\omega_-} \right) \]

and similarly

\[
\exp \{ -it [\omega_+ + q \lambda (b^\dagger + b)] \} = \exp \left( it \frac{\lambda^2}{\omega_+} \right) D^\dagger \left( q \frac{\lambda}{\omega_+} \right) \exp (-it\omega_+ b^\dagger b) D \left( q \frac{\lambda}{\omega_+} \right) \]

Substituting Eq. (C.15) and Eq. (C.16) into Eq. (C.5) and simplifying we obtain

\[
X = \exp \left[ it \lambda^2 \left( \frac{1}{\omega_+} - \frac{1}{\omega_-} \right) \right] \text{Tr}_b \left\{ \exp \left( \Omega b^\dagger b \right) D^\dagger \left( p \frac{\lambda}{\omega_-} \right) \exp \left[ it (\omega_- - \omega_+) b^\dagger b \right] \right. \\
\times \left. e^{it\omega_- b^\dagger b} D \left[ \lambda \left( \frac{p}{\omega_-} - \frac{q}{\omega_+} \right) \right] e^{-it\omega_+ b^\dagger b} D \left( q \frac{\lambda}{\omega_+} \right) \right\} \]

We simplify Eq. (C.17) further by noting that

\[
e^{it\omega_- b^\dagger b} D \left[ \lambda \left( \frac{p}{\omega_-} - \frac{q}{\omega_+} \right) \right] e^{-it\omega_+ b^\dagger b} = e^{it\omega_- b^\dagger b} \exp \left\{ \left[ \lambda \left( \frac{p}{\omega_-} - \frac{q}{\omega_+} \right) \right] (b^\dagger - b) \right\} e^{-it\omega_+ b^\dagger b} \]

\[
= \exp \left\{ \left[ \lambda \left( \frac{p}{\omega_-} - \frac{q}{\omega_+} \right) \right] (b^\dagger e^{it\omega_+} - be^{-it\omega_+}) \right\} \]

\[
= D \left[ \lambda \left( \frac{p}{\omega_-} - \frac{q}{\omega_+} \right) \right] \exp (it\omega_+) \]

Substituting Eq. (C.18) into Eq. (C.17) and simplifying, we arrive at the expression

\[
X = \exp \left[ it \lambda^2 \left( \frac{1}{\omega_+} - \frac{1}{\omega_-} \right) \right] \text{Tr}_b \left\{ \exp \left[ \Omega - it \Delta \omega \right] b^\dagger b \right\} D \left[ -\lambda P \exp (it\Delta \omega) \right] \\
\times D \left[ -\lambda (Q - P) \exp (it\omega_+) \right] D(\lambda Q) \]

\[
(C.19) \]
where we have introduced the new variables $P$ and $Q$

\[
\begin{align*}
P &= \frac{p}{\omega_-} \\
Q &= \frac{q}{\omega_+} \\
P^2 &= \frac{1}{\omega_-^2} \\
Q^2 &= \frac{1}{\omega_+^2}
\end{align*}
\]

Two displacement operators can be combined as follows

\[
D\left(\alpha e^{i\theta}\right) D\left(\beta e^{i\phi}\right) = \exp\left[i\alpha\beta \sin(\theta - \phi)\right] D\left(\alpha e^{i\theta} + \beta e^{i\phi}\right)
\]

(C.20)

The displacement operators appearing in Eq. (C.19) are thus given by

\[
D\left[ -\lambda P \exp(it\Delta\omega) \right] D\left[ -\lambda (Q - P) \exp(it\omega_+) \right] \\
= \exp\left\{i\lambda^2 (PQ - P^2) \sin[(\Delta\omega - \omega_+) t]\right\} D\left(-\lambda P e^{it\Delta\omega} - \lambda (Q - P) e^{it\omega_+}\right) \\
= \exp\left[-i\lambda^2 (PQ - P^2) \sin(\omega_- t)\right] D\left\{\lambda \left[(P - Q) e^{it\omega_+} - P e^{it\Delta\omega}\right]\right\}
\]

(C.21)

Substituting Eq. (C.21) into Eq. (C.19) and simplifying, we arrive at the following expression for $X$

\[
X = \exp\left\{i\lambda^2 \left[\frac{1}{\omega_+} - \frac{1}{\omega_-}\right] t - (PQ - P^2) \sin(\omega_- t)\right\}
\times \text{Tr}_b\left\{\exp\left[(\Omega - it\Omega)b^\dagger b\right] D\left(\lambda \left[(P - Q) e^{it\omega_+} - P e^{it\Delta\omega}\right]\right) D(\lambda Q)\right\}
\]

(C.22)

We next combine the displacement operators in Eq. (C.22), using the following identity

\[
D\left[A\left(\alpha e^{i\theta} - \beta e^{i\phi}\right)\right] D(\gamma) = \exp\left\{i\gamma A\left[\alpha \sin(\theta) + \beta \sin(\phi)\right]\right\} D\left[A\left(\alpha e^{i\theta} + \beta e^{i\phi}\right) + \gamma\right]
\]

(C.23)
and arrive at

\[ D\left\{ \lambda \left[ (P - Q)e^{it\omega^+} - Pe^{it\Delta\omega} \right] \right\} D(\lambda Q) = \exp\left\{ i\lambda Q\lambda [(P - Q) \sin(\omega_t) - P \sin(\Delta\omega t)] \right\} \]

\[ D\left[ \lambda \left[ (P - Q)e^{it\omega^+} - Pe^{it\Delta\omega} \right] + \lambda Q \right] \]

\[ = \exp\left\{ i\lambda^2 \left[ (PQ - Q^2) \sin(\omega_+ t) - PQ \sin(\omega_+ t) \right] \right\} \]

\[ D\left\{ \lambda \left[ (P - Q)e^{it\omega^+} - Pe^{i\Delta\omega t} + Q \right] \right\} \]  \hspace{1cm} (C.24)

Substituting Eq. (C.24) into Eq. (C.22) we arrive at

\[ X = \exp \left\{ i\lambda^2 \left[ \left( \frac{1}{\omega_+} - \frac{1}{\omega_-} \right) t - (PQ - P^2) \sin(\omega_- t) \right] \right\} \text{Tr}_b \left\{ \exp \left[ (\Omega - it\Delta\omega)b\dagger b \right] \right\} \]

\[ \times D\left\{ \lambda \left[ (P - Q)e^{it\omega^+} - Pe^{it\Delta\omega} \right] \right\} D(\lambda Q) \]

\[ = \exp \left\{ i\lambda^2 \left[ \left( \frac{1}{\omega_+} - \frac{1}{\omega_-} \right) \right] - (PQ - P^2) \sin(\omega_- t) + (PQ - Q^2) \sin(\omega_+ t) - PQ \sin(\Delta\omega t) \right\} \]

\[ \times \text{Tr}_b \left\{ \exp \left[ (\Omega - it\Delta\omega)b\dagger b \right] D\left\{ \lambda \left[ (P - Q)e^{it\omega^+} - Pe^{i\Delta\omega t} + Q \right] \right\} \right\} \]  \hspace{1cm} (C.25)

We next make the substitution and \( \eta = (P - Q)e^{it\omega^+} - Pe^{i\Delta\omega t} + Q \) and use the following formula to evaluate the trace (Eq. A.40),

\[ \text{Tr}_b \left\{ \exp \left[ (\Omega - it\Delta\omega)b\dagger b \right] D(\lambda\eta) \right\} = \]

\[ \frac{1}{1 - \exp(\Omega - i\Delta\omega t)} \exp \left\{ -\lambda^2 |\eta|^2 \left[ \frac{\exp(\Omega - i\Delta\omega t)}{1 - \exp(\Omega - i\Delta\omega t)} + \frac{1}{2} \right] \right\} \]  \hspace{1cm} (C.26)

Using Eq. (C.26), Eq.(C.25) is simplified to

\[ X = \exp \left\{ i\lambda^2 \left[ \left( \frac{1}{\omega_+} - \frac{1}{\omega_-} \right) \right] - (Q - P) \left[ \sin(\omega_- t) + Q \sin(\omega_+ t) \right] - PQ \sin(\Delta\omega t) \right\} \]

\[ \times \frac{1}{1 - \exp(\Omega - i\Delta\omega t)} \exp \left\{ -\lambda^2 |\eta|^2 \left[ \frac{\exp(\Omega - i\Delta\omega t)}{1 - \exp(\Omega - i\Delta\omega t)} + \frac{1}{2} \right] \right\} \]  \hspace{1cm} (C.27)
We now simplify this expression further by evaluating $|\eta|^2$ using the identity $(a+b+c)^2 = a^2 + b^2 + c^2 + 2(ab + bc + ac)$

$$
\eta = (P - Q)e^{i\omega t} - Pe^{i\Delta \omega t} + Q \quad (C.28)
$$

$$
\text{Re}[\eta] = (P - Q)\cos(\omega t) - P\cos(\Delta \omega t) + Q \quad (C.29)
$$

$$
\text{Re}[\eta]^2 = (P - Q)^2\cos^2(\omega t) + P^2\cos^2(\Delta \omega t) + Q^2
- 2P(P - Q)\cos(\omega t)\cos(\Delta \omega t) + 2Q(P - Q)\cos(\omega t) - 2PQ\cos(\Delta \omega t) \quad (C.30)
$$

Similarly for the imaginary part we obtain

$$
\text{Im}[\eta] = (P - Q)\sin(\omega t) - P\sin(\Delta \omega t) \quad (C.31)
$$

$$
\text{Im}[\eta]^2 = (P - Q)^2\sin^2(\omega t) + P^2\sin^2(\Delta \omega t) - 2P(P - Q)\sin(\omega t)\sin(\Delta \omega t) \quad (C.32)
$$

which we combine to obtain $|\eta|^2$

$$
|\eta|^2 = 2\left\{P^2 - PQ + Q^2 - PQ\cos(\Delta \omega t) - (Q - P)\left[Q\cos(\omega t) - P\cos(\omega t)\right]\right\} \quad (C.33)
$$

Substituting Eq. (C.33) into Eq. (C.27), we arrive at the following expression for $X$

$$
X = \exp\left\{i\lambda^2\left[\left(\frac{1}{\omega_+} - \frac{1}{\omega_-}\right)t - (Q - P)[Q\sin(\omega_+ t) + P\sin(\omega_- t) - PQ\sin(\Delta t)]\right]\right\}
\times \frac{1}{1 - \exp(\Omega - i\Delta \omega t)} \exp\left\{\lambda^2|\eta|^2\left[\frac{\exp(\Omega - i\Delta \omega t)}{1 - \exp(\Omega - i\Delta \omega t)} + \frac{1}{2}\right]\right\}
= \exp\left\{i\lambda^2\left[\left(\frac{1}{\omega_+} - \frac{1}{\omega_-}\right)t + (Q - P)[Q\sin(\omega_+ t) + P\sin(\omega_- t) - PQ\sin(\Delta \omega t)]\right]\right\}
\times \frac{1}{\exp(\Omega - i\Delta \omega t)} \exp\left\{\lambda^2\left\{-P^2 + PQ - Q^2 + PQ\cos(\Delta \omega t)\right\}
\times (Q - P)[Q\cos(\omega_+ t) - P\cos(\omega_- t)]\left[\frac{2\exp(\Omega - i\Delta \omega t)}{1 - \exp(\Omega - i\Delta \omega t)} + 1\right]\right\}
$$
We simplify further by substituting back for $P$ and $Q$

\[
Q - P = \frac{q}{\omega_-} - \frac{p}{\omega_-} = \frac{q \omega_- - p \omega_+}{\omega_- \omega_+}
\]

\[
PQ = \frac{pq}{\omega_- \omega_+}
\]

\[
PQ - Q^2 - P^2 = \frac{pq}{\omega_- \omega_+} - \frac{1}{\omega_-^2} - \frac{1}{\omega_+^2}
\]

\[
= \frac{1}{\omega_- \omega_+} \left( pq - \frac{\omega_-^2 + \omega_+^2}{\omega_- \omega_+} \right)
\]

and arrive at the following final expression for $X$

\[
X = \exp \left\{ i \frac{\lambda^2}{\omega_+ \omega_-} \left[ - \Delta \omega t - (q \omega_- - p \omega_+) \left( \frac{q}{\omega_+} \sin(\omega_- t) - p \frac{\sin(\omega_- t)}{\omega_-} \right) - pq \sin(\Delta \omega t) \right] \right\}
\times \frac{1}{1 - \exp(\Omega - i \Delta \omega t)} \exp \left\{ \frac{\lambda^2}{\omega_+ \omega_-} \left\{ - \frac{\omega_-^2 + \omega_+^2}{\omega_- \omega_+} + pq [1 + \cos(\Delta \omega t)] \right. \right.
\]

\[
+ (q \omega_- - p \omega_+) \left[ q \frac{\cos(\omega_+ t)}{\omega_+} - p \frac{\cos(\omega_- t)}{\omega_-} \right] \left[ 2 \exp(\Omega - i \Delta \omega t) \right] \left[ 1 - \exp(\Omega - i \Delta \omega t) + 1 \right] \right\}
\]

(C.34)

**C.3 Trace expression for the general case**

We now include the partition function $1/Z = 1 - e^{-\beta \omega}$ and quote the final answer in the most general case

\[
\frac{1}{Z} \text{Tr}_b \left( \exp \left( \Omega b^\dagger b \right) \exp \left\{ it \left[ \omega_- + p \lambda \left( b^\dagger + b \right) \right] \right\} \exp \left\{ -it \left[ \omega_+ + q \lambda \left( b^\dagger + b \right) \right] \right\} \right) =
\exp \left\{ i \frac{\lambda^2}{\omega_+ \omega_-} \Phi(\omega, J, t) \right\}
\times \frac{1 - \exp(-\beta \omega)}{1 - \exp(\Omega - i \Delta \omega t)}
\exp \left\{ \frac{\lambda^2}{\omega_+ \omega_-} \Theta(\omega, J, t) \left[ 2 \exp(\Omega - i \Delta \omega t) \right] \left[ 1 - \exp(\Omega - i \Delta \omega t) + 1 \right] \right\}
\]

where the functions $\Phi(\omega, J, t)$ and $\Theta(\omega, J, t)$ are defined as

\[
\Phi(\omega, J, t) = - \Delta \omega t - pq \sin(\Delta \omega t) - (q \omega_- - p \omega_+) \left[ \frac{\sin(\omega_+ t)}{\omega_+} + p \frac{\sin(\omega_- t)}{\omega_-} \right]
\]

(C.35)

\[
\Theta(\omega, J, t) = - \frac{\omega_-^2 + \omega_+^2}{\omega_+ \omega_-} + pq [1 + \cos(\Delta \omega t)] + (q \omega_- - p \omega_+) \left[ q \frac{\cos(\omega_+ t)}{\omega_+} - p \frac{\cos(\omega_- t)}{\omega_-} \right]
\]

(C.36)
C.3.1 Case 1: Symmetric displacement, \( p = -1 \), \( q = 1 \)

We use the following two identities to simplify the expression for specific cases

\[
-2 \frac{\exp(-z)}{1 + \exp(-z)} + 1 = \tanh \left( \frac{z}{2} \right)
\]  
(C.37)

\[
2 \frac{\exp(-z)}{1 - \exp(-z)} + 1 = \coth \left( \frac{z}{2} \right)
\]  
(C.38)

For \( \Omega = -\beta \omega \) we arrive at

\[
\frac{1}{Z} \text{Tr}_b \left[ \exp \left( -\beta \omega b^\dagger b \right) \exp \left\{ it \left[ \omega_+ - \lambda \left( b^\dagger + b \right) \right] \right\} \exp \left\{ -it \left[ \omega_+ + \lambda \left( b^\dagger + b \right) \right] \right\} \right] = 
\exp \left\{ \frac{\lambda^2}{\omega_+ \omega_-} \Phi_a(\omega, J, t) \right\} \frac{1 - e^{-\beta \omega}}{1 - e^{-\beta \tilde{\omega}(t)}} \exp \left\{ \frac{\lambda^2}{\omega_+ \omega_-} \Theta_a(\omega, J, t) \coth \left( \frac{1}{2} \beta \tilde{\omega}(t) \right) \right\}
\]  
(C.39)

and for \( \Omega = -\beta \omega + i\pi \)

\[
\frac{1}{Z} \text{Tr}_b \left[ \exp \left[ \left( -\beta \omega + i\pi \right) b^\dagger b \right] \exp \left\{ it \left[ \omega_+ - \lambda \left( b^\dagger + b \right) \right] \right\} \exp \left\{ -it \left[ \omega_+ + \lambda \left( b^\dagger + b \right) \right] \right\} \right] = 
\exp \left\{ \frac{\lambda^2}{\omega_+ \omega_-} \Phi_a(\omega, J, t) \right\} \frac{1 - e^{-\beta \omega}}{1 + e^{-\beta \tilde{\omega}(t)}} \exp \left\{ \frac{\lambda^2}{\omega_+ \omega_-} \Theta_a(\omega, J, t) \tanh \left( \frac{1}{2} \beta \tilde{\omega}(t) \right) \right\}
\]  
(C.40)

where \( \Theta_a(\omega, J, t) \) and \( \Phi_a(\omega, J, t) \) are defined to be

\[
\Phi_a(\omega, J, t) = -\Delta \omega t + \sin(\Delta \omega t) - (\omega_+ + \omega_-) \left[ \frac{\sin(\omega_+ t)}{\omega_+} - \frac{\sin(\omega_- t)}{\omega_-} \right]
\]  
(C.41)

\[
\Theta_a(\omega, J, t) = -\frac{\omega^2_+ + \omega^2_-}{\omega_+ \omega_-} + (1 + \cos(\Delta \omega t)) \left[ \frac{\cos(\omega_+ t)}{\omega_+} - \frac{\cos(\omega_- t)}{\omega_-} \right]
\]  
(C.42)

\[
\tilde{\omega}(t) = \omega + i \frac{\Delta \omega}{\beta} t
\]  
(C.43)

C.3.2 Case 2: Anti-symmetric displacements, \( p = 1 \) and \( q = 1 \)

For \( \Omega = -\beta \omega \) we arrive at

\[
\frac{1}{Z} \text{Tr}_b \left[ \exp \left( -\beta \omega b^\dagger b \right) \exp \left\{ it \left[ \omega_+ + \lambda \left( b^\dagger + b \right) \right] \right\} \exp \left\{ -it \left[ \omega_+ + \lambda \left( b^\dagger + b \right) \right] \right\} \right] = 
\exp \left\{ \frac{\lambda^2}{\omega_+ \omega_-} \Phi_a(\omega, J, t) \right\} \frac{1 - e^{-\beta \omega}}{1 - e^{-\beta \tilde{\omega}(t)}} \exp \left\{ \frac{\lambda^2}{\omega_+ \omega_-} \Theta_a(\omega, J, t) \coth \left( \frac{1}{2} \beta \tilde{\omega}(t) \right) \right\}
\]  
(C.44)
and for \( \Omega = -\beta \omega + i \pi \) we obtain

\[
\frac{1}{Z} \text{Tr}_b \left[ \exp \left( -\beta \omega b \dagger b \right) \exp \left\{ it \left[ \omega_- + \lambda \left( b \dagger + b \right) \right] \right\} \exp \left\{ -it \left[ \omega_+ + \lambda \left( b \dagger + b \right) \right] \right\} \right] = \\
\exp \left\{ i \frac{\lambda^2}{\omega_+ \omega_-} \Phi_a(\omega, J, t) \right\}
\]  
(C.45)
Appendix D

Evaluation of memory kernels

D.1 Time-dependent perturbation theory and derivation of Kenkre and Knox rate equation

In this Appendix we discuss the details of the computation of the memory kernels considered in chapter 3. We consider a Hamiltonian partitioned into a zero-order term and a time-dependent perturbation $V(t)$ where the perturbation is yet unspecified but is responsible for transfer of energy in the context of EET. We denote the eigenstates of the unperturbed Hamiltonian by $|n\rangle$, that is

$$H = H_0 + V(t)$$  \hspace{1cm} (D.1)

$$H_0|n\rangle = E_n|n\rangle.$$  \hspace{1cm} (D.2)

Next we assume that the system starts in the state $|i\rangle$ and evolves to the state $|\alpha(t)\rangle$, under the influence of the evolution operator in the interaction picture $U_I(t)$. The state
of the system at a later time is denoted by $|\alpha(t)\rangle$ and is given by

$$|\alpha(t)\rangle = U_I(t)|i\rangle$$

$$= \sum_f |f\rangle \langle f|U_I|i\rangle$$

$$= \sum_f c_{if}(t)|f\rangle \tag{D.3}$$

The amplitude $c_{if}(t)$ can be written as a perturbative expansion,

$$c_{if}(t) = \langle f|U_I|i\rangle = c_{if}^{(0)} + c_{if}^{(1)} + c_{if}^{(2)} + ... \tag{D.4}$$

The leading terms of this expansion are given by [160]

$$c_{if}^{(0)}(t) = \delta_{fi} \tag{D.5}$$

$$c_{if}^{(1)}(t) = -i \int_0^t e^{i\omega_{fi}t'} V_{fi}(t') dt' \tag{D.6}$$

$$c_{if}^{(2)}(t) = (-i)^2 \sum_m \int_0^t dt' \int_0^{t'} dt'' e^{i\omega_{fm} t'} V_{fm}(t') e^{i\omega_{mi} t''} V_{mi}(t'') \tag{D.7}$$

where $V_{fm}$ is the coupling matrix element between two eigenstates $|f\rangle$ and $|m\rangle$. The transition probability from the state $|i\rangle$ to $|f\rangle$ is given by

$$P_{i\rightarrow f} = |c_{if}^{(1)}(t) + c_{if}^{(2)}(t) + ...|^2 \tag{D.8}$$

We take the leading term of the expansion and assume a time-independent perturbation, thus arriving at the following expression for the amplitude $c_{if}^{(1)}(t)$

$$c_{if}^{(1)}(t) = V_{fi} \frac{1}{\omega_{fi}} [e^{i\omega_{fi}t} - 1]$$

$$= V_{fi} \frac{e^{i\omega_{fi}t/2}}{\omega_{fi}} [e^{i\omega_{fi}t/2} - e^{-i\omega_{fi}t/2}]$$

$$= -2i e^{i\omega_{fi}t/2} V_{fi} \frac{\omega_{fi}}{\omega_{fi}} \sin (\omega_{fi} t/2) \tag{D.9}$$

The transition probability is therefore given by

$$P_{i\rightarrow f} = 4 \frac{|V_{fi}|^2}{\omega_{fi}^2} \sin^2 (\omega_{fi} t/2) \tag{D.10}$$
and the corresponding transition rate is determined by

\[ k_{if}(t) = \frac{d}{dt} |k_{if}^{(1)}|^2 = 2 \frac{|V_{fi}|^2}{\omega_{fi}} \sin(\omega_{fi}t) \]  

(D.11)

The memory Kernel \( G_{if}(t) \) quantifies the temporal variations of the transfer rate and is defined to be

\[ k_{if}(t) = \int_0^t G_{if}(t)dt \]  

(D.12)

We therefore arrive at the following expression for the memory kernel associated with the amplitude \( c_{if}^{(1)}(t) \)

\[ G_{if}^{(1)}(t) = 2|V_{fi}|^2 \cos(\omega_{fi}t) \]  

(D.13)

To relate this formula to phonon-assisted EET, we assume that \( \{|f\rangle\} \) represents localized electronic states, and that each molecule is coupled to a ladder of vibrational modes. If the initial state is coupled to the vibrational modes \( \{|k\rangle\} \) and the final state to the modes \( \{|q\rangle\} \), the memory Kernel is modified as follows,

\[ G_{if}^{(1)}(t) = 2 \sum_{kq} \frac{e^{-\beta_k}}{Z} |\langle f, q|V|i, k\rangle|^2 \cos\left[(\omega_{kq} + \Omega_{fi})t\right) \]  

(D.14)

where the occupation probability of the mode \( k \) is written as a Boltzmann factor. The energy difference is divided into two contributions: The energy difference between the electronic states \( \Omega_{fi} \), and the change in the vibrational energy \( \omega_{kq} \). This is the result of Kenkre and Knox for the rate of energy transfer between two states via a general coupling \( V \) [86, 87]. The perturbation \( V \) is what drives the transitions and must include both the electronic and the bath part of the interaction.

### D.1.1 Linear exciton-phonon interaction

We now evaluate the leading term of the expansion of the memory kernel for the linear exciton-phonon interaction. The Hamiltonian is given by

\[ H = - \sum_{mn} J_{mn} a_m^\dagger a_n + \sum_{n,k} a_n^\dagger a_n \left[ \epsilon_n + \phi_n \omega_k (b_{k}^\dagger + b_k) \right] + \sum_{k} \omega_k b_{k}^\dagger b_k \]  

(D.15)
where $J_{mn}$ is the electronic coupling between the sites $m$ and $n$, $\{a_n^+, a_n\}$ are the molecular raising and lowering operators for site $n$, $\epsilon_n$ is the electronic transition energy at site $n$, $\{b_k^+, b_k\}$ are the bosonic creation and annihilation operators for mode $k$ of the bath, $\phi_{nk}$ is a dimensionless displacement quantifying the exciton-phonon coupling between site $n$ and mode $k$, and $\omega_k$ are the bath frequencies. To incorporate bath-induced localization we next apply a small-polaron transformation on the Hamiltonian and identify the off-diagonal element in the polaron basis as the relevant perturbation [24], that is

$$
\tilde{H} = \sum_n a_n^+ a_n \tilde{\epsilon}_n - \sum_{n \neq m} J_{mn} a_n^+ F_n F_m a_m + \sum_k \omega_k b_k^+ b_k
$$

(D.16)

The transformation induces a linear shift in the nuclear coordinates and is given by

$$
F_n = e^{-\sum_k \phi_{nk} (b_k^+-b_k)}
$$

(D.17)

where $\tilde{\epsilon}_n$ is a renormalized energy,

$$
\tilde{\epsilon}_n = \epsilon_n - \sum_k \frac{\hbar^2}{\omega_k}
$$

(D.18)

To obtain the memory kernel for this interaction Hamiltonian we make the substitution

$$
T_{nm} = F_n^+ F_m
$$

(D.19)

and write the interaction Hamiltonian as

$$
V = \sum_{m \neq n} J_{mn} a_m^+ T_{mn} a_n
$$

(D.20)

Substituting Eq. (D.20) into Eq. (D.14), we arrive at the following expression for the memory kernel

$$
G_{ij}^{(1)}(t) = 2 |J_{ij}|^2 \text{Re} \left\{ e^{i \tilde{\Omega}_{if} t} \sum_{kq} \frac{e^{\beta \epsilon_k}}{Z} \langle k | T_{if} | q \rangle \langle q | T_{fi} | k \rangle e^{i (\omega_k - \omega_q) t} \right\}
$$

$$
= 2 |J_{ij}|^2 \text{Re} \left\{ e^{i \tilde{\Omega}_{if} t} \sum_{kq} \frac{e^{\beta \epsilon_k}}{Z} \langle k | e^{i \omega_k t} T_{if} e^{-i \omega_q t} | q \rangle \langle q | T_{fi} | k \rangle \right\}
$$

$$
= 2 |J_{ij}|^2 \text{Re} \left\{ e^{i \tilde{\Omega}_{if} t} \sum_{k} \frac{e^{\beta \epsilon_k}}{Z} \langle k | e^{i H_b t} T_{if} e^{-i H_b t} | T_{fi} | k \rangle \right\}
$$

$$
= 2 |J_{ij}|^2 \text{Re} \left\{ e^{i \tilde{\Omega}_{if} t} \langle T_{if}(t) T_{fi}(0) \rangle \right\}
$$

(D.21)
where $\tilde{\Omega}_{if}$ is the energy difference between the dressed states and the angled brackets indicate an averaging with respect to the thermally equilibrated bath modes. Substituting back for the displacement operators we arrive at

$$G_{if}^{(1)} = 2|J_{if}|^2 \text{Re} \left\{ e^{i\tilde{\Omega}_{if}t} \langle F_i^\dagger(t) F_f(t) F_i^\dagger F_i \rangle \right\}$$  \hspace{1cm} (D.22)

This is a familiar expression for the memory kernel in phonon-mediated EET [24] and the expression inside the angled brackets can be identified as the correlation function of the bath.

### D.1.2 First order interference

We follow the same procedure to compute the higher order memory kernels. The first three orders in the expansion of probability are given by

$$P_{i \to n}(t) = |c_{if}^{(1)}(t) + c_{if}^{(2)}(t) + ...|^2$$

$$= |c_{if}^{(1)}|^2 + |c_{if}^{(2)}|^2 + 2\text{Re}[c_{if}^{(1)}c_{if}^{(2)}]$$

(D.23)

The associated memory kernel can be computed as

$$G_{if}(t) = \frac{d^2}{dt^2} P_{i \to f}(t)$$

(D.24)

A similar expansion can therefore be written for the memory kernel. That is.

$$G_{if}(t) = G_{if}^{(1)}(t) + G_{if}^{(12)}(t) + G_{if}^{(2)}(t) + ...$$

(D.25)

where

$$G_{if}^{(1)}(t) = \partial_t^2 |c_{if}^{(1)}(t)|^2$$

(D.26)

$$G_{if}^{(12)}(t) = 2\partial_t^2 \text{Re}[c_{if}^{(1)}(t)c_{if}^{(2)}(t)]$$

(D.27)

$$G_{if}^{(2)}(t) = \partial_t^2 |c_{if}^{(2)}(t)|^2$$

(D.28)
To compute the memory kernel associated with the interference term, we first compute the second-order amplitude $c_{i_f}^{(2)}(t)$. Simplifying Eq. (D.7) we obtain

$$
c_{i_f}^{(2)}(t) = (-i)^2 \sum_m V_{f_m} V_{m_i} \int_0^t dt' e^{i \omega_{f_m} t'} \int_0^{t'} dt'' e^{i \omega_{m_i} t''}$$

$$= (-i)^2 \sum_m V_{f_m} V_{m_i} \int_0^t dt' e^{i \omega_{f_m} t'} \frac{1}{i \omega_{m_i}} [e^{i \omega_{m_i} t'} - 1]$$

$$= (-i)^2 \sum_m \frac{V_{f_m} V_{m_i}}{i \omega_{m_i}} \int_0^t dt' e^{i \omega_{f_m} t'} [e^{i \omega_{m_i} t'} - 1]$$

$$= \sum_m \frac{V_{f_m} V_{m_i}}{\omega_{m_i}} \left\{ \frac{1}{\omega_{f_i}} [e^{i \omega_{f_i} t} - 1] - \frac{1}{\omega_{f_m}} [e^{i \omega_{f_m} t} - 1] \right\} \quad (D.29)$$

The correction to the memory function due to the first order interference can be evaluated as follows

$$G_{i_f}^{(12)}(t) = 2 \text{Re} \frac{d^2}{dt^2} \left[ c_f^{(1)}(t) c_f^{(2)}(t) \right]$$

$$= -2 \text{Re} \frac{d^2}{dt^2} \left\{ V_{i_f} \left( e^{-i \omega_{f_i} t} - 1 \right) \right\}$$

$$\times \sum_m \frac{V_{f_m} V_{m_i}}{\omega_{m_i}} \left\{ \frac{1}{\omega_{f_i}} [e^{i \omega_{f_i} t} - 1] - \frac{1}{\omega_{f_m}} [e^{i \omega_{f_m} t} - 1] \right\} \quad (D.30)$$

We multiply through and simplify to arrive at

$$G_{i_f}^{(12)}(t) = 2 \text{Re} \left\{ -2 \sum_m \frac{V_{i_f} V_{f_m} V_{m_i}}{\omega_{m_i}} \cos (\omega_{f_i} t) \right. \right.$$  

$$\left. -i \frac{d}{dt} \sum_m V_{i_f} V_{f_m} V_{m_i} \left[ \frac{e^{-i \omega_{m_i} t}}{\omega_{f_i} \omega_{f_m}} + \frac{e^{i \omega_{f_m} t}}{\omega_{f_i} \omega_{m_i}} - \frac{e^{-i \omega_{f_i} t}}{\omega_{m_i} \omega_{f_m}} \right] \right\} \quad (D.31)$$
D.1.3 Inclusion of the bath modes in the interference term

We write Eq. (D.31) as a summation of four parts and evaluate each part separately. These four parts are given by

\[
G^{(12)}_1(t) = 2 \text{Re} \left\{ -2 \sum_m V_{if} V_{fm} V_{mi} \frac{\cos (\omega_{fit})}{\omega_{mi}} \right\} \tag{D.32}
\]

\[
G^{(12)}_2(t) = 2 \text{Re} \left\{ -i \frac{d}{dt} \sum_m V_{if} V_{fm} V_{mi} \left( \frac{e^{-i\omega_{fit}}}{\omega_{fi}\omega_{fm}} \right) \right\} \tag{D.33}
\]

\[
G^{(12)}_3(t) = 2 \text{Re} \left\{ -i \frac{d}{dt} \sum_m V_{if} V_{fm} V_{mi} \left( \frac{e^{i\omega_{fit}}}{\omega_{mi}\omega_{fm}} \right) \right\} \tag{D.34}
\]

\[
G^{(12)}_4(t) = 2 \text{Re} \left\{ i \frac{d}{dt} \sum_m V_{if} V_{fm} V_{mi} \left( \frac{e^{-i\omega_{fit}}}{\omega_{mi}\omega_{fm}} \right) \right\} \tag{D.35}
\]

where the subscript \('if'\) has been dropped for brevity. We use the indices \(m_k, i_k, f_k\) to indicate the bath modes associated with the sites \(m, i,\) and \(k\). Note that Hilbert space of \(|m_k\rangle\} spans the complete modes of the bath, even those not coupled to site \(m\). We assume that the interaction takes the following form

\[
V = \sum_{m \neq f} J_{mf} a^\dagger_m T_{mf} a_f. \tag{D.36}
\]

We thus include the vibrational modes by make the following substitutions

\[
V_{fm} \rightarrow J_{fm} \sum_{f_k, m_k} \frac{e^{-\epsilon_{f_k}\beta}}{Z} \langle f_k | T_{fm} | m_k \rangle
\]

\[
\omega_{fm} \rightarrow \Omega_{fm} + \omega_{f_k m_k} \tag{D.37}
\]

where in the new notation \(\Omega_{fm}\) indicates the energy difference between the electronic levels, and \(\omega_{f_k m_k}\) is the change in the vibrational energy. We simplify and arrive at the following expression for \(G^{(12)}_1(t)\)

\[
G^{(12)}_1(t) = -4 \text{Re} \left\{ J_m e^{-i\Omega_{it}} \sum_{i_k} \sum_{m, m_k} \frac{J_{fm} J_{mi}}{\Omega_{mi} + \omega_{m_k i_k}} \langle i_k | T_{if}(-t) T_{fm} | m_k \rangle \langle m_k | T_{mi} | i_k \rangle \right\} \tag{D.38}
\]

In order to evaluate this expression we use the following identity

\[
G_0(\lambda, E) = \frac{1}{E - \epsilon_\lambda + i\delta} = -i \int_0^\infty dt' e^{it(E-\epsilon_\lambda+i\delta)} \tag{D.39}
\]
where \( G_0(\lambda, E) \) is the zero-order Green’s function and \( \delta \) is a small imaginary contribution introduced to evaluate the contour integral. After some simplification we arrive at the following expression

\[
G^{(12)}_1(t) = 4\text{Re}\left\{ iJ_{if}e^{-i\Omega_{if}t}\sum_m J_{fm} J_{mi} \int_0^\infty dt' e^{i\Omega_{mi}t'} \langle T_{if}(-t)T_{fm}T_{mi}(t') \rangle \right\} \quad (D.40)
\]

where \( \delta \) has been set to zero. Similarly we obtain the following expressions for the three remaining contributions

\[
G^{(12)}_2(t) = 2\text{Re}\left\{ i\frac{d}{dt} \sum_m e^{-i\Omega_{mt}} J_{if} J_{fm} J_{mi} \sum_{ik} \right. \\
\times \left. \int_0^\infty dt' \int_0^\infty dt'' \langle T_{if}(-t')T_{fm}(t')T_{mi}(t'') \rangle e^{i\Omega_{if}t'} e^{i\Omega_{fm}t''} \right\} \quad (D.41)
\]

The next contribution becomes,

\[
G^{(12)}_3(t) = 2\text{Re}\left\{ i\frac{d}{dt} \sum_m e^{i\Omega_{mt}} J_{if} J_{fm} J_{mi} \sum_{ik} \right. \\
\times \left. \int_0^\infty dt' \int_0^\infty dt'' \langle T_{if}(t)T_{fm}(t')T_{mi}(t'') \rangle e^{i\Omega_{if}t'} e^{i\Omega_{fm}t''} \right\} \quad (D.42)
\]

and finally the last contribution is

\[
G^{(12)}_4(t) = -2\text{Re}\left\{ i\frac{d}{dt} \sum_m e^{-i\Omega_{mt}} J_{if} J_{fm} J_{mi} \sum_{ik} \right. \\
\times \left. \int_0^\infty dt' \int_0^\infty dt'' \langle T_{if}(t)T_{fm}(t'')T_{mi}(t') \rangle e^{i\Omega_{mi}t'} e^{i\Omega_{fm}t''} \right\} \quad (D.43)
\]

### D.2 Bath correlation function

In this section we elaborate on the calculation of the correlation functions that appear in the various expressions involving the bath memory. These expressions involve exponentials of a linear combination of bosonic operators. The thermal averaging over the bath modes can therefore be carried out straightforwardly.
D.2.1 Two-time bath correlation function

In this section we evaluate the simplest correlation function that appears in Eq. (D.22). We drop the subscript $k$ for simplicity and manipulate the operators to arrive at

$$\langle F_i^\dagger(t) F_n(t) F_n^\dagger F_i \rangle = \langle \exp \{ \phi_i [b^\dagger(t) - b(t)] \} \exp \{ -\phi_n [b^\dagger(t) - b(t)] \} \rangle \exp \{ \phi_n [b^\dagger - b] \} \exp \{ -\phi_i [b^\dagger - b] \}$$

$$= \langle \exp \{ (\phi_i - \phi_n) (b^\dagger e^{i\omega t} - b e^{-i\omega t}) \} \exp \{ -(\phi_i - \phi_n) (b^\dagger - b) \} \rangle \exp \left\{ -\frac{(\phi_i - \phi_n)^2}{2} (e^{i\omega t} - e^{-i\omega t}) \right\}$$

$$= \langle \exp \{ (\phi_i - \phi_n) (e^{i\omega t} - 1) b^\dagger \} - (\phi_i - \phi_n) (e^{-i\omega t} - 1) b \rangle \langle \exp \{ (\phi_i - \phi_n) (e^{i\omega t} - 1) b^\dagger \} \rangle$$

This expression can be evaluated via expanding the bath modes in the Fock basis. We use the result [78]

$$\langle \exp \{ \eta b + \theta b^\dagger \} \rangle = \exp \left\{ -\frac{1}{2} \eta \theta \right\} \exp \{ [1 + n(\omega)] \eta \theta \}$$

$$n(\omega) = \frac{1}{e^{\beta \omega} - 1}$$

where $\eta$ and $\theta$ are constants and $n(\omega)$ is the occupation number of a bath mode with frequency $\omega$. We apply this identity to Eq. (D.44) and arrive at

$$\langle F_i^\dagger(t) F_n(t) F_n^\dagger F_i \rangle = \langle \exp \{ -\sum_k (\phi_i - \phi_n)^2 \frac{1}{1} \} \rangle \exp \left\{ \sum_k (\phi_i - \phi_n)^2 \left[ n(\omega_k) e^{\omega_k t} + n(\omega_k) + 1 \right] e^{-i\omega_k t} \right\}$$

Generalizing to multiple bath modes we arrive at the well-known expression [24]

$$I(2, t_1, t_2) = \langle F_i^\dagger(t_1) F_n(t_2) F_n^\dagger F_i \rangle$$

$$= \exp \left\{ -\sum_k (\phi_i - \phi_n)^2 \frac{1}{1} \right\} \exp \left\{ \sum_k (\phi_i - \phi_n)^2 \left[ n(\omega_k) e^{\omega_k t_1} + n(\omega_k) + 1 \right] e^{-i\omega_k t_1} \right\}$$

Note that the two-time correlation function $I(2)(t_1, t_2)$ can be obtained by making the substitution $t \rightarrow t_1 - t_2$. 
D.2.2 Continuous limit

For a continuous bath the discrete sum may be replaced by an integral with respect to the spectral density function $J(\omega)$. That is,

$$\sum_k \hbar_k^2 \rightarrow \int_0^\infty J(\omega) d\omega \quad (D.49)$$

If the vibrational bath is identical at all sites, and there are no shared vibrational modes, $I^{(2)}(t,0)$ simplifies to

$$I^{(2)}(t,0) = \exp\left\{-2 \int_0^\infty d\omega \frac{J(\omega)}{\omega^2} [1 + 2n(\omega)]\right\} \times \exp\left\{2 \int_0^\infty d\omega \frac{J(\omega)}{\omega} \left[n(\omega)e^{i\omega t} + [n(\omega) + 1]e^{-i\omega t}\right]\right\}. \quad (D.50)$$

D.2.3 Three-time bath correlation function

The next order correlation function which appears in the interference memory kernels is given by

$$I^{(3)}(t,t',t'') = \langle F_i(t) F_n(t') F_m(t') F_{m'}(t'') F_i(t'') \rangle \quad (D.51)$$

Substituting for the displacement operators we obtain

$$I^{(3)}(t,t',t'') = \left\langle \exp\left\{\varphi_{in} [b^\dagger(t) - b(t)]\right\} \exp\left\{\varphi_{nm} [b^\dagger(t') - b(t')]\right\} \times \exp\left\{\varphi_{mi} [b^\dagger(t'') - b(t'')]\right\} \right\rangle \quad (D.52)$$

where

$$\varphi_{nm} = \phi_n - \phi_m \quad (D.53)$$

We commute the operators and after some simplification arrive at the expression

$$I^{(3)}(t,t',t'') = \exp\left\{\varphi_{in} \varphi_{nm} \frac{1}{2} \left[e^{i\omega(t-t')} - e^{-i\omega(t-t')}\right]\right\} \times \left\langle \exp\left\{Ab^\dagger + Bb\right\} \exp\left\{\varphi_{mi} [b^\dagger(t'') - b(t'')]\right\} \right\rangle \quad (D.54)$$

where

$$A = \varphi_{in} e^{i\omega t} + \varphi_{nm} e^{i\omega t'} \quad (D.55)$$
\[
B = - (\varphi_{in} e^{-i\omega t} + \varphi_{nm} e^{-i\omega t'})
\] (D.56)

Next we combine the two exponentials in order to write Eq. (D.54) in the form of Eq. (D.45). After some simplification we arrive at

\[
I^{(3)}(t, t', t'') = \exp \left\{ \frac{\varphi_{in} \varphi_{nm}}{2} \left[ e^{i\omega(t-t')} - e^{-i\omega(t-t')} \right] \right\} \exp \left\{ \frac{\varphi_{mi}}{2} \left[ A e^{-i\omega t''} + B e^{i\omega t''} \right] \right\} \\
\exp \left\{ \frac{\varphi_{in} \varphi_{nm}}{2} \left[ e^{i\omega(t-t')} - e^{-i\omega(t-t')} \right] \right\} \exp \left\{ \frac{\varphi_{mi}}{2} \left[ A e^{-i\omega t''} + B e^{i\omega t''} \right] \right\} \exp \left\{ -\frac{1}{2}\eta \theta \right\} \exp \left\{ (n+1)\eta \theta \right\}
\] (D.57)

where

\[
\theta = B - \varphi_{mi} e^{-i\omega t''} \\
\eta = A + \varphi_{mi} e^{i\omega t''}
\] (D.58)

After inclusion of the mode summations we obtain

\[
I^{(3)}(t, t', t'') = \exp \left\{ \frac{1}{2} \sum_k \varphi_{ink} \varphi_{nmk} \left[ e^{i\omega_k(t-t')} - e^{-i\omega_k(t-t')} \right] \right\} \\
\times \exp \left\{ \frac{1}{2} \sum_k \varphi_{mik} \left[ (\varphi_{ink} e^{i\omega_k t'} + \varphi_{nmk} e^{i\omega_k t'}) e^{-i\omega_k t''} - (\varphi_{ink} e^{-i\omega_k t} + \varphi_{nmk} e^{-i\omega_k t'}) e^{i\omega_k t''} \right] \right\} \\
\times \exp \left\{ \frac{1}{2} \sum_k \left[ (\varphi_{ink} e^{-i\omega_k t} + \varphi_{nmk} e^{-i\omega_k t'}) + \varphi_{mik} e^{-i\omega_k t''} \right] \right\} \\
\times \left[ (\varphi_{ink} e^{i\omega_k t'} + \varphi_{nmk} e^{i\omega_k t'}) + \varphi_{mik} e^{i\omega_k t''} \right]
\] (D.59)
D.2.4 Independent bath model

We now assume that there are no shared modes between different sites and that the phonon spectrum is site independent. Eq. (D.59) simplifies as follows

\[ I^{(3)}(t, t', t'') = \exp \left\{ -3 \phi_k^2 [1 + 2n(\omega_k)] \right\} \]

\[ \times \exp \left\{ \sum_k \phi_k^2 n_k \left[ e^{i\omega_k(t-t'')} + e^{i\omega_k(t-t')} + e^{i\omega_k(t'-t'')} \right] \right\} \]

\[ \times \exp \left\{ \phi_k^2 [n(\omega_k) + 1] \left[ e^{-i\omega_k(t-t'')} + e^{-i\omega_k(t-t')} + e^{-i\omega_k(t'-t'')} \right] \right\} \]  

(D.60)

D.2.5 Continuous limit

For a continuous spectral density \( J(\omega) \), Eq. (D.60) can be written as

\[ I^{(3)}(t, t', t'') = \exp \left\{ -3 \int_0^\infty d\omega J(\omega) \frac{1 + 2n(\omega)}{\omega^2} \right\} \]

\[ \times \exp \left\{ \int_0^\infty d\omega J(\omega) \left[ e^{i\omega(t-t'')} + e^{i\omega(t-t')} + e^{i\omega(t'-t'')} \right] \right\} \]

\[ \times \exp \left\{ [n(\omega) + 1] \left[ e^{-i\omega(t-t'')} + e^{-i\omega(t-t')} + e^{-i\omega(t'-t'')} \right] \right\} \]

(D.61)

D.2.6 Checks

The three-time correlation function can be reduced to the two-time correlation function by setting two of the three time variables to zero. That is,

If \( t' = t'' = 0 \)

\[ I^{(3)}(t, 0, 0) = \langle F_i(t) F_n(t) F_n^\dagger(0) F_m(0) F_m^\dagger(0) F_i(0) \rangle \]

\[ = \langle F_i(t) F_n(t) F_i^\dagger(0) F_i(0) \rangle \]

\[ = I^{(2)}(t, 0) \]  

(D.62)
If \( t' = t = 0 \)

\[
I^{(3)}(0, 0, t'') = \langle F^\dagger_i(0) F_n(0) F^\dagger_n(0) F_m(0) F^\dagger_m(t'') F_i(t'') \rangle \\
= \langle F^\dagger_i(0) F_m(0) F^\dagger_m(t'') F_i(t'') \rangle \\
= I^{(2)}(0, t'') \tag{D.63}
\]

It is straightforward to show that Eq. (D.60) is reduced to Eq. (D.50) if this substitution is made.

### D.2.7 Evaluating the time derivatives

In this section we simplify Eq. (D.41) to Eq. (D.43) further by evaluating the time derivative of the three-time correlation function. The derivative with respect to the first time-variable is given by

\[
\partial_t I^{(3)}(t, t', t'') = I^{(3)}(t, t', t'') \times \sum_k i \omega_k \phi_k^2 \left\{ n(\omega_k) \left[ e^{i \omega_k (t-t'')} + e^{i \omega_k (t-t')} \right] - \left[ n(\omega_k) + 1 \right] \left[ e^{-i \omega_k (t-t'')} + e^{-i \omega_k (t-t')} \right] \right\} \tag{D.64}
\]

Derivatives with respect to other time variables may be evaluated in the same manner. The terms are therefore modified as follows:

\[
G^{(12)}_2 = 2 \text{Re} \left\{ i \frac{d}{dt} \sum_m e^{-i \Omega_m t} J_{if} J_{fm} J_{mi} \int_0^\infty dt' \int_0^\infty dt'' I^{(3)}(-t', t'', -t) e^{i \Omega_f t'} e^{i \Omega_f t''} \right\} \tag{D.65}
\]

\[
G^{(12)}_2(t) = 2 \text{Re} \left\{ i \sum_m e^{-i \Omega_m t} J_{if} J_{fm} J_{mi} \int_0^\infty dt' \int_0^\infty dt'' \left[ -i \Omega_m + \partial_t \right] I^{(3)}(-t', t'', -t) e^{i \Omega_f t'} e^{i \Omega_f t''} \right\} \tag{D.66}
\]

\[
G^{(12)}_3(t) = 2 \text{Re} \left\{ i \sum_m e^{i \Omega_m t} J_{if} J_{fm} J_{mi} \int_0^\infty dt' \int_0^\infty dt'' \left[ i \Omega_f + \partial_t \right] I^{(3)}(-t', t'', t) e^{i \Omega_f t'} e^{i \Omega_m t''} \right\} \tag{D.67}
\]
\( G^{(12)}_4(t) = -2 \text{Re} \left\{ i \sum_m e^{-i\Omega_{fi}t} J_{if} J_{fm} J_{mi} \int_0^\infty dt'' \int_0^\infty dt' \times \left[ -i \Omega_{fi} + \partial_t \right] f^{(3)}(t, t', t'') e^{i\Omega_{mi}t''} e^{i\Omega_{fm}t'} \right\} \) \hspace{1cm} (D.68)

Part 1 has no time derivatives and is given by

\[ G^{(12)}_1(t) = 4 \text{Re} \left\{ i J_{if} e^{-i\Omega_{fi}t} \sum_m J_{fm} J_{mi} \int_0^\infty dt'' e^{i\Omega_{mi}t''} f^{(3)}(-t, 0, t'') \right\} \] \hspace{1cm} (D.69)

These expressions are used throughout chapter 3 to compute the interference contribution to the transfer rate.
Appendix E

Hamiltonian of PE545 tetramer

Electronic couplings between all pairs of chromophores computed via the Polarizable Continuum Model (PCM) [122, 123, 124] are listed in this appendix (supplementary information in Ref. [112]).
Table E.1: Computed electronic couplings (cm\(^{-1}\)) between all chromophore pairs in the PE545 tetramer.

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## Appendix E. Hamiltonian of PE545 tetramer

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Appendix F

Hamiltonian of the FMO protein

Hamiltonian of the FMO protein with seven sites [74]. Energies and electronic couplings are quoted in cm$^{-1}$.

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<td>4.3</td>
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<td>-9.6</td>
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<td>230</td>
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Bibliography


[62] Unpublished data obtained by Dr. Tihana Mirkovich, post doctoral researcher in the Scholes group.


