Excitonic Modes and Phonons in Biological Molecules

by

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Abstract

There are two kinds of environmental modes in open quantum systems: the delocalized modes which can typically be modeled by “oscillator bath” models and the localized modes which can be mapped to “spin bath” modes. To understand the quantum phenomena in photosynthetic energy transfer, we at first conduct thorough studies of the proper modeling of light harvesting molecules as well as their interactions with the central system. These modes can couple to the system by either modulating the on-site energy (Holstein coupling) or modulating the hopping amplitude (Peierls coupling). Only the Holstein couplings of delocalized modes have been extensively studied. The importance of other types of couplings is rarely discussed in the literature.

For the spin bath, we study a particle hopping around a general lattice, coupled to a spin bath. Analytical results are found for the dynamics of the influence functional and for the reduced density matrix of the particle in various parameter regimes. Spin baths behave qualitatively differently from oscillator baths and dissipation and decoherence happen independently in different parameter regimes.

For the Peierls couplings, we start with a dimer model for light harvesting molecules, which contains a reaction center and both types of phonon couplings. We find that the effect of Peierls type coupling on the transfer rate can be significant even when it is not noticeable in the spectrum. Our study suggests that Peierls couplings cannot be easily neglected in light harvesting molecules in which the energy difference between the sites is usually much larger than the hopping amplitude. We apply our method to a real light harvesting model. Although we do not have much detailed information of the Peierls couplings in vivo, we find that vibrational phonons can affect the path-selecting of the central particles as well as increasing the transfer rate.
Lay Summary

Photosynthesis may be the single most important biochemical process on Earth, since all higher life depends on it. The underlying mechanism of photosynthesis has fascinated scientists for centuries and yet still remains controversial. Recent experiments suggest that the photosynthetic mechanism may involve the coherent quantum-mechanical transport of energy inside "light-harvesting molecules" (in a way similar to quantum coherence in, eg., lasers). We study this subject from a theoretical physics perspective, and propose a new theoretical approach. This research should help us to understand how Nature captures solar energy with such astonishing efficiency.
Preface

The original work presented in Section 2.4 was carried out by Zhen Zhu who also developed the conception, scope and methods of this research.

The original work presented in Chapter 3 is a generalization of the work done by N.V. Prokof’ev and P. C. E. Stamp[1]. Section 3.2 was published in “Pure phase decoherence in a ring geometry”[2] in Phys. Rev. A at 2010. Zhen Zhu conducted most of calculations in the manuscript. The other original work in this chapter was carried out by Zhen Zhu, with various degrees of conception, consultation and editing support from P. C. E. Stamp.

The original work presented in Chapter 4-5 was carried out by Zhen Zhu who also developed the methods of this research, with various degrees of conception, methods, consultation and editing support from P. C. E. Stamp and Mona Berciu.

Original work reported from Chapter 3-5 are under preparation for publication in the near future.
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Dedication

To my late father Miaolong Zhu
Chapter 1

Introduction

One of the most exciting experiments in the last decade is probably the discovery of coherent quantum beating behaviors in photosynthetic systems. People used to believe that quantum mechanics is generally unnecessary to understand biological systems. Due to the enormous number of environmental degrees of freedom and the high physiological temperature, quantum coherence is believed to fade away rapidly and a classical description of both dynamics and states suffices. This discovery upsets scientists. At both low temperature (77K) and room temperature (277K), quantum coherent beating is observed in various types of light harvesting molecule at a time scale comparable to the photosynthetic process. Controversies have thus arisen about the actual functional role quantum coherence plays in this photosynthesis. There is no widely accepted conclusion that has been drawn yet. To address this problem, we have to thoroughly understand the behavior of open quantum systems coupling to various types of environmental modes.

There are usually two kinds of environmental modes in mesoscopic or macroscopic systems. One can categorize the environment oscillators in insulating systems by their origins: i) delocalized modes: such as the collective movements of whole molecules; ii) localized modes: such as the intramolecule vibration modes.

Delocalized modes are usually weakly-coupled low energy modes. The number of such modes is usually huge due to the enormous number of degrees of freedom of biological molecules. They usually have a delocalized origin (representing acoustic phonons, collective movements of electrons, phonons, photons, spin waves, etc.) so they can typically be modeled by "oscillator bath" models. The oscillator bath models have been extensively studied in the literature. It is one of the fundamental topics in solid state physics, as well as many other aspects of physics. In the language of spectroscopy, acoustic phonons are usually associated with the low energy continuum in spectra. In these models, decoherence always goes hand-in-hand with dissipation because of to the fluctuation-relaxation theorem.

There are other modes that have localized microscopic origins(optical
phonons, defects, dislocations, dangling bonds, nuclear and paramagnetic impurity spins, vibrations of chemical bonds, charged amino acid residues, etc.). In spectroscopy, these modes are related to discrete peaks in spectra. Their numbers are usually fewer compared with delocalized modes (which numbers are proportional to the enormous degrees of freedom in huge biological molecules), but their energies can be much higher, sometimes even comparable to the exciton energy light harvesting molecules. Under certain circumstance, these localized modes can be mapped into “spin bath” models[1, 20]. They behave quite differently from delocalized modes, so one cannot establish a general mapping between them[20]. In spin baths models, decoherence does not necessarily come together with dissipation. These localized modes are often far from equilibrium while in oscillator bath models environmental modes are always assumed to be in thermal states.

The importance of these localized modes, especially these vibrational modes in biological molecules, has already been realized in resonant energy transfer processes in light harvesting molecules (see for example [7, 21, 22]). However, in most of these studies, only the coupling between the vibrational modes and the on-site energies are considered. This type of coupling is known as the Holstein coupling in solid state physics[23]. However, phonons could also couple to hopping amplitudes between the different sites of pigments. The phonon-modulated transitions were first mentioned by Peierls with regard to the Peierls transition[24]. They were then studied in polyacetylene[25, 26] in the form of Su-Schrieffer-Heeger (SSH) model. People found that the Peierls (and SSH) model show qualitatively different behaviors compared to the Holstein model[27]. There are already plenty of experiments suggesting that vibration modes can directly couple to the exciton creation process in photosynthetic pigments[28]. Therefore, in principle, these modes should also couple to the hopping amplitude of excitons between pigments. Unfortunately, this type of coupling has never been discussed in biological molecules. Although the role of oscillator baths in biological systems has already been extensively studied[29–32], most studies only include the diagonal couplings, a.k.a, the modulation of the on-site energy.

On the other hand, although oscillator baths have been studied in-depth for various systems during the last half century, research on spin baths is scattered in the literature. Many previous works focus on either mapping spin baths into oscillator baths [17] or studying some simplified spin toy models such as the "central spin model" (a central 2-level system (TLS) coupled to a background spin bath; for examples, see [1, 20, 33, 34]).

In this thesis, we are going to address the following four objectives: (i) Understand the limitation of existing approaches in this newly found
1.1 Biological Systems with Quantum Phenomena

quantum biology field; (ii) Extend the existing theoretical and numerical techniques of spin bath models; (iii) Study the role of vibrational modes in resonant energy transfer, with both diagonal and non-diagonal couplings; (iv) Apply these studies in biological systems and understand the role of large scale quantum coherence in these systems.

This thesis is organized as follows: the rest of this section serves as an introduction to quantum phenomena in biological systems. The proper quantum modeling of biological systems is also reviewed in this chapter. We give the outline of this thesis and point out our contributions. In Chapter 2, we review the current popular approaches for quantum open systems and their limitations in application to biological systems. We also introduce the path integral formalism which is used later in this thesis. In Chapter 3, we study the spin bath model coupled to a general lattice model. We develop methods to solve the model in different parameter regions systematically. In Chapter 4, we study the role of vibrational modes in resonant energy transfer. We include both the diagonal (Holstein) couplings, the non-diagonal (Peierls) couplings as well as the two-phonon couplings. In Chapter 5, we propose a complete quantum Hamiltonian for excitons coupled to phonons in Fenna-Matthew-Olson complexes (FMO). We apply the theoretical and numerical techniques developed in the previous chapters to address the various terms in this Hamiltonian. Although the lack of knowledge of the detailed phonon spectrum in FMO prevent us from doing a thorough research, we still find some interesting mechanisms introduced by the coupling to environmental modes.

1.1 Biological Systems with Quantum Phenomena

In principle, quantum mechanics ultimately dictates the atomic and molecular details of biological systems, as the correct underlying theory. But such quantum effects are "trivial" at the biological level. In this section we review three specific biological systems which shows interesting quantum phenomena at time scales which are relevant to their biological functionality. In these cases, a proper quantum description of biological molecules is important to study the biological functionality. Such "non-trivial" quantum effects are the main motivation of this thesis. Although in this thesis, we mainly focus on the first system, i.e. the Fenna-Matthew-Olson complexes, a brief review of this new field of quantum biology could help understanding the overall context of the following research.
1.1 Biological Systems with Quantum Phenomena

1.1.1 Fenna-Matthew-Olson Complexes

Photosynthesis happens in various stages. The first stage is the absorption of light. Excitations are created in antennae called light harvesting complexes (LHC), usually in form of excitons [35]. The excitations are then transferred to reaction centers (RC) where the photosynthetic chemical reactions eventually happen. The transfer efficiency of LHC, i.e. the ratio between the amount of photons transported to RC and the amount of photons absorbed by the antennae, is fantastically high, almost 100% efficient [4]. The typical time for the whole exciton transfer process in LHCs is at the order of several pico seconds [36].

The Fenna-Matthew-Olson (FMO) complex is an LHC which exists in the purple bacteria *Chlorobium tepidum*. It was the first pigment-protein complex whose structure was solved by X-ray crystallography [37, 38]. The recently refined structure of FMO can be found in [3]. It has a global C3 symmetry with an arrangement of three identical subunits. People used to believe that each subunit contains seven bacteriachlorophylls (BChls) with the nearest neighbor distance of 11.3 to 14.4 Å, while the distance between nearest neighbors in different subunits of the trimer is about 24 Å [39, 40]. An eighth BChls has been found recently [41]. They are almost not interacting with Bchls in two different subunits [37]. FMO complexes act as "antennae" in photosynthetic process. Their main function is to transport photon energies into the RC for photosynthesis chemical reactions.

In 2007, Engel et al observed the quantum beating in FMO complexes at 77K by using a 2D femtosecond nonlinear spectroscopy. They found that the quantum coherence time of energy transfer is unexpectedly longer than any previous theoretical predictions (> 660fs [9]). This coherence time is comparable to the previous mentioned transfer time, which makes it ineligible to fully understand the functionality of LHCs. Shortly after, similar experiments were repeated under room temperature, which also showed long coherence time [13]. Furthermore, people found that this quantum coherent transfer is stable against the change of the structures of biological molecules by cultivating mutations of light harvesting molecules [42].

The existing theory of photosynthesis is based on the Förster theory [43]. The Förster is a semi-classical theory which only assumes classic energy transfer. Therefore it is insufficient to study the newly-found quantum beating phenomenon. Due to the amorphous nature of the biological molecules, the couplings to delocalized modes are also not negligible [30] (e.g., to local distortion of the molecule around pigments). The fact that the total transfer process takes less than several pico-seconds suggests that localized
modes probably play an important role here, although the incoherent oscillator bath-mediated transition would take over at longer times [1]. To compare with experiments, both localized and delocalized modes have to be included to study this macroscopic quantum coherent phenomenon. Furthermore, biological systems mostly operate away from equilibrium, which also renders most existing oscillator bath approaches questionable [44], since these approaches all rely on the assumption that baths are always in the thermal equilibrium state. The Markovian approximation also becomes questionable since the hopping amplitude of excitons in this central system is typically $10 \sim 10^2 \text{cm}^{-1}$ which is the same order as the coupling to the environment modes. Many theories have been proposed to describe the dynamics of light harvesting molecules. We are going to review them in detail later.

![Figure 1.1: The illustration of the molecular structure of FMO complexes. The left panel shows the three identical subunits of the FMO trimer. The right panel is the structure of each subunit. It is composed by 8 bacteriachlorophylls. Reprinted (adapted) with permission from [3]. Copyright (2011) American Chemical Society.](image-url)
1.1.2 Light Harvesting System I,II

Another interesting light harvesting system besides FMO is the light harvesting complex I (LH1) and light-harvesting complex II (LH2) found in the photosynthetic bacterium *Rhodopseudomonas acidophila* [35, 36, 45–48]. The LH2 complex serves as an antenna, which transfer photon energies towards LH1. Their molecular structures are shown in Fig.1.2. Each LH2 consists of 24 bacteriochlorophylls (BChls). These BChls have a C8 global symmetry as illustrated in Fig. 1.2 [49]. Sixteen of the BChls in a complex form a ring structure that is responsible for the strong absorption peak around 850 nm (B850) at room temperature, and the remaining eight BChls are bound near the cytoplasmic surface, and are responsible for another absorption peak around 800 nm (B800). LH1 surrounds a reaction center (RC) which is the destination of incoming excitons. LH1 contains 32 Bchls and forms a larger ring with C16 symmetry. The overall diameter of LH1 is 118 Å [36]. The large LH1 ring lies in the center of the process of photosynthesis. It absorbs excitations from LH2 networks and send them into the RCs. Similar quantum coherent beating phenomena were recently found in both LH1 [50] and LH2 [11]. Compared to FMO, these types of light harvesting complex has more BChls and therefore more computationally challenging. However their ring-like symmetric property can let us avoid the localization problem in FMO complexes. The calculation of this kind of central systems is also useful in other condensed matter system such as superconductors [51], which may also contain a flux threading the ring, which gives an interesting Aharonov-Bohm syle interference [2].

1.1.3 Avian Compass

The mechanism of avian navigation and bacteria guidance has been studied for hundreds of years. The once popular explanation is that certain magnetite particles exist in bacteria and birds. However it cannot explain the observation that the primary navigation mechanism is light activated [52, 53]. A novel magnetoreception explanation has arisen based on the radical-pair-based mechanism in cryptochrome [54]. Similarly to photosynthetic process, the chromophore flavin adenine dinucleotide (FAD) absorbs a photon and is excited to FAD* state [55]. After protonation to form FAD*, an electron-hole paired excitation is formed and the electron is allowed to hop within the cryptochrome. The spin configuration of this pair is initially singlet (or triplet in a different kind of cryptochrome [56]). The hopping electron’s spin is constantly altered by the external magnetic field, i.e. the earth’s
magnetic field, while the spin of the hole is fixed. Meanwhile, the electron spin is also interacting with surrounding nucleus spins through hyperfine couplings. The strength of hyperfine couplings in FAD molecules is from $10^1 \sim 10^2 \mu T$ while the earth magnetic field is from $23 \mu T$ to $68 \mu T$ [57]. When the spin configuration of this electron-hole pair is singlet(or triplet) again, they might recombine to produce FAD again and thus terminate the reaction. Therefore, the yield of the final product (FADH) of this reaction is controlled by the angles between the earth’s magnetic field and the hyperfine fields. Since the direction of hyperfine fields is fixed in the cryptochrome in birds’ eyes, birds are allowed to sense the angle between their lines of sight and the earth’s magnetic field, and know the right direction to go for. The structure of this cryptochrome is illustrated in Fig. 1.3. There is already some convincing experimental evidence which support this radical-pair explanation[58].

The electrons are interacting with a large number of nucleus spins dur-
1.2. Quantum Model for Photosynthetic Energy Transfer

In light harvesting molecules, the energy is usually transferred as Frenkel excitons, which are localized around each chromophore pigment. Therefore, the system is usually depicted as a particle (exciton) hopping between different sites (chlorophylls) while coupling to the surrounding environment. This phenomenon of resonant energy transfer (RET) was first observed at the beginning of last century. Before the breakthrough of the recent quantum biology experiments, the most successful theory about RET was the...
1.2. Quantum Model for Photosynthetic Energy Transfer

Förster theory, which was proposed by Förster in the late 1940’s. He derived an equation that relates the interchromophore distances to the spectroscopic properties of chromophores[43]. The Förster theory then became the standard way of spectroscopic distance determination in biology[36,60–62]. The Förster theory is a semi-classical theory which involves incoherent hopping between different sites. Förster assumed weak inter-site couplings and assumed that one can use the equilibrium Fermi Golden Rule to treat the electron coupling between site to site. In Förster theory, the probability $P_i$ to find a molecule $i$ excited at time $t$ can be determined by

$$\frac{d}{dt} P_i = \sum_j (W_{ij} P_j - W_{ji} P_i)$$  \hspace{1cm} (1.1)

Here $W_{ij}$ is the Förster transfer rate from molecule $j$ to molecule $i$. Using the Fermi Golden rule, we can get $P_i$ as a function of the electronic coupling $V_{ij}$, i.e.,

$$W_{ij} = \frac{\pi \hbar}{\hbar} \int_0^\infty d\varepsilon |V_{ij}|^2 J_{ij}(\varepsilon).$$  \hspace{1cm} (1.2)

Here $J_{ij}(\omega) \propto \int d\lambda \tilde{f}_i(\lambda) \tilde{f}_j(\lambda) \lambda^4$ is the overlap integral integral between the normalized emission spectrum $\tilde{f}_i(\lambda)$ and the normalized emission spectrum $\tilde{f}_j(\lambda)$. This theory was rather successful in the past. The sixth-power dependence of $P_i$ on the inter-molecular distance was verified experimentally in 1978 [63]. People are still working on this model and trying to improve its performance in photosynthetic systems (e.g. [64]). Incoherent hopping between sites is a central assumption in Förster theory, so it is not applicable for the study of the newly observed quantum effects.

Fortunately, there are already studies on the exciton transport, since it is a well-known phenomenon which is important in solid state physics. But there are many difference between these two fields of science. The biological systems usually contain a huge number of degrees of freedom and are much ”dirtier” (a huge number of environmental modes). In contrast with low temperature physics experiments, quantum biological experiments are usually conducted at either 77K or room temperature. The environment in biological experiments is also more complex and less controllable. It is crucial for us to establish proper models for these biological systems with their environments before we study the actual behaviour of this exciton transfer process with the tools in quantum physics.

Thanks to the recent development of refined experiments, we are provided with new tools to look into this fragile and sensitive quantum environment. In this section, we review the microscopic origins of various
environmental modes and their coupling to either the on-site energy of the exciton (diagonal couplings) or to the hopping amplitude (off-diagonal couplings). We take the FMO complexes and the associated Bacteriochlorophylls (BChls) as a typical example. We can see that both delocalized and localized modes are important in biological systems and they couple to the central system through both diagonal and off-diagonal couplings. We also believe that the two-phonon interaction terms beyond the linear approximation might also be relevant.

1.2.1 Single Chlorophyll Excitations and Diagonal couplings

Most chlorophylls are planar molecules which have a Magnesium coordinate atom as their centres. The illustration for Bacteriochlorophyll a (Bchl-a) in purple photosynthetic bacteria is shown in Fig.1.4. It is a quasi-planar molecule with a big hydrocarbon tail. There are four pyrrole rings surround the central Magnesium atom. These pyrrole rings form a chlorin macrocycle around the coordinate atom, and form a multi-band \( \pi \)-bonded system along the molecular plane, in the language of the molecular orbital theory\[6\].

The transition in the Bchl-a which is relevant to the biological process is believed to be the \( \pi \rightarrow \pi^* \) transitions in the conjugated \( \pi \) system. There are many different types of such transitions among these bands, which can be seen from their absorption spectra. A simplified theoretical model is the “four orbits” model\[6\]. Only the two lowest unoccupied molecular orbitals and the two highest occupied molecular orbitals are principally involved in these transitions. The two lower energy transitions are called “Q bands” and the two higher energy transitions are called “B bands” or “Soret Bands” (see Fig. 1.4). These “bands”, which are actually transitions, have different electronic transition dipole moments \( \mu_{ij} = e \langle i | r | j \rangle \) associated with each of them. For the lowest energy \( Q_y \) band, the polarization is along the direction of the solid Mg-N bond in Fig. 1.4 with a slight deviation; the \( Q_x \) band polarization is not as big as the \( Q_y \) band polarization and theoretical calculations also suggest that it is not perpendicular to the \( Q_y \) polarization. The Soret bands have mixed polarizations which are scarcely discussed. The transition dipole moment of the \( Q_y \) transition is 6.1\( D \) in vacuo\[29\]. Though there is more than one excitation in the system, in almost every previous calculation, the \( Q_y \) “band” is the only transition to be included in the exciton transfer.

After being embedded into the protein, the exact excitation energy of a single Bchl changes due to the effect of the surrounding charges and sol-
1.2. Quantum Model for Photosynthetic Energy Transfer

Figure 1.4: The structure and the absorption/fluorescence spectrum of a single Bchl-a. The structure of a single Bchl-a is illustrated in the left panel (without the hydrocarbon tail). The left panel is the absorption spectrum of Bchl-a and the left panel is its fluorescence spectrum. We can see that there are two major peaks in the absorption: the Soret Bands and the Only the \( Q_y \) “band” transition is included in the current calculations of excitonic energy transfer. Reprinted with permission from [6].
vent dielectricities. In experiments, the excitation energy is determined by fitting its absorption spectrum. It is generally believed that the major influence on the excitation energy \( \epsilon_i \) of each single Bchl \( a \) comes from the surrounding charged amino acid residues of the protein. The calculation based this assumption is quite accurate compared to the experimental data[29]. By applying the dipole approximation, the electric field created by the surrounding charges would give an extra term to the single electron Hamiltonian of the \( Q_y \) orbital in the form of

\[
\Delta H = \frac{e}{\epsilon} \sum_j q_j \vec{r}_i \cdot \vec{R}_{ij} \frac{R_{ij}^3}{R_{ij}^4},
\]

(1.3)

where \( j \) are the indices of all different amino residues, \( q_j \) is the charge of the amino residues, \( \epsilon \) is the optical dielectric constant in the protein and \( R_{ij} \) is the distance between the central chlorophyll and the \( j \)th residue. In first order approximation, this term gives an energy shift to the single electron state \( \sum_j \frac{q_j \vec{\mu} \cdot \vec{r}_{ij} R_{ij}^3}{R_{ij}^4} \). Here \( \vec{\mu} = \int d^3 r \phi(r) \vec{r} \phi^*(r) \) is the permanent dipole moment of a particular single electron state. Therefore, in the Hartree-Fork approximation, the shift to the exciton energy is

\[
\Delta \epsilon_i = \frac{1}{\epsilon} \sum_j \frac{q_j \Delta \vec{\mu} \cdot \vec{R}_{ij}}{R_{ij}^4},
\]

(1.4)

where \( \Delta \vec{\mu} = \vec{\mu}_1 - \vec{\mu}_0 \) is the difference of the permanent dipole moments between the ground state and the excited state(\( Q_y \) transition). The absolute value of \( \Delta \vec{\mu} \) is around 1.6\( D \) to 2.4\( D \). There are more than 100 amino acid residues which have significant effects on the excitation energy (> 20\( cm^{-1} \)). These residues are mainly from the protein frame in which the Bchls are embedded. The net energy shift ranges from \(-105 cm^{-1}\) to 195\( cm^{-1} \). Since the energy shift depends on the relative distance between the Bchls and the amino acid residues, it couples to the phonons in the system, i.e. the quantized movements of atoms in biological molecules. This is the microscopic origin of the diagonal couplings of the phonon modes in the Hamiltonian.

1.2.2 Exciton Propagation and Off-Diagonal Couplings

In the photosynthetic energy transfer process, the excitation is transferred from one chlorophyll to another. The system in which the coherent quantum beating phenomenon is found is actually quite compact. For example, the minimum distance between two BChls in one FMO complex is around 11\( \AA \)
1.2. Quantum Model for Photosynthetic Energy Transfer

This is the centre to centre distance. The distance measured between the closest atoms is much smaller, which ranges from 3.8 Å (Bchl 1 to Bchl 2) to 11.3 Å (Bchl 2 to Bchl 7)\(^{[65]}\). For comparison, the C–C single bond length is around 1.5 Å. For the long range Coulomb interaction, we can use the point-dipole approximation and assume the inter-Bchl coupling

\[
V_{mn} = f \frac{\mu_{\text{vac}}}{r_{ij}^3} (\hat{e}_i \cdot \hat{e}_j - 3(\hat{e}_i \cdot \hat{e}_{ij})(\hat{e}_j \cdot \hat{e}_{ij})),
\]

where \(f = \frac{1}{\epsilon} \frac{\mu(\epsilon)^2}{\mu_{\text{vac}}^2} \) is the term representing the screening effect of dielectric molecular environment; and \(\mu(\epsilon)\) is the transition dipole moment of \(Q_y\) transition after screening. The empirical value of \(f\) is 0.8 and we can simply use this to calculate the dipole interaction between Bchl-1 and Bchl-2 as 111 cm\(^{-1}\). This is also called the Förster picture in which there is no real particle exchange in this type of interaction. The statistical property of the electron is irrelevant here.

However, there are several drawbacks to the model. At first, the Mg-N distance is around 2.0 Å to 2.2 Å\(^{[65]}\), which is quite comparable to the closest atomic distance between two different pyrrole rings. This fact leads to several problems for this simple picture: i) the effect of higher order multipole interaction is not negligible.\(^{[66]}\) ii) the screening factor \(f\) becomes a function of distance rather than a constant\(^{[29]}\); iii) electrons can be directly exchanged between \(\pi\) orbitals in different Bchls.\(^{[67]}\)

This can be understood in the Hartree-Fock picture. The interaction between the two electrons on two neighboring Bchls can be written as

\[
V = V_{ij} c_{j,e}^\dagger c_{i,g} c_{i,e} c_{j,g}.
\]

Here \(i, j\) are indices for different Bchls; \(g\) represents the ground state of each Bchl and \(e\) represents the first excited state. The interaction term \(V_{ij}\) can be written as

\[
V_{ij} = \int \! dr_1 \! dr_2 \psi_{j,e}(r_1) \psi_{j,g}(r_1) \frac{e^2}{|r_1 - r_2|} \psi_{i,g}(r_2) \psi_{i,e}(r_2)
- \int \! dr_1 \! dr_2 \psi_{j,e}(r_1) \psi_{i,e}(r_1) \frac{e^2}{|r_1 - r_2|} \psi_{i,g}(r_2) \psi_{j,g}(r_2)
= \langle \psi_{j,e} | \psi_{j,g} | \psi_{i,g} | \psi_{i,e} \rangle - \langle \psi_{j,e} | \psi_{i,e} | \psi_{i,g} | \psi_{j,g} \rangle
= V_{ij}^c - V_{ij}^{ex},
\]

where \(\psi_{i,e}(r)\) is the single electron wave function for the \(e\) state of the \(i\)th
1.2. Quantum Model for Photosynthetic Energy Transfer

Bchl. Here we denote

\[ (\psi_a|\psi_b|\psi_c|\psi_d) \equiv \int d\vec{r}_1 d\vec{r}_2 \psi_a(r_1)\psi_b(r_1) \frac{e^2}{|r_1 - r_2|} \psi_c^*(r_2)\psi_d(r_2). \]  

(1.8)

The first term \( V_{ij}^c = (\psi_{i,e}\psi_{j,e}|\psi_{i,g}\psi_{j,g}) \) can lead to the usual dipole-dipole interaction form by expanding \( r_i, r_j \) around \( R_{i,j} \). The wave functions \( \psi_{i,e(g)} \) are centred near \( R_i \) which is the position of the center of the Bchl, so the first nonzero order gives the dipole-dipole interaction in (1.5) with the transition dipole moments \( \vec{\mu} = \int d\vec{r}\psi_{i,e}^*(r)\vec{r}\psi_{i,g}(r) \). The second part \( V_{ij}^{ex} \) is called the exchange interaction. Its value depends on the overlap of wave functions at different Bchls. By applying the Mulliken’s approximation of multcentre integrals, we can write it as

\[ V_{ij}^{ex} \approx \langle i,e|j,e\rangle \langle i,g|j,g\rangle \frac{2}{[(\psi_{j,e}\psi_{j,e}|\psi_{i,g}\psi_{i,g}) + (\psi_{i,e}\psi_{i,e}|\psi_{i,g}\psi_{i,g})]} \]  

(1.9)

The \( \pi \) orbitals are composed of \( p_z \) orbitals, therefore the overlap of wave functions \( \langle i,e|j,e\rangle \) decays exponentially by distance. As we mentioned the closest atom-atom distance between different Bchls is around 3.8\( \AA \). At this scale, the integral actually is not necessarily small. For example, the overlap integral between two \( p_z \) orbitals which is displaced in the \( x \) direction by \( d \) is illustrated in Fig. 1.5.

The exchange interaction \( V^{ex} \) has a different dependence on the distance compared to the dipole interaction \( V^c \) (\( V^c \propto \frac{1}{R^3} \) and \( V^{ex} \propto e^{-R/R_c} \), in which \( R_c \) is the extension of the molecular orbital wavefunction). Whether the extra exchange term \( V^{ex} \) is important or not still remains unknown. But both terms couple to the distances between Bchls, and thus to the phonon modes in the system. Since \( V^{ex} \) modulates the hopping amplitude of excitations, this is the origin of the off-diagonal phonon interaction in the Hamiltonian.

1.2.3 Vibrational Modes

Now we look at the details of the wave functions and their dependence on the atomic distances. The actual state wave function \( \psi_{e(g)} \) can be approximately calculated in the Pariser-Parr-Pople Hamiltonian given by [68],

\[ H = \sum_{i,\sigma} (-I_i - \sum_{j \neq i} R_{ij}) n_{i,\sigma} + \sum_{i \neq j,\sigma} t_{ij} c_{i,\sigma}^c c_{j,\sigma} + \frac{1}{2} \sum_{i \neq j,\sigma,\sigma'} R_{ij} n_{i,\sigma} n_{j,\sigma'}. \]  

(1.10)
1.2. Quantum Model for Photosynthetic Energy Transfer

Here $i, j$ are the indices for different $\pi$ orbitals. $\sigma, \sigma'$ are spin indices, $I_i$ is the ionization energy of orbital $i$, $R_{ij}$ is the effective Coulomb interaction integral, and $t_{ij}$ is the hopping integral between different orbitals. The Hamiltonian (1.10) is a semi-classical empirical Hamiltonian. For a single Bchl-a pigment, it takes into account for $24 \pi$ orbitals (18 C atoms, 2 O atoms and 4 N atoms) and 26 electrons (two extra electrons from the coordinate atoms Mg in the center). Solving this Hamiltonian would give the wave function $\psi_{e(g)}$ and the associated eigen-energy. In (1.10), both $R_{ij}$ and $t_{ij}$ depend on the relative distance $r_{ij}$ between the different atoms. In contrast with the collective movement of the molecules, the distances between atoms are affected by the vibration movements between Bchls, i.e. the vibrational modes. These modes are localized intra-chlorophyll phonon modes, which can have high frequencies. Vibrational modes are significant in the spectrum (see Fig. 1.6). We can see the sharp peaks ranging from $200cm^{-1}$ to $1700cm^{-1}$ in addition to the low energy continuum. The strongest peak around $1500cm^{-1}$ is associated with the C=O and C=C double bonds in the Bchl structure[7]. As a result, these modes also change the wave function $\psi(r)$ in equation (1.7) and hence couple to the off-diagonal terms $V_{ij}$. That is the microscopic origin of off-diagonal couplings to the vibrational modes.

These intra-chlorophyll vibrational modes are fundamentally different from the collective modes which have been extensively studied in the literature continuum modes described in the previous two sections. They have dif-
1.2. Quantum Model for Photosynthetic Energy Transfer

Figure 1.6: The spectral function $J(\omega)$ for each Bchl in FMO complex. The result is acquired by fitting the auto-correlation function of the absorption spectrum. Reprinted with permission from [7]. Copyright (2011) American Chemical Society.

Different dispersion relations and their numbers are small. Furthermore, these modes also couple to the transition dipole moments $\mathbf{d} = \int d\mathbf{r} \psi^*_g(\mathbf{r}) \mathbf{r} \psi_g(\mathbf{r})$. Therefore, when a single chlorophyll is excited by incoming photons, the vibrational modes are also excited by the phonons. In experiment, people usually use coherent light signals to excite the Bchls and they could construct a particularly structured vibrational states, which could make the decoherence being significantly slower due to the existence of vibrational modes[69]. Vibrational modes could introduce new physics into the system. It is important to study this type of environmental modes individually.

1.2.4 Two-Phonon Interaction

Another comment we have to make is about the possible effect from the higher order phonon couplings. Most of the time we only keep the linear terms for the interactions between the bath and the system for the following three reasons: i) The weak interaction: the interaction between the system and a single mode in the environment is usually small. ii) The $n > 2$ multi-phonon processes do not introduce new physics: they only give a weak renormalization to the parameters in the influence function kernel[17] for acoustic phonons at low temperature. iii) The Gaussian assumption: since the number of modes couples to the central system is huge, one can utilize the central limit theorem to justify the elimination of any cumulants higher
1.3. The Proposed Hamiltonian for Energy Transfer

than second order. The effect of a two-phonon interaction can be absorbed into linear terms if it is pure Gaussian.

However, these reasons are not applicable in these biological systems, especially with the addition of vibrational modes. Although Fig. 1.6 does not include the off-diagonal couplings, we can still see that the couplings to theses vibrational modes could be much stronger than the couplings of delocalized modes (for example $g \approx 0.1eV$ for the $0.21eV$ peak, compared with those $g \approx 0.02$ to the continuum), which are also strong compared with the net shift of the on-site energy from $-105cm^{-1}$ to $195cm^{-1}$. Furthermore, the number of such mode is also much fewer than the collective movement of the environment. The coupling strength for a single vibrational modes could be even stronger than the coupling to the continuum, which has a huge number of modes due to the enormous degrees of freedom. Therefore, we cannot assume weak interactions and a huge number of modes.

In addition, we cannot assume the low temperature condition for biological molecules either: the system is either at 77 K (in experiments) and 300K (in real life). Meanwhile, the coupling strength and hopping amplitude of excitons are both $\sim 10^2cm^{-1} \sim 100K$ which are comparable to the ambient temperature. Also the vibrational modes in photosynthetic molecules have a completely different spectrum compared to the acoustic phonons in solid state physics.

Therefore, if we include the couplings to the vibrational modes, we cannot use the usual argument to neglect the effect the two phonon interactions. We shall see in this thesis that the two-phonon process can introduce new physics into the system.

1.3 The Proposed Hamiltonian for Energy Transfer

In this thesis, we are going to focus on the exciton energy transfer in light harvesting molecules. Based on the previous review, we propose the appropriate complete Hamiltonian for an exciton coupling to vibrational modes
1.3. The Proposed Hamiltonian for Energy Transfer

of the environment as

\[ H = H_0 + H_1 + H_2 \]  (1.11)

\[ H_0 = \sum_i \varepsilon_i c_i^\dagger c_i + \sum_{\langle ij \rangle} (t_{ij} c_i^\dagger c_j + h.c.) + t_0 (c_1^\dagger d_0 + d_0^\dagger c_1) + H_B \]  (1.12)

\[ H_B = \sum_{\langle ij \rangle} V (d_i^\dagger d_j + h.c.) \]  (1.13)

\[ H_2 = \sum_k \Omega_k a_k^\dagger a_k. \]  (1.14)

\[ H_1 = \sum_i \left( \sum_k g_{H,i,k}^{(1)} (a_k^\dagger + a_k) + \sum_{k,k'} g_{H,i,k,k'}^{(2)} (a_k^\dagger + a_k) (a_{k'}^\dagger + a_{k'}) \right) c_i^\dagger c_i \]

\[ + \sum_{\langle ij \rangle} \left( \sum_k g_{P,i,k,\langle ij \rangle}^{(1)} (a_k^\dagger + a_k) + \sum_{k,k'} g_{P,i,k,k',\langle ij \rangle}^{(2)} (a_k^\dagger + a_k) (a_{k'}^\dagger + a_{k'}) \right) c_i^\dagger c_j + h.c. \]  (1.15)

where \( H_0 \) is the bare molecular Hamiltonian without coupling to phonons, and \( \{c_i^\dagger, c_i\} \) are the creation and annihilation operators of local excitons on the \( i \)-th chromophore. Here \( H_B \) is the phenomenological Hamiltonian of the reaction center (RC) and \( t_0 \) is the transfer amplitude to RC. The details of this reaction center model will be discussed in details in Chapter 4 and Appendix D.2.

The “\( g \)”s are the couplings to vibrational phonon modes. The couplings with subscript \( H \) stand for the diagonal couplings (which is known as the Holstein coupling in solid state physics[23]) and the couplings with subscript \( P \) stand for the off-diagonal couplings (which was first mentioned by Peierls [24] with regard to the Peierls transition). The superscripts (1) and (2) stand for the first order phonon coupling and for the second order phonon coupling.

The environmental modes are represented by operators \( \{a_k^\dagger, a_k\} \), including both the delocalized modes (acoustic phonons) and localized modes (e.g. vibrational modes). Together we have a complete description of the energy transfer model in light harvesting molecules in (5.1).

These equations are difficult to solve. Phonon couplings with different coupling strengths and frequencies require different theoretical and numerical techniques to address. Different parameters can have a huge impact on the qualitative behaviour of the model. The implication of exciton-phonon
1.3. The Proposed Hamiltonian for Energy Transfer

Coupling has been examined by many authors using many methods over the past few years. In the latter part of this sub-section, we will give a review of the prior work, and outline our approaches in this thesis.

1.3.1 Coherence in light harvesting molecules

In experiments, coherence is detected by specialized measurements. Short laser pulses are applied to the sample consecutively, creating superpositions of excitations, which can be detected using two-dimensional spectroscopy\(^\text{[70]}\). In principle, the cross-peak in the 2-D spectrum is the Fourier transform over \(t\) and \(\tau\) in the following expression:

\[
\frac{i}{\hbar} 3 (\vec{\mu}_{ij} \cdot \vec{E}_1)(\vec{\mu}_{ji} \cdot \vec{E}_2)(\vec{\mu}_{kl} \cdot \vec{E}_3)(\vec{\mu}_{lk} \cdot \vec{E}_4) \times (G_{ij}(\tau)G_{jk}(T)G_{kl}(t)). \quad (1.16)
\]

Here the \(\vec{\mu}_{ij}\) are the absorption dipole moments of the eigenstate \(|i\rangle\); the \(\vec{E}_{1,2,3,4}\) are polarization vectors of laser pulses; and \(G_{ij}(t)\) is the free propagator of the density matrix element \(\rho_{ij}\). If there is no decoherence, this latter is simply \(\exp (-i\omega_{ij}t)\) with \(\omega_{ij} = \omega_i - \omega_j\). When one takes the Fourier transform over \(\tau\) and \(t\), this term gives a cross-peak at \((\omega_{ij}, \omega_{kl})\) and oscillates in a time \(T\). In the real world, the oscillation does not last forever because of decoherence. In FMO complex experiments, the observed oscillation time is comparable with the time of the relevant biological process, i.e. the exciton transport time.

However, whether or not these results indicate coherent energy transport \textit{in vivo} remains controversial. All of the experiments are done in laboratories. The sample FMO complexes are extracted from the membranes of cells. The light signals to create excitons are not incoherent solar-like light, but ultrashort coherent laser pulses. Some have argued that the dynamics observed from ultra-short coherent excitation does not reflect what happens in processes induced by solar-like radiation\(^\text{[69]}\). It is suggested that electronic coherence decays significantly faster for incoherent light than for coherent ultrafast excitation. Furthermore, simply describing decoherence based on the damping of oscillations of off-diagonal elements of density matrix can be misleading, since such damping can also describe “False decoherence”\(^\text{[71]}\). In “False decoherence”, although one still observes damping of the reduced density matrix, the coherence information is actually not lost but preserved in the surrounding environmental modes. If one restores the interaction with the environment, one can restore the coherence as well. In Section 2.4, we will have a detailed discussion of False decoherence.

Although whether or not the beating phenomena indicates quantum coherence remains controversial, various experiments confirm the failure of
1.3. The Proposed Hamiltonian for Energy Transfer

the old semi-classical picture. Some work suggested that the observed beating has properties of quantum mechanics rather than a classical coherence picture\cite{72}. Experimental approaches that certify the non-classical nature of coherence in chemical and biophysical systems require us to employ a quantum model to understand its functions.

1.3.2 Acoustic Modes and Vibrational Modes

Many attempts have been made to understand the role of coherence in light harvesting molecules, despite the controversies. The traditional Förster theory \cite{43} and Markovian Redfield theory \cite{73} cannot predict the newly found long coherence time. New methods have been developed for the so called “non-Markovian” region for intermediate phonon-exciton couplings. The Hierarchy Equation of Motion (HEOM) is an exact method to deal with a spectral density of Drude type\cite{30,74,76}. The Non-Markovian quantum state diffusion (NMQSD) method is also applied to address more structured spectra (those with weakly interacted high frequency modes)\cite{77}. These methods are mainly employed to deal with the phonon modes in the low energy continuum.

Later on, people started to notice the importance of vibrational modes\cite{21}. The coherent beating amplitude is amplified by the resonance between the exciton energy difference and vibrational frequencies\cite{78}. The effects of these vibrational modes on the 2-D spectroscopy has been extensively examined\cite{79,80,81}. The results suggest that these resonant vibrational modes greatly increase the coherence time of the energy transfer.

Regarding the functionality of the biological molecules, it is generally believed that a balance of coherent and incoherent energy transfer is required to achieve the fastest transfer rate. Many works show that there is an optimal decoherence rate, which leads to an optimal transfer rate(e.g.\cite{82}). In the pure coherent limit, one can have constructive interference between multiple pathways for back reactions, therefore decreasing the transfer rate. In the pure classical limit, the exciton can be easily trapped in energy landscapes. These two competing mechanisms yield an optimal transfer rate with an intermediate decoherence rate. The transition between these two limits is smooth and seems robust against small parameter changes.

There are certain drawbacks to the work already appearing in the literature. First, we note that most of this work is based on the quantum master equation approach. The quantum master equation, based on the Born approximation and a Markov approximation, is successful for weakly interacted phonon modes, but not appropriate for strong couplings. This is
1.3. The Proposed Hamiltonian for Energy Transfer

especially important if we are going to deal with the strongly coupled vibrational modes. Mapping these modes into a spin bath model can greatly simplify the calculation in certain parameter regimes. In Chapter 2, we critically review the limitations of the popular master equation approaches, and in Chapter 3, we study the spin bath model which is useful in related calculations.

Second, in the context of biological functionality, we note that the quantity most often studied is the transfer rate, i.e., the exciton population transferred into the reaction center. In most of the literature, the population of the lowest energy site in FMO complexes is used as an indication of the transfer rate instead. However, as the exciton can be trapped by the strong phonon-exciton coupling, the population on the lowest energy site is not a proper indication of the transfer rate. In our thesis, we are going to use a quantum model for the reaction center, which allows possible back reaction processes.

Last but not least, only the diagonal phonon coupling is included in all previous studies. In the next paragraph, we will give a brief review of both diagonal and off-diagonal phonon couplings in physics.

1.3.3 Diagonal Coupling and Off-Diagonal Coupling

The polaron problem, i.e., the problem of a particle dressed by an environment, is an old problem in physics. It was firstly introduced by Landau in 1933 and later by Pekar in 1946.[83–85]

The diagonal coupling models (such as the Holstein model[23], the Fröhlich model[86] and the breathing-mode model[87]) show qualitatively similar results: the stronger coupling leads to a bigger dressing cloud, and hence create a heavier polaron. It involves a smooth crossover between weak and strong couplings, with no sharp transition in between. This is called the “polaron paradigm[88]. This is expected for diagonal couplings, where phonons only modulate the potential energy of the exciton. Therefore, a stronger coupling means it is harder for the exciton to ”climb out” the potential well created by the polarization cloud. It actually can be shown that for diagonal models having gapped bosonic modes, sharp transitions in the polaronic properties are impossible; all physical quantities must vary smoothly with coupling strength [89]. Therefore, we can see that the robustness and optimal transfer rate in light harvesting molecules is actually a common feature for all the diagonal phonon coupling models.

The off-diagonal coupling to phonons was first mentioned by Peierls [24], with regard to the Peierls transition. It was then studied in polyacetylene[25].
The proposed Hamiltonian for energy transfer using the Su-Schrieffer-Heeger (SSH) model. Unlike diagonal models, off-diagonal models do allow sharp transitions between different regimes. The polarons can be very light even at very strong coupling because hopping integrals can be larger in the presence of phonons. The polaron dispersion in these models can be quite different from that of the bare particle. In this thesis, we are going to compare the effects of both diagonal couplings and off-diagonal couplings in biological models. We will show that the local spectra can be changed qualitatively with the presence of off-diagonal couplings. This property allows us to engineer various macroscopic properties such as the transfer pathways selecting mechanism (see Chapter 5).

### 1.3.4 Two-Phonon Terms

Most theories about polaron physics only contain linear terms. Studies of quadratic phonon coupling are rarely found in the literature. Due to the particular symmetry of certain systems, pure quadratic phonon coupling is expected to occur in certain intramolecular modes of vibration, such as the out-of-plane bending modes in aromatic hydrocarbons. These couplings are estimated to be of importance in exciton transport but probably not in charge-carrier transport. For the large polaron case (weak interaction), we can use second order perturbation theory to show that the effective mass of the polaron is barely changed by quadratic phonon couplings [92]. In these cases, the quadratic phonon interaction term can be captured by a linear Hamiltonian with renormalized parameters, although the effective mass and transition rate have different dependence on the temperature [93, 94]. However, for medium and strong linear coupling, even small quadratic electron-phonon coupling terms are found to lead to very significant quantitative changes in the properties of the Holstein polaron [95]. These results suggest that the linear approximation is likely to be inappropriate to model systems with strong electron-phonon coupling. Actually, going back to 1989, it was already realized that the most important quadratic phonon couplings are the couplings between the modes with close frequencies [96]. In Section 4.6, we show that the only non-trivial effects from the two-phonon interactions come from the cross-interaction terms $g_{k,k',(ij)}^{(2)}(a_k + a_k^\dagger)(a_{k'} + a_{k'}^\dagger)$ when $k \neq k'$ and $\Omega_k \approx \Omega_{k'}$. These can be mapped into the spin bath interaction $(\Omega_k - \Omega_{k'})\sigma^z + g_{k,k',(ij)}^{(2)}\sigma^x$, in which the $\sigma_k$s are the operators of spin $\frac{1}{2}$ systems.
Chapter 2

Limitations of Master Equation Approaches to Open Quantum Systems and Decoherence

An open quantum system is a quantum system $S$ (the central system) coupled to another quantum system $B$ (the environment/bath). They form a closed quantum system $S + B$ with $S$ as the subsystem. Although the total system still obeys Hamiltonian dynamics, the evolution of the subsystem can no longer be represented as unitary Hamiltonian dynamics. The theories of open quantum system aim to derive the dynamics of the reduced system $S$. The quantum dynamics of such mesoscopic or macroscopic systems is always complicated due to their coupling to environments. In light harvesting system, the central system is a Frenkel exciton propagating in the light harvesting molecules and the environment is all the surrounding phonon modes with the aforementioned coupling to the transfer of such a exciton. Despite the biological significance, the understanding of the dynamics of quantum systems in contact with different kind of environment modes is also an important topic in physics. It has already been noticed that there are fundamental differences between a system coupled to a spin bath or an oscillator bath\[97\]. A thorough study is needed to compare these two models, each of which has its own theoretical importance.

The studies of biological systems focus on the their biological functionality, namely the energy transfer rate, efficiency, robustness, etc. After the discovery of the quantum beating phenomenon, quantum decoherence became another aspect to study in this field. Quantum coherence is a measure of how much a quantum state differs from a classic state and decoherence is the loss of quantum coherence. The concept of decoherence was introduced since 1953 \[98,103\] and has been a subject of active research since 1980s\[104\]. Many kinds of decoherence mechanisms exist, for example, environment-
induced decoherence; 3rd-party decoherence; intrinsic decoherence due to gravity, etc.[105]. Here we are only interested in the environment-induced decoherence, in which the quantum coherence is lost by interacting with environmental modes. People usually refer to the decoherence as the reduction of the off-diagonal elements of the density matrix, after “averaging over” the environment modes. However the definition of decoherence is not quite so straightforward that there are subtleties involved.

In this chapter, we would like to review the two most commonly used approaches for open quantum systems: the method of master equations and the path integral formalism. In the first part of this chapter, we review the key steps in deriving the famous Redfield equation and point out the limitation of the master equation approach. Although historically it has been successful in various fields, it could be questionable if we blindly apply it into any open quantum system. In latter part of this chapter, we use the central spin model as an example to show the danger when not using the appropriate method for the system we are studying. After that we show the path integral formalism and the influence functional method, which will be used in the later chapter on the spin bath model. We then use a slightly different central spin model to show the subtleties in the definition of quantum decoherence.

2.1 A Brief History of Studies on Open Quantum Systems

The traditional way to deal with open quantum systems started from Anderson and Kubo’s pioneering works on the spectrum of nuclear magnetic resonance in 1954 [106, 107]. They treated the environment as a source of random forces which act on the central system. They introduced a time-dependent effective hamiltonian $H(t) = H_0 + H_I(\Omega(t))$ in which $H_0$ is the bare Hamiltonian and $H_I(\Omega(t))$ is the effective influence of a bath with stochastic variables $\Omega(t)$. By making a Gaussian-Markov assumption (i.e. $\langle \Omega(t)\Omega(0) \rangle \propto e^{-\gamma t}$) on the stochastic evolution, they got a stochastic Liouville equation for the central system. This method is successful in diverse topics such as NMR, ESR, muon spin rotation, Mössbauer spectroscopy, dielectric relaxation, and linear and nonlinear spectroscopies[108].

However, this phenomenological model ignores the microscopic nature of the bath modes and the back reaction of the central system on the baths. It cannot describe a system with non-Markovian dynamics. The research on a dynamic bath model was started near the end of 1950s [109–113],
2.1. A Brief History of Studies on Open Quantum Systems

including the important work by Feynman & Vernon in 1963[14]. However, this work did not attract major attention until Caldeira & Leggett’s famous work on quantum tunneling in dissipative systems[15]. They modeled the environment as \( N \) uncoupled harmonic oscillators, which was originated by Feynman & Vernon. By employing the path integral method to take into account the intrinsic dynamics of the bath, they got effective interactions between classical paths, and demonstrated the quantum microscopic nature of friction.

Tanimura and Kubo then included this path integral formalism of an oscillator bath to overcome the drawbacks of the stochastic theory[114]. They derived a set of hierarchy equations of motion (HEOM) for the evolution of the reduced density matrix. By introducing auxiliary stochastic variables, they showed that the HEOM is actually a generalization of the previous quantum stochastic Liouville equation[115]. The HEOM has recently been widely used in quantum chemistry, especially in treating the spectrum of a biological molecule with strong interactions to the environment [30, 75, 76, 116, 117].

However, in these models, quantum decoherence always happens together with the relaxation, due to the fluctuation-dissipation theorem. The loss of phase is associated with friction from the environment which makes it impossible to study dissipation and decoherence separately. Furthermore, the whole work is based on the oscillator bath model. As Feynman showed, this is only valid when the coupling is weak [14, 118]; only under the weak coupling limit can we linearize the couplings and neglect high order cumulants. The derivation of the HEOM is based on the Gaussian-Markovian property of the spectral function, i.e. \( \langle q(t)q(0) \rangle \propto e^{-\gamma t} \). The delocalized modes couple to the central system with couplings \( \sim N^{-1/2} \) (\( N \) as the number of environmental modes). Their couplings are automatically weak for large \( N \). The couplings to the localized modes, on the other hand, are often independent of \( N \) and not necessarily small. The localized modes can have various microscopic origins such as nuclear spins, topological defects, and various more subtle modes associated with frustration, boundaries and intrinsic disorder. These modes are usually discrete and can be mapped into a spin system with spin \( S \) such that \( 2S+1 = M \), where \( M \) is the number of energy levels of each discrete mode. The decoherence in spin bath models is due to the precession of spins in time-variant fields coming from the central system, which allows us to study the pure phase decoherence without dissipation.

Unfortunately, spin baths have not been studied as completely as oscillator baths. One usual approach is to omit any cumulant higher than two
Such treatment eliminates the non-Gaussian behavior and is therefore unable to capture the strong nonlinearity of spin baths. Even if we include the higher level cumulants, it is still far from an exact method since the commutators between spin operators $S^{x,y,z}$ are spin operators themselves, not the c-number commutators like the Fermion or Boson cases.

Another approach is the cluster expansion of spin correlators. Though varying in details, cluster expansion methods are aiming at dealing with the expectation value of $T \exp(\int_0^t dt' H(t'))$ for an interactive bath Hamiltonian $H(t') = V_{ij}^{\alpha \beta} \sigma_i^{\alpha} \sigma_j^{\beta}$. By expanding the exponent we can get a cluster expansions based on the series of the commutators between spin operators. This model is computationally friendly and has been applied to spin decoherence experiments. In these works, the interactions between bath spins and the central systems are always assumed not to flip the central spin. Therefore, there is no “real” interaction between the bath and the central systems; the decoherence is due to the mismatch of phases between spins under the different effective spin Hamiltonians which are associated with different eigenstates of the central system. Obviously, this assumption is not always correct for any real system.

A more general form of spin-environment interaction is considered in spin star models. In order to compensate for the complexity of general interactions, the intrinsic dynamics of the spin itself are usually omitted, in some cases even the dynamics of the central system is not included. Since exact results can be usually acquired in these models, people already found some peculiar properties of spin baths which have never been found among oscillator ones, such as ballistic long time behavior and incomplete decoherence. However the problems considered still lack generality.

Prokof'ev and Stamp have done a thorough study on a central spin model coupled to a spin bath and their work has been successfully supported by various experiments. Their technique is based on a path integral and instanton operator method. However many experimental systems do not have such a simple central system (a two level system), and the path counting is generally not as straightforward as the TLS. It is even more different if we study the decoherence of quantum walks in an infinite lattice. The peculiarities found in a study of a spin bath on a lattice system have already been noticed by them but have yet been studied systematically.
2.2 Quantum Master Equation Approaches

As we reviewed in last section, the quantum master equation has been the center of the studies in open quantum systems. The master equation approach is widely used in quantum optics and quantum chemistry, as well as in quantum biology, with both phenomenological and microscopic models (e.g.,[32, 136, 137]). In this chapter we are going to derive the master equation and show the limitation of this approach.

The master equation is a probability equation to describe the time evolution of a system that can be modeled as being in a probabilistic combination of states at any given time, and in which the switching between states is determined by a transition rate matrix,

$$\frac{d}{dt}P_{ij}(t) = \sum_k A_{ik}(t, t') P_{kj}(x', t'). \tag{2.1}$$

In mathematics it is called the Kolmogorov equation for his contribution to Markov processes. The master equation is usually used with a discretized phase space. By replacing discrete indices $i,j$ with continuous variables $x,y$, we can obtain its counterpart for the continuous phase space, namely the Fokker-Planck equation. A quantum master equation is a generalization of the master equation, involving a differential equation for the entire density matrix. Its continuous counterpart, a quantum Fokker-Planck equation, is a differential equation for the Wigner quasi-distribution function [138] of the quantum system.

The common derivation of a quantum master equation is usually based on the Liouville equation of the whole quantum system

$$\frac{d}{dt}\rho(t) = \mathcal{L}\rho(t) = [H, \rho]. \tag{2.2}$$

We can start by writing the Hamiltonian as

$$H = H_0 + H_B + H_I, \tag{2.3}$$

where $H_0$ is the Hamiltonian of the central system, $H_B$ is the bath Hamiltonian and $H_I$ is the interaction between them. In most cases we can write $H_I$ as

$$H_I = \sum_i F_i L_i. \tag{2.4}$$

Here $F_i$ are the operators acting on the bath and $L_i$ are the operators acting on the central system. We can define the Hamiltonian in the interaction
picture as
\[ H_I(t) = e^{i(H_0 + H_B)t} H_I e^{-i(H_0 + H_B)t}. \] (2.5)

The ultimate goal is to calculate the reduced density matrix of the central system
\[ \rho_S(t) = tr_B [\rho(t)], \] (2.6)
where \( \rho(t) \) is the density matrix of the whole system. We start with the most general master equation: the Nakajim-Zwanzig Master Equation [139, 140] (NZME). The core idea of the NZME is to using the following projection operators to divide the Hamiltonian into “relevant” part (central system plus a fixed bath) and “irrelevant” part (the bath variation part):
\[ P\rho = tr_B [\rho] \otimes \rho_B, \] (2.7)
\[ Q\rho = (1 - Q)\rho. \] (2.8)

Then solving the reduced density matrix \( \rho_S(t) \) is equivalent to finding \( P\rho(t) \). Here \( \rho_B \) is a constant density matrix for the bath. In principle it can be chosen arbitrarily, but usually one chooses \( \rho_B \) to be a state which is close to the actual bath state. In some cases, the choice for \( \rho_B \) is obvious: for example, a thermal state for a thermal bath. The dynamics of the total system can be written as
\[ \frac{d\rho}{dt} = L(t)\rho \equiv [H_I(t), \rho], \] (2.9)
where \( L(t) \) is the time evolution operator in the interaction picture. We then get
\[ \frac{d}{dt} P\rho = P\mathcal{L} P\rho + P\mathcal{L} Q\rho, \] (2.10)
\[ \frac{d}{dt} Q\rho = Q\mathcal{L} P\rho + Q\mathcal{L} Q\rho. \] (2.11)

The solution of (2.11) can be formally written as
\[ Q\rho(t) = G(t, 0)Q\rho(0) + \int_0^t ds G(t, s) Q\mathcal{L} P\rho(s) \] (2.12)
with \( G(t, 0) \) as the propagator of the “irrelevant” part of the system:
\[ G(t, 0) = T_+ \left[ e^{i \int_0^t ds \mathcal{L}(s)} \right]. \] (2.13)
2.2. Quantum Master Equation Approaches

Here $T_+$ is the time ordered operator. Plugging $T_+$ into (2.10), we can write the exact master equation as

$$\frac{d}{dt} \rho(t) = P\mathcal{L}(t)P\rho(t) + \mathcal{P}\mathcal{L}(t)G(t,0)Q\rho(0) + \int_0^t ds P\mathcal{L}(t)G(t,s)Q\mathcal{L}(s)P\rho(s).$$

(2.14)

This equation is the Nakajima-Zwanzig Master Equation (NZME). It is an exact equation. The right hand side contains an inhomogeneous term depending on the initial state of the bath and a time convolution integral. The mixture of time evolution operator and projections actually makes it extremely difficult to solve analytically. The first term on the right hand side of (2.14) is a dynamic term. To simplify the equation, we can assume that

$$P\mathcal{L}(t)P\rho(t) = 0.$$  

(2.15)

This is equivalent to assuming that for any eigenstate in the bath’s Hilbert space, the expectation value of the bath operators involved in the bath-system coupling vanishes:

$$\langle b| F_i |b \rangle = 0,$$

(2.16)

where $|b\rangle$ are the states of the bath. However, this condition is not necessary since even if it is not zero, we can just add a renormalization term

$$\sum_i tr_B[\rho_B F_i] [L_i, \ldots]$$

to the time evolution super operator $\mathcal{L}$ (see for example [141]). In the rest of this chapter, we always assume (2.15) holds.

2.2.1 Redfield Master Equation

The NZME (2.14) is exact but difficult to solve. In practice people employ several approximations to mitigate the difficulty. The Redfield equation is among one of the most popular quantum Markovian master equations. The derivation of the Redfield equation involves multiple approximation procedures which are popular in many master equation approaches. In this section we would like to review the derivation of the Redfield master equation and review the critical steps. Although the Redfield equation has been successful in history, there are several drawbacks which makes it applicable to many real world systems.

To begin with, we assume that the initial state of the system is a product state, i.e.

$$\rho(0) = \rho_S(0) \otimes \rho_B.$$  

(2.17)
Therefore $Q\rho(0) = 0$, i.e. the inhomogeneous term which depends on the initial state is gone. This assumption is quite common when people are dealing with open quantum systems. However, in reality, validating this assumption requires either the central system and the environment to be prepared separately, or the relaxation time of the bath to be much shorter than the other time scales of the system. Actually in most cases the bath and the central system are initially entangled due to interactions.

Secondly, we introduce the weak coupling assumption: $H_I(s) t \ll 1$. We assume that there is no evolution for the “irrelevant” part of the Hamiltonian, i.e.

$$G(t, 0) = T_e \int_0^t ds QL(s) \approx 1.$$ \hspace{1cm} (2.18)

This is the zeroth order perturbation of the superoperator $QL$, which means (2.18) is only valid in the weak interaction regime and for a short time scale. This weak interaction assumption is sometimes called the Redfield limit[30]. We can see later that this is also a Gaussian approximation: you eliminate any cumulant higher than two for the bath correlation function. The master equation then becomes

$$\frac{d}{dt} P\rho(t) = \int_0^t ds P\mathcal{L}(t)\mathcal{L}(s) P\rho(s).$$ \hspace{1cm} (2.19)

We can write out the operators explicitly to get the familiar master equation:

$$\frac{d}{dt} \rho_S(t) = -\int_0^t d\tau B[H_I(t), [H_I(s), \rho_S(s) \otimes \rho_B]].$$ \hspace{1cm} (2.20)

In the literature, (2.20) is usually referred as the second-order time-convolution equation(TC2). It still contains memory effect of the past in the convolution integral explicitly.

The next step is to introduce the Markov approximation to make the master equation local in time:

$$\rho_S(s) \approx \rho_S(t).$$ \hspace{1cm} (2.21)

We can then write the master equation in the form of the commonly used Redfield equation:

$$\frac{d}{dt} \rho_S(t) = -\int_0^t d\tau \left( [L_i(t), L_j(t - \tau)\rho_S(t)] G_{ij}(\tau) - [L_i(t), \rho_S(t)L_j(t - \tau)] G_{ji}(-\tau) \right).$$ \hspace{1cm} (2.22)
2.2. Quantum Master Equation Approaches

In the literature, (2.22) is sometimes called the second-order perturbative time-convolutionless equation (TL2). If the bath energy level is continuous and infinite, one can expect the correlation function $G(\tau)$ to decay in time. We denote the bath correlation time $\tau_B$ as the decay time scale. The Markov approximation is usually justified by assuming that $t \gg \tau_B$. The TL2 seems like a further approximation of TC2. However, one can show that (2.22) is actually the second order correction to the time convolutionless form of the NZME. They should be at the same level of accuracy since they are both the second-order perturbations of the original master equation. The details can be found in [142].

Although the TL2 does not include the time convolution integral, it is still not a completely Markovian equation since the integral is over a particular time span $\tau \in \{0, t\}$. To transform it to a completely Markovian form, we put the upper limit of the integral from $t$ to $\infty$. The reasoning is still based on the assumption that $G(\tau)$ decays in time and $t \gg \tau_B$. The result is the Redfield equation:

$$\frac{d}{dt} \rho_S(t) = -\int_0^\infty d\tau \left( [L_i(t), L_j(t - \tau)\rho_S(t)]G_{ij}(\tau) - [L_i(t), \rho_S(t)\rho_j(t - \tau)]G_{ji}(\tau) \right). \quad (2.23)$$

One thing we need to comment on here is that (2.23) is a time local Markov master equation but not in Lindblad form, which means the resulting density matrix can be non-physical. One can easily verify that the Redfield equation preserves the trace as well as the Hermicity of the reduced density matrix. But it does not preserve the positivity. One has to be careful about the possible resulting negative density matrix.

To transform the equation into the Lindblad form, we need to perform a secular approximation. We project the equation onto the eigenstates of $H_0$ denoted as $|s\rangle$ such that $H_0|s\rangle = E_s|s\rangle$. In this case,

$$\frac{d}{dt}[\rho_S(t)]_{ss'} = \sum_{pp'} K_{ss'pp'}(t)[\rho_S(t)]_{pp'} \quad (2.24)$$

with

$$K_{ss'pp'}(t) = e^{-iE_{ss'}t} \sum_k \left( \delta_{s'p} \Gamma_{kkp}^+ + \delta_{sp} \Gamma_{kksp}^- \right) - \Gamma_{ps'p}^+ - \Gamma_{ss'p}^- \quad (2.25)$$
where
\[
\Gamma_{ss'pp'}^{+} = \sum_{ij} \langle s|L_i|s'\rangle \langle p|L_j|p'\rangle \int_{0}^{\infty} d\tau e^{i(E_p^{'}-E_p)\tau} G_{ij}(\tau),
\]
(2.26)

\[
\Delta E_{ss'pp'} = E_s - E_{s'} + E_p - E_{p'}
\]
(2.27)

and \(\Gamma_{ss'pp'}^{-} = (\Gamma_{p'ps}s')^*\). We define the intrinsic dynamic time scale of the central system as \(\tau_S \propto \frac{|E_s - E_{s'}|}{E_s - E_{s'}}\). If \(\tau_S \ll t\), we may neglect the fast oscillatory terms when \(E_s - E_{s'} \neq 0\) since these terms oscillate rapidly during an appreciable time scale. In quantum optics this is also called the Rotating Wave approximation. If we only include terms where \(\Delta E_{ss'pp'} = 0\), the right hand side does not depend on time explicitly and it can be easily rewritten into a form which is consistent with Fermi’s Golden Rule:

\[
\frac{d}{dt}[\rho_S(t)] = \sum_{\omega} \sum_{ij} \Gamma_{ij}(\omega) (L_i(\omega)\rho_S(t)L_j(\omega) - (L_i(\omega)L_j(\omega)\rho_S(t))) + h.c,
\]
(2.28)

where the operator \(L_i\) is defined as

\[
L_i(\omega)_{ss'} = \sum_{E_s - E_{s'}=\omega} \langle s|L_i|s'\rangle
\]
(2.29)

and

\[
\Gamma_{ij}(\omega) = \int_{0}^{\infty} d\tau e^{i\omega\tau} G_{ij}(\tau)
\]
(2.30)

Now (2.28) is a Markov master equation. We can diagonalize the matrix \(\Gamma_{ij}\) to transform this equation into the standard Lindblad form [142].

**Summary**: We have three typical time scales in the system: the time scale of the intrinsic dynamics of the central system \(\tau_S\), the bath correlation time \(\tau_B\) and the appreciable time span \(t\). \(t\) is usually replaced by the so-called bath relaxation time \(\tau_R\), which represents the time scale of the bath system interactions.

To simplify the NZME (2.14) to get a time-local Markov master equation (2.28), we assume: i) The product initial state \(\rho(0) = \rho_S(0) \otimes \rho_B\); ii) A weak interaction between the bath and the system so as to make a 2nd order perturbation to get both TL2 (2.22) and TC2 (2.20); iii) The Born-Markov approximation by sending the the integral limit to \(\infty\); iv) A secular approximation to eliminate the fast oscillatory terms.

The first and second steps both depend on the weak interaction assumption and the first term also requires that the bath and the system be prepared
separately as well as $\tau_S \gg \tau_B$. The third step rely on the assumption that $G_{ij}(\tau)$ decays in time, and that the decay rate $\tau_B \ll \tau_R$. However, it is only well-defined if the bath is infinitely large and its energy levels contains a continuum. However, in an ideal non-interacting spin bath model, the bath energy levels are discretized and their numbers are finite. As a result, the bath is pseudo-periodic in time and the Poincaré recurrence time is always finite which means the definition of $\tau_B$ can be pathological. In the last step, the secular approximation requires $\tau_S \ll \tau_R$ to allow us to ignore fast oscillatory components in the master equation.

We notice that this whole process imposes a strong restriction on the applicable systems: a infinitely large bath with continuous energy levels, a hierarchy of time scales $\tau_B \ll \tau_S \ll \tau_R$, as well as the weak interactions. There are tons of literature working on different forms of Redfield equations (2.20), (2.22), (2.28), trying to compare the accuracy of the aforementioned approximations (for example [30] [143]). However, most of them are only tweaking the relevant size between these three time scales but not touching anything else in the model. For example, the hierarchy equation of motion technique developed by Ishizaki and Tanimura [30][76][75] is an exact method for such systems. But it has a even stronger restriction on the bath model: not only has it to obey all previous restrictions, but the bath spectral function also has to be the particular Drude form $J(\omega) \propto \frac{\gamma^2 \omega}{\omega^2 + \gamma^2}$. This bath itself exhibits Markov properties and therefore it is not a surprise that one can write the final hierarchy equation of motion in time local fashion. Unfortunately, most system in the real world do not falls into this exact category. Just as we reviewed in the first chapter, there are all kinds of different environmental modes, which requires us to employ different techniques. In most systems, the three time scales $\tau_B, \tau_S, \tau_R$ might not be easily defined. For example, in spin systems, although the spin-lattice relaxation time $t_1$ is analogous to the $\tau_R$ in damped oscillators, the spin-spin relaxation time $t_2$ has a different microscopic origin and does not have any analogous in oscillator baths. Writing every model into the Redfield master equation actually homogenizes the difference between systems and it might lead to artificial results. In the next subsection, we would like to show how disastrous this can be when we blindly apply the master equation to every open quantum systems.

2.2.2 Example: Central Spin Model

To see the limitation of the approaches of master equations, we are going to use the central spin model as a simple example. It will be shown how
2.2. Quantum Master Equation Approaches

Master equation approaches lead to unphysical results. The simplest case of the central spin model can be written as

\[ H = \sum_{k} g_{k} \sigma_{k}^{z} \tau^{z}, \]

where \( \tau \) is the central spin and the \( \sigma_{k}s \) are the operators of environmental spins. There is no dynamics either for the bath or for the central spin. This model can be solved exactly, therefore it is useful for us to compare results from different methods.

**Exact Result** Assume that the initial state of the system is

\[ |\psi(0)\rangle = (a|\uparrow\rangle + b|\downarrow\rangle) \otimes_{k=1}^{N} (\alpha_{k}|\uparrow_{k}\rangle + \beta_{k}|\downarrow_{k}\rangle). \]

It is easy to show that the reduced density matrix is then

\[ \rho(t) = \begin{pmatrix} |a|^{2} & a^{*}b\kappa(t) \\ ab^{*}\kappa^{*}(t) & |b|^{2} \end{pmatrix}. \]

We can see that the system has no dissipation– the diagonal elements do not change in time. The off-diagonal elements of the reduced density matrix are tuned by a decoherence factor

\[ \kappa(t) = \prod_{k=1}^{N} (|\alpha_{k}|^{2}e^{-ig_{k}t} + |\beta_{k}|^{2}e^{ig_{k}t}). \]

Since \(|\alpha_{k}|^{2} + |\beta_{k}|^{2} = 1\), we can write

\[ \kappa(t) = \prod_{k=1}^{N} \left( \cos g_{k}t + i\sin g_{k}t(\alpha_{k}^{2} - \beta_{k}^{2}) \right). \]

It can be shown that in the large \( N \) limit, this factor can be approximated as a Gaussian decay, i.e.

\[ \kappa(t) \approx e^{iBt}e^{-s_{N}^{2}t^{2}/2}, \]

where

\[ B = \sum_{k} g_{k}(|\alpha_{k}|^{2} - |\beta_{k}|^{2}) \]

\[ s_{N}^{2} = \sum_{k} 4g_{k}^{2}(|\alpha_{k}|^{2} - |\beta_{k}|^{2}). \]

This derivation can be found in [144]. It can also be easily seen by using the central limit theorem: without dynamics, the spins now act on the central spin as a random field, and if the number is large enough the distribution of the field is always Gaussian.
2.2. Quantum Master Equation Approaches

**Master equation: Born Approximation** Actually in this simple case, TL2 and TC2 are the same. We can simply write the equation of motion as

\[
\frac{d}{dt}\rho = -\int_0^t ds \sum_{k \neq k'} 2g_k g_{k'} (|\alpha_k|^2 - |\beta_k|^2)(|\alpha_{k'}|^2 - |\beta_{k'}|^2)(\rho - \tau^z \rho \tau^z). \tag{2.39}
\]

Since

\[
\rho - \tau^z \rho \tau^z = \begin{pmatrix} 0 & 2\rho_{10} \\ 2\rho_{01} & 0 \end{pmatrix}, \tag{2.40}
\]

the diagonal matrix elements do not change. But the evolution of the off-diagonal element satisfies

\[
\frac{d}{dt}\rho_{10} = -\sum_{k \neq k'} 4g_k g_{k'} (|\alpha_k|^2 - |\beta_k|^2)(|\alpha_{k'}|^2 - |\beta_{k'}|^2) t \rho_{10}. \tag{2.41}
\]

Its solution has an exponential decay:

\[
\rho_{10}(t) = \rho_{10}(0) e^{-\lambda_R t^2}, \tag{2.42}
\]

with the decoherence factor

\[
\lambda_R = \sum_{k \neq k'} 2g_k g_{k'} (|\alpha_k|^2 - |\beta_k|^2)(|\alpha_{k'}|^2 - |\beta_{k'}|^2). \tag{2.43}
\]

Although this correctly recovers the Gaussian decay of the exact result \((2.36)\), the decay rate \(\lambda_R\) is not correct. Actually, the master equation approach only captures this lowest order information and discards the rest: the first order perturbation over coupling strength \(g_k\) for the decay rate \(r(t) = \prod_{k=1}^N (\cos g_k t + i \sin g_k t(|\alpha_k|^2 - |\beta_k|^2))\) is proportional to \(g_k(|\alpha_k|^2 - |\beta_k|^2)\).

One might argue that since there is no dynamics of the central spin, the Redfield equation, which is only valid in the weak interaction region, can certainly fail in this region. However, even when we add the dynamics to the central spin, i.e. set the field \(\hbar\) non-zero, the factor \(\lambda_R\) does not change. The Born approximation always leads to the following coefficient

\[
tr_B[\sum_k \sigma_k^z \sum_{k'} \sigma_{k'}^z \rho_B] = \sum_{k \neq k'} 2g_k g_{k'} (|\alpha_k|^2 - |\beta_k|^2)(|\alpha_{k'}|^2 - |\beta_{k'}|^2). \tag{2.44}
\]

We can also see that for finite \(N\), the exact result is a pseudo-periodic function in time. But in the master equation approach, in this case, the TC formalism of Redfield equations always gives Gaussian decay and the time-local Lindblad form always gives exponential decay. These are the intrinsic
properties embedded in these methods: as long as your central system is a two-level system one always gets such behavior, regardless of the nature of the problem. Therefore, we cannot apply the master equation approach to any open quantum systems without looking at the detailed structures of their environments.

In the next part, we would like to introduce another approach to the open quantum system: the path integral formalism, which we are going to use later in this thesis. In contrast to the Markovian master equation approaches, it preserves the memory effect explicitly and allows us to do the perturbation with different parameters. We can see later that it can be useful in certain models.

### 2.3 Path Integral Formalism

The path integral was developed by Feynman in 1948 [145]. The idea is to generalize the action principle in classical mechanics and write the evolution operator of a quantum state as a functional integral over all possible paths for the classic actions. The path-integral approach has been proved to be equivalent to the other forms of quantum mechanics and quantum field theory.

In this section, we are going to introduce path integral method using the Feynman and Vernon formalism[14]. We again assume the Hamiltonian for a central system couples to the bath as

\[
H = H_0(x) + H_B(q) + H_I(x, q).
\]  

where the subscripts \( f, i \) indicate final and initial states respectively. The time evolution of the whole system’s density matrix \( \rho \) can be written as

\[
\rho(x_f, q_f; x'_f, q'_f) = \int dq_i dq'_i dx_i dx'_i \rho(x_i, q_i; x'_i, q'_i) 
\times J(x_f, q_f; x'_f, q'_f; t; x_i, q_i; x'_i, q'_i, 0),
\]

where the subscripts \( f, i \) indicate final and initial states respectively. The
2.3. Path Integral Formalism

integration kernel can be written as

\[
J(x_f, q_f; x'_f, q'_f; x_i, q_i x'_i, q'_i, 0) = \int_{q(0) = q_i}^{q(t) = q_f} Dq \int_{q'(0) = q'_i}^{q'(t) = q'_f} Dq' \int_{x(0) = x_i}^{x(t) = x_f} Dx \int_{x'(0) = x'_i}^{x'(t) = x'_f} Dx' \\
\cdot \exp\left\{ \frac{i}{\hbar} (S[x, q] - S[x', q']) \right\},
\]

(2.47)

where \( Dx \) means functional integration for all possible paths \( x \) from time 0 to \( t \). \( S \) is the action corresponds to the total Hamiltonian \( H \). Similarly we could write it as

\[
S[x, q] = S_0[x] + S_B[q] + S_I[x, q].
\]

(2.48)

Suppose that the density operator of the global system at the initial time \( t = 0 \) is in product form, i.e.

\[
\rho(0) = \rho_S(0) \otimes \rho_B(0).
\]

(2.49)

We can take a partial trace over \( B \) in equation (2.46) and get

\[
\rho_S(x_f, x'_f; t) = \int dx_i dx'_i \int_{q(0) = q_i}^{q(t) = q_f} Dq \int_{x(0) = x_i}^{x(t) = x_f} Dx \int_{x'(0) = x'_i}^{x'(t) = x'_f} Dx' \\
\cdot \exp\left\{ \frac{i}{\hbar} (S_0[x] - S_0[x']) \right\} \mathcal{F}[x(t), x'(t)] \rho_S(x_i, x'_i; 0),
\]

(2.50)

with the kernel

\[
\mathcal{F}[x(t), x'(t)] = \int dq_f dq_i dq'_i \int_{q(0) = q_i}^{q(t) = q_f} Dq \int_{q'(0) = q'_i}^{q'(t) = q'_f} Dq' \\
\cdot \exp\left\{ \frac{i}{\hbar} \left[ S_B[q] + S_I[q, x] - S_B[q'] - S_I[q', x'] \right] \right\} \rho_B(q, q'; 0)
\]

(2.51)

Since we take a trace over system \( B \), the final state of \( B \) should be the same \( q_f \) for both \( q(t) \) and \( q'(t) \). This method is called the influence functional method and \( \mathcal{F}[x(t), x'(t)] \) is the so-called “influence functional”. Notice that since \( q'(t) = q(t) = q_f \), the integral over \( q_f \) is actually equivalent to the partial trace over all bath states. Although we still use the product initial state condition \( \rho(0) = \rho_S(0) \otimes \rho_B(0) \), it is actually not necessary. We use it mainly for simplicity. One can write down the influence functional for a general initial state: absorb the term \( \rho_S(x_i, x'_i; 0) \) into \( \mathcal{F}[x(t), x'(t)] \) in (2.50) and replace the \( \rho_B(q, q'; 0) \) in (2.51) with \( \rho(x_i, x'_i; q, q'; 0) \).
Path integral and Master equation approaches

The influence functional $F[x(t), x'(t)]$ is a functional over the path $x(t), x'(t)$. It does not only depend on the initial and the end point of the path $x(t)$ but also on the positions at any time between them. For a superoperator $K(t, t')$ which is defined as $\rho(t) = K(t, t')\rho(t')$, this situation means that the quantum semi-group assumption does not hold:

$$K(t, 0) \neq K(t, t')K(t', 0); \quad 0 < t' < t. \quad (2.52)$$

In other words, we cannot write it as a Markovian time local master equation. But one can still derive master equations (or quantum Fokker-Planck equations) from the path integral formalism under certain conditions. We can take a simple example to see how this is achieved. Consider a 1-D free particle with a friction term caused by the environment. We have its action:

$$S_0[x] = \int_0^t d\tau \left( \frac{1}{2} M \dot{x}^2(\tau) \right), \quad (2.53)$$

and the influence functional with pure friction:

$$F[x(t), x'(t)] = \frac{1}{A} \exp \left[ -\int_0^t d\tau \gamma (x(\tau) - x'(\tau))^2 \right]. \quad (2.54)$$

For a short interval of time $(t, t+\epsilon)$, we can assume that $\int_t^{t+\epsilon} f(\tau)d\tau \approx f(t)\epsilon$ and $\dot{x} = \frac{x(t+\epsilon)-x(t)}{\epsilon}$, and also eliminate the functional integral

$$\int d\Delta x' \int_{x(t)=x}^{x(t+\epsilon)=x'} Dx \rightarrow \int d\Delta x. \quad (2.55)$$

Then we can write the simplified path integral in this period of time as

$$\rho_S(x, x'; t+\epsilon) \approx \frac{1}{A} \int d\Delta x d\Delta x' \exp \left[ \frac{i}{\epsilon} \frac{1}{2} M \left( \frac{\Delta x}{\epsilon} \right)^2 - i \frac{1}{2} M \left( \frac{\Delta x'}{\epsilon} \right)^2 \right]$$

$$\cdot e^{-\epsilon\gamma (x-x'^2)} \rho_S(x-\Delta x, x'-\Delta x'; t)$$

$$\approx \frac{1}{A} \int d\Delta x d\Delta x' \exp \left[ \frac{iM}{2\epsilon} \Delta x^2 - \frac{iM}{2\epsilon} \Delta x'^2 \right] \left[ 1 - \epsilon\gamma (x-x')^2 \right]$$

$$\cdot \left[ \rho_S(t) - \frac{\partial \rho}{\partial x} \Delta x - \frac{\partial \rho}{\partial x'} \Delta x' + \frac{\partial^2 \rho}{\partial x^2} \Delta x^2 + \frac{\partial^2 \rho}{\partial x'^2} \Delta x'^2 + \frac{\partial^2 \rho}{\partial x \partial x'} \Delta x \Delta x' \right]. \quad (2.56)$$
2.3. Path Integral Formalism

The integral is of the Fresnel type and the dominant term comes from \( \exp \left( \frac{iM}{2}\Delta x^2 - \frac{iM}{2}\Delta x'^2 \right) \), which shows that \( \Delta x \) is on the order of \( \epsilon^{1/2} \). Therefore, we can expand the path integral in order of \( \epsilon \). The zeroth order terms are only \( \exp \left( \frac{iM}{2}\Delta x^2 - \frac{iM}{2}\Delta x'^2 \right) \), which gives the renormalization factor

\[
A = \frac{2\pi\epsilon}{M}.
\]  

The first order of \( \epsilon \) gives the equation

\[
\frac{d\rho_S}{dt} = \rho_S(t + \epsilon) - \rho_S(t) = -\frac{i}{2M} \frac{\partial^2 \rho_S}{\partial x^2} + \frac{i}{2M} \frac{\partial^2 \rho_S}{\partial x'^2} - \frac{\gamma}{2} (x - x')^2 \rho_S,
\]  

(2.58)

which can be written in the operator form of (2.28):

\[
\frac{d\rho_S}{dt} = -i[H_0, \rho_S] - \gamma [x, [x, \rho_S]].
\]  

(2.59)

We can introduce the Wigner distribution

\[
W(x, p) = \frac{1}{2\pi} \int dy e^{ipy} \langle x + y/2 | \rho_S | x - y/2 \rangle
\]  

(2.60)

to write (2.59) as the quantum Fokker Planck equation

\[
\frac{dW}{dt} = \frac{d}{dx} pW + \gamma \frac{d^2W}{dp^2}.
\]  

(2.61)

By assuming a proper type of influence functional \( F \), we can actually write the path integral as a Gaussian time local master equation. However, this procedure is only valid for a Ohmic oscillator bath at high temperature\[146\], in which case one can get the Markov influence functional kernel \( F \). The HEOM mentioned in the previous chapter can also be derived from the path integral formalism by assuming a Drude-Lorentz form spectrum, which can be used to acquire a Markov influence functional kernel which is proportional to \( e^{-\gamma t} \) \[147\]. In the path integral approach, the Markov approximation can be applied by choosing a specific form of bath spectrum.

Summary

Formally, equation (2.50) gives the exact time evolution of the reduced density matrix of the central system. Unfortunately, just as in the exact NZME, in most cases it is very difficult to calculate. We can only do the functional integration analytically for a limited class of Hamiltonians. One of the most extensively studied Hamiltonian is a harmonic oscillator bath coupled linearly to the central system. In this case the integrals are
2.4 Decoherence and False Decoherence

The standard technique to determine the decoherence is to look at the reduced density matrix, in which one has traced out the environmental variables in an open quantum system. If the state changes from a pure state to a mixed state one argues that the system has lost quantum coherence, and quantum interference effects are suppressed. In most experiments, there is no good measure to quantify the coherence for a general mixed state. Decoherence is usually referred as the decreasing of the off-diagonal elements. However this criterion is vague and sometimes too strong.

In this section we again use a central spin model coupled to different baths as an example. By choosing different bath structures and adiabatically coupling/decoupling the system from the bath, we study the “decoherence” phenomenon in detail. We can see that in some instances the information of the quantum coherence is not truly lost with apparent decreasing of off-diagonal elements. We claim that the decoherence is a more subtle subject and that people might be misled by the so-called “False Decoherence”.

2.4.1 Central Spin Couples to a Spin Chain

The environment is modeled as a 1-D spin chain $\{\sigma_i\}$ and our central system is a single spin $\tau$. All Gaussian and can be solved analytically. It can be mapped into a master equation or a Fokker-Planck equation by assuming a Markov spectral function for the bath, which is equivalent to doing the Born-Markov approximation in the previous section. The influence functional method is often used with a continuous Hilbert space to take advantage of continuous dynamical variables. The discretized model, both for the central system and the bath, are barely touched in the literature. In this dissertation, we are going to use the path integral method for discretized models extensively in Chapter 3. Although we cannot get a closed form for a single spin if it is exposed to a time-dependent field, we can still make approximations for the influence functional under certain limits. In Section 4 we are going to use the general continuous path integral formalism to deal with two-phonon interactions.
2.4. Decoherence and False Decoherence

Model 1

The first case we are considering for the environment is a spin chain with Hamiltonian

\[ H = J \tau^y \sigma^y_0 + V \sum_{i=0}^{N-1} \sigma^z_i \sigma^z_{i+1}, \]  

(2.62)

where \( \tau^y \) is the central spin operator and the \( \{ \sigma_i \} \) are operators for \( N \) bath spins; \( J \) is the coupling and \( NV \) is the band width of the bath spins. We do NOT use the periodic boundary condition here. Similar to the central spin model in 2.2.2, we have the reduced density matrix

\[
\begin{pmatrix}
|a|^2 & a^* b \kappa(t) \\
ab^* \kappa^*(t) & |b|^2
\end{pmatrix}.
\]  

Again, we can see that since the total Hamiltonian commutes with the central spin operator \( \tau^y \), the diagonal component (represented in \( \tau^y \) eigenstates) of the reduced density matrix does not change in time. Only the off-diagonal components \( \rho_{12}(t) \) and \( \rho_{21}(t) \) might decay in time. Also, we have

\[ \rho_{12}(t) = \kappa(t) \rho_{12}(0), \]  

(2.64)

with \( \kappa(t) \) being the “decoherence factor”

\[ \kappa = \text{tr}_b \left( e^{-iH+b} \rho_b e^{-iH-b} \right), \]  

(2.65)
2.4. Decoherence and False Decoherence

where $H^\pm$ are the block Hamiltonians in the $\tau^y = \pm 1$ subspaces respectively.

$$H^+ = J\sigma^y_0 + V \sum_{i=0}^{N-1} \sigma^z_i \sigma^z_{i+1}$$

(2.66)

$$H^- = -J\sigma^y_0 + V \sum_{i=0}^{N-1} \sigma^z_i \sigma^z_{i+1}.$$  

(2.67)

This model can be solved exactly. The result is

$$\kappa(t) = \frac{V^2 + J^2 \cos 2\sqrt{1 + J^2/V^2}t}{V^2 + J^2} = 1 - \frac{2J^2 \sin^2 \sqrt{1 + J^2/V^2}t}{V^2 + J^2}.$$  

(2.68)

But for convenience for the next model, we introduce the Jordan-Wigner transformation to diagonalize this Hamiltonian:

$$\sigma^z_i = -\prod_{j<i}(1 - 2c_j^\dagger c_j)(c_i^\dagger + c_i),$$  

(2.69)

$$\sigma^x_i = 1 - 2c_i^\dagger c_i,$$  

(2.70)

$$\sigma^y_i = i\prod_{j<i}(1 - 2c_j^\dagger c_j)(c_i^\dagger - c_i).$$  

(2.71)

Substituting this back to the Hamiltonian (2.62) gives

$$H = iJ\tau^y(c_0^\dagger - c_0) + V \sum_{i=0}^{N-1} (c_i^\dagger c_{i+1}^\dagger - c_i c_{i+1} + c_i^\dagger c_{i+1} - c_i c_{i+1}).$$  

(2.72)

We can make Fourier transforms:

$$c_{kn} = \frac{1}{\sqrt{N}} \sum_j c_j e^{ijk_n}$$  

(2.73)

$$c_{kn}^\dagger = \frac{1}{\sqrt{N}} \sum_j c_j^\dagger e^{-ijk_n}; \ k_n = \frac{2\pi n}{N}$$  

(2.74)

$$k_n = \frac{2\pi n}{N}.$$  

(2.75)

as well as a Bogoliubov transformation:

$$\gamma_{kn} = e^{-i\frac{kn}{2}} \left( \cos \frac{k_n}{2} c_{kn} - i \sin \frac{k_n}{2} c_{kn}^\dagger \right),$$  

(2.76)

$$c_{kn} = \cos \frac{k_n}{2} e^{i\frac{kn}{2} \gamma_{kn}} + i \sin \frac{k_n}{2} e^{i\frac{kn}{2} \gamma_{kn}^\dagger}.$$  

(2.77)
2.4. Decoherence and False Decoherence

The resulting Hamiltonian is

\[
H = \sum_n \left( V(2\gamma_k^\dagger \gamma_n - 1) + \frac{iJ}{\sqrt{N}} \tau^y (\gamma_k^\dagger - \gamma_n) \right)
\]

\[
= \sum_n H_n, \tag{2.78}
\]

with \( H_n = V(2\gamma_k^\dagger \gamma_n - 1) + \frac{iJ}{\sqrt{N}} \tau^y (\gamma_k^\dagger - \gamma_n). \) It looks block-diagonal but it actually is not. The problem here is that the individual Hamiltonians \( H_n \) do not commute with each other, i.e.

\[
[H_n, H_n'] = -\frac{2J^2}{N}(\gamma_k^\dagger - \gamma_n)(\gamma_{k'}^\dagger - \gamma_n). \tag{2.79}
\]

It can be shown that for the weak interaction limit \( J/\sqrt{NV} \ll 1 \), the commutators between \( H_n \) can be neglected as they are higher order in \( O(J^2/NV^2) \). The details can be found in Appendix A. If we ignore the commutators in (2.79), the Hamiltonian (2.78) becomes block diagonal. In each \( \{\gamma_k^\dagger, \gamma_n\} \) subspace, we have that

\[
H_n(\tau^y = +1) = \begin{pmatrix} 1 & \frac{iJ}{\sqrt{NV}} \\ -\frac{iJ}{\sqrt{NV}} & -1 \end{pmatrix}
\]

\[
H_n(\tau^y = -1) = \begin{pmatrix} 1 & -\frac{iJ}{\sqrt{NV}} \\ \frac{iJ}{\sqrt{NV}} & -1 \end{pmatrix}. \tag{2.80}
\]

We assume the bath is in a fully mixed state \( \rho_b = \frac{1}{2} I \). It is then straightforward to calculate the decoherence factor \( \kappa(t) \) as

\[
\kappa = 1 - 2 \sin^2 \left( \sqrt{1 + \frac{J^2}{NV^2} t} \right) \frac{J^2}{NV^2 + J^2}
\]

\[
\approx 1 - 2 \sin^2 t \frac{J^2}{NV^2}. \tag{2.82}
\]

For the \( N \to \infty \) limit, we have the total decoherence factor as

\[
\kappa = \lim_{N \to \infty} \left( 1 - 2 \sin^2 t \frac{J^2}{NV^2} \right)^N = e^{-2J^2 \sin^2 t/V^2}. \tag{2.83}
\]

We can see that \( \kappa \) gives the correct result compared with the exact result (2.68) up to order \( J^2/V^2 \).
2.4. Decoherence and False Decoherence

As we can see from both results, $\kappa$ is periodic in time, which means it will come back to its initial state without real loss of coherence in time (see Fig. 2.2). There is no real decoherence happening in this model if you are given sufficient time for observation. Although in practice, you might observe the initial drop of the off-diagonal elements and apparently, “decoherence”.

![Graph showing periodic nature of $\kappa(t)$](image)

Figure 2.2: Decoherence factor $\kappa(t)$ (2.83) of model 1 as a function of time. There is no real decoherence and $\kappa$ goes back to 1 periodically.

Model 2

The last model is rather simple and in fact, equivalent to a two-spin model. But the method we develop is useful. In this part, we change the structure of the bath spins to

$$H = J y \sigma_0^y + V \sum_{i=0}^{N-1} (\sigma_i^+ \sigma_{i+1}^- + h.c.).$$

(2.84)

The trick we introduced in the last subsection is used here to transform the Hamiltonian into

$$H = \sum_n \left( 2V \cos k_n (\gamma_{k_n}^\dagger \gamma_{k_n} - \frac{1}{2}) - \frac{iJ}{\sqrt{N}} y (\gamma_{k_n}^\dagger - \gamma_{k_n}) \right).$$

(2.85)

It has the same structure as (2.78), except that now the spectrum is $\cos k_n V$ instead of a constant. Unfortunately, there is no exact result for this model. But we can follow the approximate procedure in the previous section to get
the decoherence factor up to order $J^2$:

$$
\frac{1}{2} \text{tr} \left( e^{-iH_n t} e^{-iH_n^\dagger t} \right) = 1 - \frac{2\sin^2 \sqrt{V^2 \cos^2 k_n + \frac{J^2}{NV^2} t}}{\cos^2 k_n + \frac{J^2}{NV^2}} \cdot \frac{J^2}{NV^2} \\
\approx 1 - \frac{2\sin^2 (Vt \cos k_n) J^2}{NV^2 \cos^2 k_n}; \quad (N \to \infty) \quad (2.86)
$$

After including all the $H_n$'s, we have

$$
\kappa(t) = \exp \left( - \sum_n \frac{2\sin^2 (Vt \cos k_n) J^2}{NV^2 \cos^2 k_n} \right) \\
\approx \exp \left( - \frac{J^2}{\pi V^2} \int_{-\pi}^{\pi} \frac{dk}{2\pi} \frac{\sin^2(Vt \cos k)}{\cos^2 k} \right); \quad (N \to \infty) \quad (2.87)
$$

$$
= \exp \left( -2J^2 t^2 {}_1 F_2 \left( \frac{1}{2}; \frac{3}{2}; -V^2 t^2 \right) \right).
$$

The behaviour of $\kappa(t)$ is illustrated in Fig. 2.3 Its long time asymptotic behaviour can still be studied. When $t \to \infty$, we can expand the generalized hypergeometric function as

$$
(Vt)^2 {}_1 F_2 \left( \frac{1}{2}; \frac{3}{2}; -V^2 t^2 \right) = Vt + \frac{1}{2} \sqrt{\frac{1}{\pi Vt}} \cos \left( 2Vt - \frac{\pi}{4} \right) + O \left( \frac{1}{(Vt)^{\frac{3}{2}}} \right). \quad (2.88)
$$

Therefore, $\kappa \to e^{-J^2 t/V} \to 0$ as $t \to \infty$. We can see now in this model the system is completely decohered and different from our previous case; it never goes back to its initial condition. In model 2, the quantum information is truely lost into the environment. We can see the main difference now is that the eigenstates of the bath spins are spin waves. The “information” is propagating through the whole spin chain and if the chain is long enough, it never feeds back to the central system.
2.4. Decoherence and False Decoherence

Figure 2.3: This is the decoherence factor of model 2 as a function of time. The loss of coherence is clear over time.

Adiabatic Decoupling

Now we still consider the same system, but make the coupling between the central system and the bath vary in time:

\[ H = J(t) \gamma \sigma^y_0 + H_{bath}, \] (2.89)

where \( J(t) \) is the time-varying coupling with \( J \to J_0 \) as \( t \to -\infty \) and \( J \to 0 \) as \( t \to \infty \). We choose our \( J(t) \) as

\[ J(t) = \frac{J_0}{e^{kt} + 1}. \] (2.90)
2.4. Decoherence and False Decoherence

Figure 2.4: Figure of the coupling $J(t)$ over time. These lines represent $k = 0, 0.5, 1, 10$ respectively.

Therefore, $\frac{d}{dt} J(t) = -J_0 k e^{kt}/(e^{kt} + 1)^2$. When $k \to 0$, $\frac{d}{dt} H_0 \propto \frac{d}{dt} J(t)$ will go to zero; when $k \to \infty$, it will become a Heaviside step function with a jump at $t = 0$ (see Fig. 2.4). Therefore, the $k = 0$ limit means that we adiabatically decouple the system from the bath. Meanwhile the $k \to \infty$ limit refers to the sudden turn-off of the coupling. For this sudden decoupling case, the result should be the same as what we get from previous sections since the central system stops evolving after the turn-off. But for the adiabatic decoupling case, it is more complicated.

With time dependent coupling $J(t)$, we can still follow the same procedure to transform the Hamiltonian to

$$H = \sum_n 2E_n (\gamma_n \dagger \gamma_n - \frac{1}{2}) + \sum \frac{i J(t)}{\sqrt{N}} (\gamma_n \dagger - \gamma_n),$$  \hspace{1cm} (2.91)

where $E_n = V$ for our first model and $E_n = V \cos k_n$ for our second model. Then

$$H_n^\pm = \begin{pmatrix} 2E_n & \mp \frac{i J(t)}{\sqrt{N}} \\ \pm \frac{i J(t)}{\sqrt{N}} & 0 \end{pmatrix}.$$  \hspace{1cm} (2.92)

Our goal is to solve this Hamiltonian in each $\{\gamma_n \dagger |0\rangle, |0\rangle\}$ subspace. A vector $(a(t), b(t))$ in this subspace evolves as

$$-i \left(\frac{d}{dt} a(t) \right) = \begin{pmatrix} 2E_n & \mp \frac{i J(t)}{\sqrt{N}} \\ \pm \frac{i J(t)}{\sqrt{N}} & 0 \end{pmatrix} \begin{pmatrix} a(t) \\ b(t) \end{pmatrix}.$$  \hspace{1cm} (2.93)
2.4. Decoherence and False Decoherence

It can be rewritten as

\[ a(t) = \mp \frac{\sqrt{N}}{J(t)} b(t), \tag{2.94} \]

\[ \ddot{b}(t) - (iE_n + \frac{J(t)}{J(t)}) \dot{b}(t) + \frac{J^2(t)}{N} b(t) = 0. \tag{2.95} \]

The derivation is lengthy, and can be found in Appendix A. At the end, we can find for the long time asymptotic limit \( t \to \infty \) of the decoherence factor:

\[ \kappa(t) = \prod_n (1 - \frac{2J^2}{NE_n^2}). \tag{2.96} \]

For our first bath model, \( H_{bath} = V \sum_{i=0}^{N-1} \sigma_i^z \sigma_{i+1}^z, E_n = V \) for all subspaces. Then the decoherence factor is

\[ \kappa_1(t) = (1 - \frac{2J^2}{NE_n^2})^N = e^{-2J_0^2}. \tag{2.97} \]

For our second bath structure \( H_{bath} = V \sum_{i=0}^{N-1} (\sigma_i^+ \sigma_{i+1}^- + h.c.), E_n = V \cos k_n \) for each subspaces. The decoherence factor is

\[ \kappa_2(t) = e^{-\frac{1}{\sqrt{2}} \int_0^{2\pi} \frac{J^2}{V^2 \cos^2 k} \to 0}. \tag{2.98} \]

So we find “partial decoherence” for model 1 (\( \kappa \to e^{-2J^2} \)) and “complete decoherence” for model 2 (\( \kappa \to 0 \)) in the adiabatically decoupled limit. Apparently, the system would end up in a mixed state and the coherence is eventually lost. But we can still ask the question: is the information truly lost? Or equivalently, is this real decoherence?

To see this, we should reverse the system back to its original condition, by further looking at a general slow-varying \( J(t) \). In this case (2.95) still holds.

i) For our first model, \( E_n = V \). If the coupling is varying slowly, \( J(t) \ll J(t)E_n \), we can safely neglect the \( \dot{J}(t) \) term in (2.95) and have

\[
\begin{align*}
    b(t) &= C_1 e^{-iVt/2 - iVt/2 \sqrt{1 + \frac{4J^2(t)}{NV^2}}} + C_2 e^{-iVt/2 + iVt/2 \sqrt{1 + \frac{4J^2(t)}{NV^2}}} ,
    \\
    a(t) &= -i2C_1 \sqrt{N} \frac{J(t)}{J(t)} (V + V \sqrt{1 + \frac{4J^2(t)}{NV^2}}) e^{-iVt/2 - iVt/2 \sqrt{1 + \frac{4J^2(t)}{NV^2}}} e^{-iVt/2 + iVt/2 \sqrt{1 + \frac{4J^2(t)}{NV^2}}},
    \\
    &\quad -i2C_2 \sqrt{N} \frac{J(t)}{J(t)} (V - V \sqrt{1 + \frac{4J^2(t)}{NV^2}}) e^{-iVt/2 + iVt/2 \sqrt{1 + \frac{4J^2(t)}{NV^2}}}.
\end{align*}
\]
We can see that in this adiabatic limit, the result has no dependence on \( \dot{J}(t) \). The decoherence factor \( \kappa_1(t) \) should be solely dependent on \( J(t) \). This means that if one slowly changes the coupling strength back to its original value, \( \kappa_1(t) \) would go back to its original value regardless of the apparent loss of decoherence we obtained from (2.97). One can recover the full coherence if by decoupling the model 1 to its environment and recoupling it back adiabatically. Roughly speaking, in this case, the coherence is not truly lost from the environment. It is encoded in the bath and can be transferred back to the central system as long as the interaction recovers.

ii) For model 2, on the other hand, we cannot neglect the \( \dot{J}(t) \) term since \( E_n = V \cos k_n \) can be zero. The slow varying condition \( \dot{J}(t) \ll J(t)E_n \) breaks down for the modes in the center of the band. Actually it is easy to prove that \( \kappa(t) \) would stay at 0 after adiabatically decoupling from the environment and never come back to its initial state even if one recover the interaction. In this case, the coherence is truly lost through the modes near \( k_n \approx \frac{\pi}{2}, \frac{3\pi}{2} \).

**Discussion** From the study of these two central-spin models, we can see that decoherence is a subtle subject and cannot be easily judged by the behaviour of the off-diagonal elements during a certain period of time. For true decoherence to happen, the “information” has to be carried away by the environment, separated from the system by some mechanism so that it cannot come back into the system. In model 2, the spin wave modes with \( k_n \approx \frac{\pi}{2}, \frac{3\pi}{2} \) serve this purpose. In model 1, the apparent loss of decoherence is actually encoded in the environment and if one adiabatically restores the interaction, coherence is fully restored. This usually referred as “False Decoherence” in the literature \[71\], which was initially discussed for high frequency modes in the environment. These high frequency modes do not affect the dynamics of low energy physics, but formally can still introduce false decoherence. This suggests the importance of not making quick conclusions about the decoherence of the system, especially for these systems which strongly couple to certain localized modes in the environment.
Chapter 3

Spin Bath Model

Both oscillator and spin bath models map to many important models in physics. For example, the spin-boson model mentioned before can be mapped into the Kondo model, Sine-Gordon models, and various other 2-dimensional field theories for specific parameter values. Although for the spin bath model, similar mappings have yet to be exploited in great detail, they will obviously be very useful for, e.g. lattice spin models. Actually, as mentioned in the introduction, lattice spin models are important in understanding the role of quantum phenomena in various biological systems. Physicists need to understand the mechanisms of decoherence and quantum dissipation in nature, and the crossover to (or the “emergence of) classical behaviour from quantum physics as one increases either size, temperature T, external fields, or couplings to the environment. Such quantum-classical crossover phenomena are not only relevant to the traditional low temperature microscopic systems, but also observed in high temperature macroscopic biological systems.

The oscillator bath model as an environment has been studied extensively in the literature. Meanwhile, spin lattice models has not been studied in depth, although people have already noticed the peculiarity of spin bath dynamics (e.g.[97]). We shall see in this chapter that it is even more different if we study the decoherence of quantum walks in a general lattice.

The general model for a particle moving between a set of sites through a spin bath can be written as

\[ H = H_{band} + H_{SB}, \]

where

\[ H_{band} = \sum_{ij} [\Delta_{ij} c_i^\dagger c_j e^{iA_{ij}^o} + \sum_k (\phi_k^{ij} + \alpha_k^{ij} \sigma_k) + H.c.] \]

\[ + \sum_j (\epsilon_j + \sum_k \lambda_j^k \cdot \sigma_k) c_j^\dagger c_j, \]
3.1. The Model of a Discretized System Coupled to a Spin Bath

and

\[ H_{SB} = \sum_k h_k \cdot \sigma_k + \sum_{k,k'} V_{k,k'}^{\alpha\beta} \sigma_k^\alpha \sigma_{k'}^\beta. \]  \hspace{1cm} (3.4)

Here \(i,j\) are the site indices. The operator \(c_j^+\) creates a particle at site \(j\); in this chapter we assume a single particle only, which means the statistical property of the particle is irrelevant. \(\sigma_k\) is the spin operator. \(k\) is the bath spin index. In the following section, the microscopic origin of this model is discussed.

The dynamics of the spin bath depends on the size of the system parameters: the central particle parameters \(\Delta_{ij}, \epsilon_i\), and the spin bath parameters \(V_{k,k'}^{\alpha\beta}, h_k\), as well as both the diagonal couplings \(\lambda_j^k\) and off-diagonal coupling \(\alpha_{k,j}^i\) to the spin bath. In this chapter, we are going to explore the dynamics of the central particle in various parameter regimes. Some analytical results are acquired by taking the system into certain asymptotic limits. These results already show the extraordinary behavior of spin baths compared with oscillator ones. General techniques are given afterwards, with some numerical results. Although the most general Hamiltonian for a spin bath has not yet been solved, we are trying to cover most parameter regions.

3.1 The Model of a Discretized System Coupled to a Spin Bath

In this section, we discuss the microscopic origin of spin bath models. The behavior of the model depends on the ratios between parameters. We will outline the various dynamics of the model in different parameter regimes.

At first we look at the bare system Hamiltonian. We can truncate the following high-energy Hamiltonian of form:

\[ H_V = \frac{1}{2M}(\mathbf{P} - \mathbf{A}(\mathbf{R}))^2 + U(\mathbf{R}), \]  \hspace{1cm} (3.5)

into the discretized effective Hamiltonian:

\[ H_o = -\sum_{<ij>} \left[ \Delta_{ij} c_i^\dagger c_j e^{iA_{0j}} + H.c. \right] + \sum_j \epsilon_j c_j^\dagger c_j. \]  \hspace{1cm} (3.6)

This “1-band” Hamiltonian is the result of truncating to low energies. The Hamiltonian (3.5) describes a particle of mass \(M\) moves in a potential \(U(\mathbf{R})\) characterized by \(N\) potential wells in a certain configuration. Then \(\epsilon_j\) is the energy of the lowest state in the \(j\)-th well, and \(\Delta_{ij}\) is the tunneling
amplitude between the \(i\)-th and \(j\)-th wells. In path integral language, this tunneling is over a semiclassical “instanton” trajectory \(R_{\text{ins}}(\tau)\), and this occurs over a timescale \(\tau_B \sim \frac{1}{\Omega_0}\) (the “bounce time” \([148]\)), where \(\Omega_0\) is roughly the small oscillation frequency of the particle in the potential wells. In a semiclassical calculation, the phase \(A_{ij}^0\) is that incurred along the semiclassical trajectory by the particle, moving in the gauge field \(A(R)\).

The second step is to add the interaction to the environment. The most obvious interaction between the particle and a set of bath spins has the local form \([124]\):

\[
H_{\text{int}}(R) = \sum_k F(R - r_k) \cdot \sigma_k = \sum_k H_{\text{int}}^k(R)
\]

(3.7)

where \(F(r)\) is some vector function, and \(r_k\) is the position of the \(k\)-th bath spin. The diagonal coupling \(F_{ij}^k\), or its linearized form \(\omega_{ij}^k\), is then easily obtained from (3.7) when we truncate to the single band form. But the term (3.7) must also generate a non-diagonal term, which is more subtle. We can see this by defining the operator

\[
\hat{T}_{ij}^k = \exp \left[ -\frac{i}{\hbar} \int_{\tau_{\text{in}}(R_i)}^{\tau_f(R_j)} d\tau \ H_{\text{int}}^k(R, \sigma_k) \right],
\]

(3.8)

where the particle is assumed to start in the \(i\)-th potential well centered at position \(R_i\), at the initial time \(\tau_{\text{in}}\), and finish at position \(R_j\) in the adjacent \(j\)-th well at time \(\tau_f\); the intervening trajectory is the instanton trajectory (which in general is modified somewhat by the coupling to the spin bath). Now we operate on \(\sigma_k\) with \(\hat{T}_{ij}^k\), to get

\[
|\sigma_k^f\rangle = \hat{T}_{ij}^k |\sigma_k^{\text{in}}\rangle = e^{i(\phi_{ij}^k + \alpha_{ij}^k \cdot \sigma_k)} |\sigma_k^{\text{in}}\rangle,
\]

(3.9)

where we note that both the phase \(\phi_{ij}^k\) multiplying the unit spin operator \(\sigma_k^0\), and the vector \(\alpha_{ij}^k\) multiplying the other 3 spin operators \(\sigma_k^x, \sigma_k^y, \sigma_k^z\), are in general complex. In this way the instanton trajectory of the particle acts as an operator in the Hilbert space of the \(k\)-th bath spin \([1, 149]\). Note that one important implication of this derivation is that typically \(|\alpha_{ij}^k| \ll 1\), in fact exponentially small, since the interaction energy scale set by \(|F(R - r_k)|\) is usually much smaller than the “bounce energy” scale \(\hbar/|\Omega_0|\) set by the potential \(U(R)\), i.e. the tunneling of the particle between wells is a sudden perturbation on the bath spins \([1]\).

Therefore, the most general coupling terms between the particle and the spin bath has the form

\[
H_{\text{int}} = \sum_k N_k \left[ \sum_j F_j^k(\sigma_k) c_j^\dagger c_j + \sum_{<ij>} (G_{ij}^k(\sigma_k) c_i^\dagger c_j + H.c.) \right]
\]

(3.10)
3.1. The Model of a Discretized System Coupled to a Spin Bath

in which both the diagonal coupling $F^k_j$ and the non-diagonal coupling $G^k_{ij}$ are vectors in the Hilbert space of the $k$-th bath spin.

Starting with the particle-bath interaction given in (3.7), we will end up with an effective Hamiltonian for the interaction terms in form given in (3.10), in which the non-diagonal interaction $G^k_{ij}(\sigma_k)$ has assumed a rather special form.

One can in fact have a more general form for $G^k_{ij}(\sigma_k)$ in the lowest-band approximation, provided one also introduces in the microscopic Hamiltonian a coupling

$$H_{\text{int}}(P) = \sum_k G(P, \sigma_k) = \sum_k H^k_{\text{int}}(P)$$

(3.11)

to the momentum of the particle. This can include various terms, including functions of $P \times \sigma_k$ and $P \cdot \sigma_k$; a detailed analysis is fairly lengthy. The main new effect of these is to generate terms in the band Hamiltonian which couple the spins to the amplitude of $t_{ij}$ as well as to its phase; these do not appear in (3.15).

The spin bath itself, independent of the particle, has the Hamiltonian

$$H_{\text{SB}} = \sum_k h_k \cdot \sigma_k + \sum_{k,k'} V_{\alpha\beta}^{k,k'} \sigma_k^\alpha \sigma_{k'}^\beta.$$  

(3.12)

Each environment spin has some local field $h_k$ acting on it, and the interactions $V_{\alpha\beta}^{k,k'}$ are typically rather small because the spin bath represents localized modes in the environment.

Considering the origin of these terms, we can combine the bare Hamiltonian (3.6) and the interaction terms (3.10) to get the band Hamiltonian as

$$H_{\text{band}} = H_o + H_{\text{int}}$$

(3.13)

$$= \sum_{ij} [\Delta_{ij} c_i^\dagger c_j e^{iA^j_{ij}} + \sum_k (\phi_{ij}^j + \alpha_{ij}^j \sigma_k) + H.c.]$$

(3.14)

$$+ \sum_j (\epsilon_j + \sum_k \lambda_k^j \cdot \sigma_k) c_j^\dagger c_j$$

(3.15)

in which the diagonal couplings to the spin bath assume a “Zeeman” form, of strength $|\lambda_k^j|$, linear in the $\{\sigma_k\}$, and the non-diagonal couplings appear in the form of extra phase factors in the hopping amplitude between sites.

### 3.1.1 Parameter Regions

Solving the general Hamiltonian (3.1) and (3.15) analytically is difficult. But we can study the behaviour of the central system in different parameter
regions. We are going to outline and discuss them briefly in this section. The detailed calculations are provided in the next two sections of this chapter.

I. Off-diagonal Coupling: Pure phase decoherence region  If $h_k \cdot \sigma_k$ commutes with the off-diagonal coupling $\alpha^{ij}_k \cdot \sigma_k$, the interactions with the central system will not flip the bath spins between the eigenstates of the bath Hamiltonian $H_{SB} = h_k \cdot \sigma_k$. Therefore there is no dissipation in this region since there is no energy transfer between the bath and the system. The interaction terms only add time dependent phase factors to bath spin states which cause the decoherence. This is one of the major differences from the oscillator bath case where decoherence always happens together with dissipation due to the fluctuation-dissipation theorem. Therefore, we call this region the pure phase decoherence region. It has been studied for a ring system [2] and there is no difficulty to generalize it to an arbitrary lattice by using the influence functional technique. We can see that the influence functional kernel in this case smears the phase correlation between different paths and eventually leads to a non-dissipative decoherence of the reduced density matrix.

II. Off-diagonal Coupling: High field region  If $h_k \cdot \sigma_k$ does not commute with $\alpha^{ij}_k \cdot \sigma_k$ and the commutators are much larger than $|\alpha^{ij}_k \Delta_{ij}|$, bath spins are completely driven by this effective “external field”. The technique we are going to use for this region is the orthogonal blocking approximation which was originally discussed for the TLS central system[1]. We generalize the method here to deal with general lattices. We divide the total Hilbert space of bath spins into different polarization groups. Those polarization groups are the sets of bath states which have similar eigenvalues of $\sum_k h_k \cdot \sigma_k$. Since $|h_k|$s are large, the energy difference between different polarization groups is usually large too. Due to such large energy gaps, the transitions between different polarization groups rarely happen. We can do a perturbation expansion on the maximum number of transitions allowed. Since these transitions are naturally correlated in nature, we can find effective interactions between different paths and derive an effective influence functional kernel. This method can be systematically generalized to the intermediate parameter region. We can see that the bath spins behave differently compared with those in the pure phase decoherence region. Combining them together give a complete description of a spin bath with only off-diagonal coupling.
3.2. Pure Phase Decoherence Region

III. Diagonal Coupling: Anderson localization and beyond  The diagonal coupling \( \sum_j (\epsilon_j + \sum_k \lambda_j^k \cdot \sigma_k) c_j^\dagger c_j \) is more complicated to deal with. The site energy \( \{\epsilon_j\} \) is generally not homogeneous and therefore we expect the localization phenomenon in the bare Hamiltonian. In fact, this problem can be converted into the famous Anderson model\[150\]. In mathematics, it is also called the random Jacobi problem\[151\]. The wave function of the central particle can be localized by a randomly distributed set of \( \{\epsilon_j\} \) due to the interference between multiple paths. This localization mechanism impedes the energy transfer of the central system.

If the diagonal coupling term \( \lambda_j^k \cdot \sigma_k \) commutes with \( h_k \cdot \sigma_k \), again there is no energy transfer into the bath. If the spin bath is initially in a high temperature state, this interaction basically gives a decoherence kernel \( \propto \exp(-\lambda^2) \) to each path in the path integral. This decoherence kernel can destroy the mentioned interference between different paths and therefore eventually destroy the localization. In biophysics, this destruction of weak localization is also called an “environment-assisted” transition \[32, 136\].

Anderson localization with quantum environments is a huge topic which has tons of literature about it. If the commutator between \( \lambda_j^k \cdot \sigma_k \) and \( h_k \cdot \sigma_k \) is not negligible, this problem becomes even more complicated. If \( h_k \to \infty \), we can imagine that the “orthogonality blocking approximation” method is still valid. For large but finite \( h_k \), a perturbation expansion method can be made based on the path integral, but the convergence of the expansion strongly depends on the geometry of the lattice which is beyond the scope of this thesis. Therefore, in this thesis we are not going to follow this direction in any depth, which could be useful for various lattice models.

3.2 Pure Phase Decoherence Region

If only off-diagonal couplings are considered, and \( h_k \cdot \sigma_k \) commutes with \( \alpha_{ij}^k \cdot \sigma_k \), we get the “Pure Phase Decoherence Region”. It is useful to look at models in this region since the environment causes pure phase decoherence, with no dissipation.

Such models become particularly interesting when the decoherence is acting on systems propagating in ‘closed loops’. Models of rings coupled to oscillator baths have already been studied \[152\]. However such models, where decoherence is inextricably linked to dissipation, do not capture the largely non-dissipative decoherence processes that dominate many solids at low \( T \).

In this section we are going to illustrate the character of spin bath in
3.2. Pure Phase Decoherence Region

this region on a ring structure (see Fig. 3.1). As we reviewed in Section 1.1, the light harvesting systems I and II also have these ring-like structures. In theory, by making $\epsilon_i$ identical at each site, we can eliminate the unnecessary localization effect to focus on the effect of the pure phase decoherence. And the 1-D ring is the smallest possible structure we can study to showcase this phenomenon. This calculation can be easily generalized to other lattices.

Figure 3.1: Illustration of truncation to discretized system: At left, an 8-site ring with nearest-neighbour hopping between sites. At right a potential $U(R)$ with 8 potential wells (shown here symmetric under rotations by $\pi/4$), depicted as a contour map (with lower potential shown darker). When truncated to the 8 lowest eigenstates, this is equivalent to the 8-site model.

3.2.1 Bare System Behaviour

We first consider the dynamics of a particle in some initial state moving on the $N$-site ring without bath. In (3.6), we assume a symmetric ring so that $\Delta_{ij}$ is only nonzero for neighboring sites and identical for every such pair. The gauge potential is given by

$$A^\circ_{ij} = \frac{e}{2} \mathbf{H} \cdot \mathbf{R}_i \times \mathbf{R}_j = \Phi/N$$  \hspace{1cm} (3.16)

(We use MKS units, in which $\hbar = 1$.) Here, $\mathbf{H}$ is the magnetic field, and $\mathbf{R}_i$ is the radius-vector to the $i$th site; in cylindrical coordinates

$$\mathbf{R}_j = (R_o, \Theta_j)$$
$$\Theta_j = 2\pi j/N$$  \hspace{1cm} (3.17)
3.2. Pure Phase Decoherence Region

for a ring of radius $R_o$. We now define operators

$$c^\dagger_j = \sqrt{\frac{1}{N}} \sum_{k_n} e^{ik_n j} c^\dagger_{k_n},$$

$$c^\dagger_{k_n} = \sqrt{\frac{1}{N}} \sum_{\ell} e^{-ik_n \ell} c^\dagger_{\ell},$$

$$k_n = \frac{2\pi n}{N}, \quad n = 0, 1, \ldots, N - 1,$$  \hspace{1cm} (3.18)

(we have slightly switched notation from the last section, now denoting momenta by $k_n$ instead of $p_n$). The bare Hamiltonian is then

$$\mathcal{H}_o = \sum_{k_n} 2\Delta_o \cos(k_n - \Phi/N)c^\dagger_{k_n} c_{k_n}.$$  \hspace{1cm} (3.19)

For this free particle the dynamics is entirely described in terms of the bare 1-particle Green function

$$G^o_{jj'}(t) \equiv \langle j | G^o(t) | j' \rangle \equiv \langle j | e^{-i\mathcal{H}_o t} | j' \rangle = \frac{1}{N} \sum_n e^{-i2\Delta_o t \cos(k_n - \Phi/N)} e^{ik_n (j' - j)}.$$  \hspace{1cm} (3.20)

which gives the amplitude for the particle to propagate from site $j'$ at time zero to site $j$ at time $t$. This can be evaluated in various ways (see Appendix B.1); the result can be usefully written as

$$G^o_{jj'}(t) = \sum_{p=-\infty}^{+\infty} J_{Np + j' - j}(2\Delta_o t) e^{-i(Np + j' - j)(\Phi/N + \pi/2)}.$$  \hspace{1cm} (3.21)

where $\sum_p$ is a sum over ‘winding numbers’ around the ring. The ”return amplitude” $G^o_{00}(t)$ is then given by

$$G^o_{00}(t) = \sum_p e^{ip\Phi} (-i)^{|Np|} J_{|Np|}(2\Delta_o t)$$

$$= \sum_p e^{ip\Phi} I_{Np}(-2i\Delta_o t).$$  \hspace{1cm} (3.22)

where in the last form we use the hyperbolic Bessel function.

It is often more useful to have expressions for the density matrix; even though these depend trivially for a free particle on the Green function, they
3.2. Pure Phase Decoherence Region

are essential when we come to compare with the reduced density matrix for the particle coupled to the bath. One has, for the ‘bare’ density matrix of the system at time \( t \),

\[ \rho^{o}(t) = e^{-i\mathcal{H}_o t} \rho_{o}(0) e^{i\mathcal{H}_o t}. \]  

(3.23)

Thus, suppose we have an initial density matrix \( \rho_{l,l'}^{o} = \langle l|\rho(t=0)|l' \rangle \) at time \( t = 0 \) (where \( l \) and \( l' \) are site indices), then at a later time \( t \) we have

\[ \rho_{jj'}^{o}(t) \equiv \langle j|\rho^{o}(t)|j' \rangle = \langle j|e^{-i\mathcal{H}_o t}|l \rangle \rho_{l,l'}^{o} \langle l'|e^{i\mathcal{H}_o t}|j' \rangle = \rho_{l,l'}^{o} G_{jl}^{o}(t) G_{j'l'}^{o}(t)^{\dagger}. \]  

(3.24)

where we use the Einstein summation convention (summing over \( l, l' \)). In what follows we will often choose the special case where the particle begins at \( t = 0 \) on site 0, so that \( \rho_{l,l'} = \delta_{0l} \delta_{l'0} \), and then we have

\[ \langle j|\rho_{o}(t)|j' \rangle = G_{j0}^{o}(t) G_{j'0}^{o}(t)^{\dagger}. \]  

(3.25)

Figure 3.2: A particular path in a path integral for the particle, shown here for an \( N = 3 \) ring. This path, from site 0 to site 1, has winding number \( p = 1 \).

The evaluation of the time-dependent density matrix for the free particle turns out to be quite interesting mathematically. As discussed in the Appendix [B.2] one can evaluate \( \rho_{jj'}^{o}(t) \) as a sum over winding numbers, to produce either a sum over pairs of paths in a path integral, to give a double sum over winding numbers, or as a single sum over winding numbers (see Fig. 3.2). Consider first the double sum form; for the special case where
3.2. Pure Phase Decoherence Region

\( \rho_{l,l'} = \delta_{l0} \delta_{l'0} \) (the particle starts at the origin), this can be written as

\[
\rho_{0,jj'}(t) = \sum_{pp'} e^{i(p-p')\Phi} e^{i\Phi(j-j')/N} (-i)^{Np+j} e^{i\Phi(j-j')/N} \times J_{Np+j}(2\Delta_0 t)J_{Np'+j'}(2\Delta_0 t),
\]

(3.26)

where \( p, p' \) are winding numbers (see Appendix B.2 for the derivation for a general initial density matrix). This form has a simple physical interpretation - the particle propagates along pairs of paths in the density matrix, one finishing at site \( j \) and the other at site \( j' \), and the order of each Bessel function simply gives the total number of sites traversed in each path, with appropriate Aharonov-Bohm phase multipliers for each path.

Consider now the answer written as a single sum over winding numbers; again assuming \( \rho_{l,l'} = \delta_{l0} \delta_{l'0} \), we get:

\[
\rho_{0,jj'}(t) = \frac{1}{N} \sum_{m=0}^{N-1} \sum_{p=-\infty}^{\infty} J_{Np'+j'-j}[4\Delta_0 t \sin(k_m/2)] e^{\Phi[p'+(j'-j)/N]-ik_m(j+j'-Np')/2}.
\]

(3.27)

The physical interpretation of this form is less obvious, but the sums are much easier to evaluate since they only contain single Bessel functions instead of pairs of them. Thus wherever possible we reduce double sum forms to single sums. Notice that for these finite rings, the bare density matrix is of course strictly periodic in time. Notice also that the diagonal elements of \( \rho(t) \) are generally periodic with \( \Phi \). However, the off-diagonal elements are only periodic in \( \Phi/N \). In contrast, \( e^{i\Phi[p'+(j'-j)/N]-ik_m(j+j'-Np')/2} \) is periodic in \( \Phi \), with period \( 2\pi \). This latter is the quantity needed for calculating the currents, as we will see below.

From either \( G_{j,j'}^o(t) \) or \( \rho_{j,j'}^o(t) \) we may immediately compute two useful physical quantities. First, the probability \( P_{j0}^o(t) \) to find the particle at time \( t \) at site \( j \), assuming it starts at the origin; and second, the current \( I_{j,j+1}(t) \) between adjacent links as a function of time. This probability \( P_{j0}^o(t) \) is given by

\[
P_{j0}^o(t) = \langle j | \rho_o(t) | j \rangle = |G_{j0}^o(t)|^2.
\]

(3.28)

which from above can be written in double sum form as

\[
P_{j0}^o(t) = \sum_{pp'} J_{Np+j}(2\Delta_0 t)J_{Np'+j}(2\Delta_0 t) \times e^{-iN(p'-p)(\Phi/N + \frac{\pi}{2})}.
\]
or in single sum form as

\[ P^0_{j0}(t) = \frac{1}{N} \sum_{m=0}^{N-1} \sum_{p=-\infty}^{\infty} e^{ip(\Phi+Nk_m/2)} \times J_{Np}[4\Delta_o t \sin(k_m/2)] . \]

Figure 3.3: Results for the free particle for \( N = 3 \) and for a particle initially on site 1. Left: The probabilities to occupy site 1 (full line), 2 (large dashes), and 3 (small dashes). Right: the current from site 1 to site 2. Top: \( \Phi = 0 \). Bottom: \( \Phi = \pi/2 \) (i.e. \( \phi = \pi/6 \)).

One may also compute moments of these probabilities (e.g., the 2nd moment \( \sum_j j^2 P^0_{j0}(t) \) tells us the rate at which a density matrix spreads in time), by a simple generalisation of these formulas.

To give some idea of how for the free particle behaves, it is useful to look at these results for a small 3-site ring, where the oscillation periods are quite
3.2. Pure Phase Decoherence Region

short. One then has, for the case where the particle starts at the origin, that

\[
\begin{align*}
P_{j_0}^o(t) &= \frac{1}{3}(1 + (3\delta_{j,0} - 1)[J_0(2\Delta_o \sqrt{3}t) \\
&\quad + 2 \sum_{p=1}^{\infty} J_{6p}(2\Delta_o \sqrt{3}t) \cos(2p\Phi)] \\
&\quad + (\delta_{j,1} - \delta_{j,2})2\sqrt{3} \sum_{p=1}^{\infty} J_{6p-3}(2\Delta_o \sqrt{3}t) \sin((2p - 1)\Phi))
\end{align*}
\]

(3.29)

In Fig. 3.3 the return probability \( P_{j_0}^o(t) \) is plotted for \( N = 3 \), using (3.29); we see that the periodic behaviour depends strongly on the flux \( \Phi \).

Turning now to the current \( I_{j,j+1}^o(t) \) between site \( j \) and site \( j+1 \), this is given by

\[
I_{j,j+1}^o(t) = 2 \Im \left[ \Delta_o e^{-i\Phi/N} \rho_{j+1,j}^o(t) \right] = -i\Delta_o \sum_{pp'} e^{i(p-p')\Phi} \left( I_{Np+j+1}(x)I_{Np'+j}(x^*) - I_{Np+j}(x)I_{Np'+j+1}(x^*) \right)
\]

(3.30)

where we define \( x = -2i\Delta_o t \). Again, one can write the current as either a double sum over pairs of winding numbers, or as a single sum (see Appendix B.2 for the general results and derivation). For the case where the particle starts from the origin, these expressions reduce to

\[
I_{j+1,j} = 2\Delta_o \sum_{pp'} J_{Np+j}(2\Delta_o t)J_{Np'+j+1}(2\Delta_o t) \cos\left[\left(\frac{\pi}{2}N + \Phi\right)(p' - p)\right] \\
= \frac{2\Delta_o}{N} \sum_{m=0}^{N-1} \sum_{p} J_{Np+1}(4\Delta_o t \sin \frac{k_m}{2}) e^{-ikm(N/2+j) \lambda Np+1} \cdot \cos\left[\left(\frac{\pi}{2}N + \Phi\right)p\right]
\]

(3.31)

for the double and single sums respectively.

Again, the currents across any links must be strictly periodic in time; and again, it is useful to show the results for a 3-site system. For this case \( N = 3 \), and assuming that the particle begins at the origin, we find

\[
I_{0,1} = \frac{2\Delta_o}{3} \sum_{m=1}^{2} \sum_{p} J_{3p+1}(4\Delta_o t \sin \frac{m\pi}{3}) \times e^{-im\pi(3p+1)/3} 3^{3p+1} \cos\left[\left(\frac{3\pi}{2} + \Phi\right)p\right]
\]

(3.32)
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which we can also write in the form

\[ I_{0,1} = \frac{2\Delta_0}{3} \sum_p J_{3p+1} (2\sqrt{3}\Delta_0 t)^{3p+1} \cos(\frac{3\pi}{2} + \Phi) p ] \]

\[ \times \sum_m (e^{-i\pi(3p+1)/3} + e^{-i2\pi(3p+1)/3}) \]  (3.33)

Now let us write \( e^{-i\pi(3p+1)/3} + e^{-i2\pi(3p+1)/3} = (-)^p e^{-i\pi/3} + e^{-2i\pi/3} \). If \( p \) is even, this becomes \(-i\sqrt{3}\) and \( \cos([\frac{3\pi}{2} + \Phi] p] = (-)^{3p/2} \cos(\Phi p) \); If \( p \) is odd, it becomes \(-1\) and \( \cos([\frac{3\pi}{2} + \Phi] p] = (-)^{3(p-1)/2} \sin(\Phi p) \). Therefore, we have

\[ I_{0,1} = \frac{2\Delta_0}{3} \sum_{p=-\infty}^{\infty} J_{3p+1} (2\Delta_0 \sqrt{3} t) K(p, \Phi), \]

\[ K(p, \Phi) = \sin(p\Phi) \text{ if } p = \text{ odd}, \]

\[ K(p, \Phi) = \sqrt{3} \cos(p\Phi) \text{ if } p = \text{ even}. \]  (3.34)

These results are shown in Fig. 3.4. Notice that in this special case the result is periodic in \( \Phi \); this is not however true for a general initial density matrix \( \rho_{l,l'} \), when the periodicity is in \( \Phi/N \).

Figure 3.4: Plot of \( P_{j1}(t) \) for a 3-site ring, for a particle initially on site 1, in the strong decoherence limit. Left: The probability to occupy site 1 (full line), 2 (large dashes), and 3 (small dashes). Right: the current from site 1 to site 2 (compare Fig. 3.3). The results do not depend on \( \Phi \).

3.2.2 System Plus the Bath

We now wish to solve for the dynamics of the particle once it is coupled to the bath, via the Hamiltonian

\[ H_\phi = -\Delta_0 \sum_{\langle ij \rangle} \left[ c_i^\dagger c_j e^{i(A_{ij}) + \sum_k \alpha_{ij}^{l_k} \sigma_k} + H.c. \right]. \]  (3.35)
3.2. Pure Phase Decoherence Region

Here we neglect the $\sigma_k$ term since it commutes with the full Hamiltonian. Before going to the actual calculation, it is useful to note what are the important parameters in this problem. Consider first the simplest completely symmetric case where $\alpha_{nk} \rightarrow \alpha_k$ for all links $\{mn\}$. Assuming that $|\alpha_k| \ll 1$ for all $k$, as discussed in section II, then it has been usual to define a parameter $\lambda$ \cite{1,149}

$$\lambda = \frac{1}{2} \sum_k |\alpha_k|^2$$

(3.36)

which is intended to measure the strength of the pure phase decoherence (this parameter has been referred to as the ‘topological decoherence strength’ in the literature$[1]$). If the number $N$ of bath spins is large, then we can have $\lambda \gg 1$; this is the limit of strong phase decoherence. However we shall see in what follows that under certain circumstances the decoherence characteristics depend on the function

$$F_0(p) = \prod_k \cos(Np|\alpha_k|)$$

(3.37)

which, depending on the values of the $|\alpha_k|$, can show very interesting properties.

In the more general case where the couplings $\{\alpha_{nk}\}$ differ from one link to another, one can in principle define a set of decoherence parameters $\lambda_{mn}$ for each link, but this turns out to be not very useful.

We now wish to solve for the reduced density matrix of the particle once it is coupled to the spin bath, assuming the system to be described by $H_\phi$ in (3.35). This is most easily done in a path integral framework, because for the tight-binding model of the ring we are using, the particle paths are very simple (see Fig. 3.2).

As shown in Appendix B.2, the reduced density matrix for the particle can be written as follows. We begin by writing the “bare” free particle density matrix as a double sum over winding numbers:

$$\rho_{jj'}^0(t) = \sum_{pp'} \rho_{jj'}^0(p,p';t)$$

(3.38)

Then one finds that in the presence of phase coupling to the spin bath, the reduced density matrix takes the form

$$\rho_{jj'}(t) = \sum_{pp'} \sum_{ll'} \rho_{jj'}^0(p,p';t) F_{ll'}^{j,j'}(p,p')$$

(3.39)
where the influence functional has now reduced to a much simpler weighting function \( F_{l,j}(p,p') \), which we call the ‘influence function’. In the same way as the original influence functional, it depends in general on the initial state \( \rho_{l,l'} \) of the density matrix at time \( t = 0 \). In the appendix the full expression for \( F_{l,j}(p,p') \) is given; but here we will only use it for the usual case where \( \rho_{l,l'} = \delta_{0l}\delta_{0l'} \), i.e., the particle starts at the origin. We will also assume the purely symmetric case where \( \alpha_{ij} \rightarrow \alpha_{k} \) for every link. In this case the influence function reduces to (see Appendix B.2):

\[
F_{j,j'}(p,p') = \langle e^{-iN[(p-p')+(j-j')]\sum_k \alpha_k \cdot \sigma_k} \rangle \quad (3.40)
\]

Notice that \( F_{j,j'}(p,p') \) is a function only of the distance \( j - j' \) between initial and final sites. We may easily evaluate \( F_{j,j'}(p,p') \) by assuming the usual thermal initial bath spin distribution, with equally populated states; we then get:

\[
F_{j,j'}(p,p') = \prod_k \cos((N[p-p'] + j - j')|\alpha_k|) \quad (3.41)
\]

Other initial distributions for the spin bath are easily evaluated from (B.23). From expressions like (3.41) one can then write down expectation values of physical quantities as a function of time. The simplest example is the probability for the particle to end up at some site after a time \( t \), having started at another. Thus, e.g., the probability \( P_{j,0}(t) \) to move to site \( j \) from the origin in time \( t \) is now given by

\[
P_{j,0}(t) = \rho_{jj}(t) = \sum_{pp'} J_{Np+j}(2\Delta_o t)J_{Np'+j}(2\Delta_o t) \times e^{-iN(p'-p)(\Phi/N + \frac{\pi}{2})} F_0(p,p')
\]

which is a simple generalization of the free particle result in (3.29); we note that only the term

\[
F_0(p,p') = \prod_k \cos(N(p-p')|\alpha_k|) \quad (3.42)
\]

in the influence function survives in this expression. Note that since this function depends only on the difference \( p - p' \), it is identical to the function \( F_0(p) \) defined in (3.37) above (letting \( p' = 0 \)). We shall see below that the ring current is also controlled by this function, and that it is therefore of

\[
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\]
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quite general use in discussing the decoherence in this system. Note that it has a complex multiperiodicity, as a function of the $N$ different parameters $p\lambda_k = Np|\alpha_k|$; we do not have space here to examine the rich variety of behaviour found in the system dynamics as we vary these parameters.

To give something of the flavour of this behaviour, suppose we have a Gaussian distribution for the $|\alpha_k|$, given by

$$P(|\alpha_k|) = e^{-|\alpha_k|^2/2\lambda_o/\sqrt{2\pi\lambda_o}}$$

(3.43)

so that

$$F_0(p) = e^{-\lambda p^2/2}, \quad \lambda = N\lambda_o$$

(3.44)

The limit $\lambda \to \infty$ is the “strong decoherence” limit for this distribution, where we have $F_0(p) \to \delta_{p,0}$. In this limit the behaviour does not depend on flux at all.

Now consider the results away from this limit - to be specific we take the case where $N = 3$ again. For this 3-site ring one has

$$P_{11}(t) = \frac{1}{3} \left[ 1 + 2\frac{2A}{\sqrt{\pi\Delta_o\sqrt{3}t}} \cos(2\Delta_o\sqrt{3}t - \pi/4) \right]$$

(3.45)

To analyse this result, note that for $x \gg (6p)^2$, we can use $J_{6p}(x) \approx (-1)^p \sqrt{2/(\pi x)} \cos(x - \pi/4)$. If the function $F_0(6p)$ truncates terms with $p > p_{\text{max}}$ then for $2\Delta_o\sqrt{3}t \gg (6p_{\text{max}})^2$ we have e.g.

$$P_{11}(t) \approx \frac{1}{3} \left[ 1 + \frac{2A}{\sqrt{\pi\Delta_o\sqrt{3}t}} \cos(2\Delta_o\sqrt{3}t - \pi/4) \right],$$

$$A = 1 + 2\sum_{p=1}^{\infty} (-1)^p \cos(2p\Phi) F_0(6p) \right).$$

(3.46)

For $\Phi = 0$ (or $\pi/2$), the sum in the amplitude $A$ reduces to $\sum (-1)^p F_0(6p)$ [or to $\sum F_0(6p)$]. Clearly, switching from $\Phi = 0$ to $\Phi = \pi/2$ causes a large increase in $A$. As $\lambda$ increases, $p_{\text{max}}$ decreases, and Eq. (3.46) applies at shorter times. However, if $\lambda > 0.1$ the whole sum becomes negligible, and we are left with the $\Phi$–independent asymptotic result. In fact, the inverse Fourier transform of the amplitude $A(\phi)$ can be used to measure the decoherence function $F_0(6p)!$

Turning now to the current through the ring, we generalize the free particle results in the same way as above. Quite generally one has

$$I_{j,j+1} = -i(\tilde{\Delta}_{j,j+1}\rho_{j+1,j} - \tilde{\Delta}_{j+1,j}\rho_{j,j+1})$$

(3.47)
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where one averages over the operator

\[ \tilde{\Delta}_{j,j+1} = \Delta_0 e^{i\Phi/N} e^i \sum_k \alpha_k^{i,j+1} \sigma_k \]  (3.48)

This expression is evaluated in detail in the Appendix B.2. Here we consider only the special case where the particle starts from the origin, and \( \alpha_k^{ij} \to \alpha_k \).

Then one has

\[ I_{j,j+1}(t) = \frac{2\Delta_0}{N} \sum_{m=0}^{N-1} \sum_p J_{Np+1} (4\Delta_0 t \sin \frac{k_m}{2}) e^{-ik_m (Np+1+j)/\frac{N}{2}} \cdot F_0(p) \cos[(\frac{\pi}{2}N + \Phi)p] \]  (3.49)

One can also analyse these results as a function of the decoherence strength and of the flux. Here we only quote the result in the strong decoherence limit - then one has

\[ I(j,j+1) \to \frac{2\sqrt{3}}{3} \Delta_0 (\rho_{j,j} - \rho_{j+1,j+1}) J_1(2\Delta_0 \sqrt{3}t) . \]  (3.50)

for some general initial density matrix \( \rho_{l,l} \). Again we see that the result is completely independent of the flux.

### 3.2.3 Wave Package Interference

It is interesting to now turn to the situation where two signals are launched at \( t = 0 \) from 2 different points in the ring. The idea is to see how the spin bath affects their mutual interference, and how, by effectively coupling to the momentum of the particle, it destroys the coherence between states with different momenta. We do not give complete results here, but only enough to show how things work.

We therefore start with two-wave-packets which will initially be in a pure state, and will then gradually be dephased by the bath. In the absence of a bath, we will assume the wave function of this state to be the symmetric superposition

\[ \Psi(t) = \frac{1}{\sqrt{2}} (\psi_1(t) + \psi_2(t)) \]  (3.51)

where the two wave-packets are assumed to have Gaussian form:

\[ |\psi_1(t)\rangle = \sum_{n=0}^{N-1} e^{-(k_n-\pi/2)^2 D/2} \times e^{i\chi_0 k_n - i2\Delta_0 t \cos(k_n - \Phi/N)} |k_n\rangle \]  (3.52)
3.2. Pure Phase Decoherence Region

\[ |\psi_2(t)\rangle = \sum_{n=0}^{N-1} e^{-(k_n-\pi/2)^2D/2} |2\pi - k_n\rangle \]  

(3.53)

where we assume the usual symmetric ring with flux \( \Phi \). At \( t = 0 \), one of the packets is centred at the origin, and the other at site \( j_o \). Note that the velocity of each wave-packet is conserved. At times such that \( \Delta_o t = 2n \), the two wave packets cross each other. From (3.52) we see that the main effect of the flux is to shift the relative momentum of the wave-packets. It also affects the rate at which the wave-packets disperse in real space - this dispersion rate is at a minimum when \( \phi = \frac{\pi}{2} \).

The free-particle wave function in real space is then

\[ |\Psi_j(t)\rangle = \sum_{n=0}^{N-1} e^{-(k_n-\pi/2)^2} \left( e^{i(j-j_0)k_n} e^{-2i\Delta_o t \cos (k_n+\Phi/N)} + e^{-ijk_n e^{-2i\Delta_o t \cos (k_n-\Phi/N)}} \right) |j\rangle \]  

(3.54)

so that the probability to find a particle at time \( t \) on site \( j \) is \( P(j) = |\Psi_j(t)|^2 \).

Let us now consider the effect of phase decoherence from the spin bath. Using the results for \( P_{jj'}(t) \) from the last section, with an initial reduced density matrix given by

\[ \rho(j,j'; t = 0) = |\Psi_j(t = 0)\rangle \langle \Psi_{j'}(t = 0)| \]  

(3.55)

we find a rather lengthy result for the probability that the site \( j \) is occupied at time \( t \):

\[ P_j(t) = \sum_{n,n'=0}^{N-1} \sum_{m=-\infty}^{+\infty} e^{-(k_n-\pi/2)^2+(k_n'-\pi/2)^2}D/2 F_0(m) \times \left\{ e^{i(j-j_0)(k_n-k_n')} J_m(4\Delta_o t \sin ((k_n - k_n')/2)) e^{im(k_n+k_n')/2+\Phi/N} + e^{-i(k_n-k_n')} i J_m(4\Delta_o t \sin ((k_n - k_n')/2)) e^{im(k_n+k_n')/2-\Phi/N} + e^{i(j-j_0)k_n+jk_n'} J_m(4\Delta_o t \sin ((k_n + k_n')/2)) e^{im(k_n-k_n')-\Phi/N} + h.c. \right\} \]  

(3.56)

Here we have used the generating series for Bessel functions, viz.,

\[ e^{ix \sin \theta} = \sum_{m=-\infty}^{+\infty} J_m(x)e^{im\theta} \]  

(3.57)

to separate the parts depending on flux in the final expression.
3.2. Pure Phase Decoherence Region

Figure 3.5: Interference between 2 wavepackets in the strong decoherence limit. The packets start at site 0 and site \( j_0 = 50 \) at \( t = 0 \), and their relative velocity is \( \frac{\pi}{2} \), in phase units.
3.3. High Field Region

One can also, in the same way, derive results for the current in the situation where we start with 2 wave-packets. We see that expressions like (3.56) are too unwieldy for simple analysis. However in the strong decoherence limit (3.56) simplifies to:

$$P(j) = N - 1 \sum_{n,n'} e^{-((k_n - \pi/2)^2 + (k_{n'} - \pi/2)^2)D/2}$$

\[ \cdot \left\{ e^{i(j-j_0)(k_n - k_{n'})}J_0(4\Delta t \sin ((k_n - k_{n'})/2)) 
+ e^{-ij(k_n - k_{n'})}J_0(4\Delta t \sin ((k_n - k_{n'})/2)) 
+ [e^{i(j-j_0)k_n + jk_{n'}}]J_0(4\Delta t \sin ((k_n + k_{n'})/2)) + h.c.\right\} \right) \] (3.58)

and again we see that the flux has disappeared from this equation. This result is shown in Fig 3.5.

We notice 2 interesting things here. First, the interference between the two wave-packets is completely washed out, as one might expect. However notice also that each wave packet splits into parts which move in opposite directions. This is because the interaction with the fluctuating bath flux can actually change the direction of parts of each wave-packet (note that the transformation $\Phi \rightarrow \Phi + \pi$ reverses the momentum).

One can also derive results for the current dynamics in the situation where we start with 2 wave-packets.

3.3 High Field Region

In this section, we are going to study the effect of the ‘transverse field’ term $\sum_k h_k \cdot \sigma_k$, if $h_k \cdot \sigma_k$ does not commute with $\alpha_k^{ij} \cdot \sigma_k$. If the commutators are much larger than $|\alpha_k^{ij} \Delta_{ij}|$, bath spins are significantly driven by the fields acting on them. The large fields divide surrounding bath spins into certain polarization groups, which are the sets of bath states which have similar eigenvalues of $\sum_k h_k \cdot \sigma_k$, and make the hoppings between different polarization groups forbidden. That is the reason we call it the “High Field Region” in the first section of this chapter.

In this section, we mainly use the “Orthogonal Blocking Approximation” (OBA) to explore this problem. We start with the lowest order of OBA with only perpendicular couplings before we generalize the method into general couplings as well as general initial states. At the end we discuss the technique of finite $h_k$ expansion which allow us systematically generalizing the OBA to a wide parameter region. Together with the last section,
3.3. High Field Region

we can obtain a complete description of the effect of off-diagonal couplings in the spin bath model.

The Hamiltonian we are considering in this section can be written as

\[ H = \sum_{\langle ij \rangle} \Delta e^{i(\phi_{ij} + \sum k \alpha^{ij} \cdot \sigma_k)} c_i^\dagger c_j + \sum_k h_k \cdot \sigma_k. \]  \hspace{1cm} (3.59)

For simplicity we are assuming \( \Delta_{ij} = \Delta_0 \) for all non-zero \( \langle ij \rangle \) pairs, although the result can be generalized to arbitrary \( \Delta_{ij} \) without difficulty. The fields \( h_k \) act on each spin in bath may not always point in the z-direction since this effective “magnetic field” has various origins. But we can rotate every \( \sigma_k \) to let \( h_k \) acting along its “z-direction”. Now the dynamics of the spin bath is entangled with the central system. We have a rough argument on this issue. When \( \alpha_k \) is small then \( e^{i\alpha_k \cdot \sigma_k} \approx 1 + i\alpha_k \cdot \sigma_k \). The dynamic terms of the \( k \)th surrounding spin are

\[ (h_k + i\Delta_0 \sum_{ij} \alpha^{ij}_k c_i^\dagger c_j) \cdot \sigma_k. \]  \hspace{1cm} (3.60)

We can see that the external field acting on a bath spin is affected by the path chosen by the central particle. By each hopping of the central particle, the environmental spins precess along different axes. Let’s write the interaction vector \( \alpha^{ij} = \alpha^{ij}_\parallel + \alpha^{ij}_\perp \). Here \( \alpha^{ij}_\perp \) is the component perpendicular to \( h_k \) and \( \alpha^{ij}_\parallel \) is the component parallel to \( h_k \).

**Parallel Coupling**  The parallel component \( \alpha^{ij}_\parallel \) does not change the direction of the “effective field” \( (3.60) \). If there is only a parallel component, all the bath spin related terms commute with each other. As a result, the effect of the spin bath should be the same as the pure phase decoherence case in the previous chapter: it only changes the relative phase of different paths of the central spin. The trajectory of the central particle does not mix bath spins in different polarization groups. In the latter part of this section, we are going to show in detail that this is also true if both components are nonzero.

**Perpendicular Coupling**  The \( \alpha^{ij}_k \) term, however, changes the precession axis of the bath spins while the particle is hopping within the lattice. Therefore, the Berry phase of the environmental spin is entangled with the path which the central particle chooses. This kind of entangled precession is a unique source of decoherence in the spin bath which cannot be reproduced...
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in oscillator bath models. In this section we are going to focus more on the $\alpha_{k,\perp}^{ij}$ terms.

### 3.3.1 Orthogonal Blocking Approximation

In this high field limit, we start with the “Orthogonal Blocking Approximation” (OBA), which was originally discussed in [1] with a TLS as the central system. In this section, we are going to generalize this approximation to a general lattice in a formal way.

Consider a time-independent Hamiltonian which can be separated into two parts, i.e. $H = H_0 + H_1$, with $H_1$ as the perturbation term. We expand the time evolution operator $U(t) = e^{-iHt}$ in orders of $H_0$,

$$e^{-iHt} = e^{-i(H_0+H_1)t} = 1 + \sum_{\{n_i\}} \frac{(-it)^L}{(L + \sum_{i=0}^L n_i)!} (-iH_1t)^{n_0}H_0(-iH_1t)^{n_1} \cdot H_0...(-iH_1t)^{n_{L-1}}H_0(-iH_1t)^{n_L} + ....$$  (3.61)

Noticing that

$$\sum_{n} \frac{x^n}{(n+m)!} = \frac{e^x}{(m-1)!} \int_0^x dt \ t^{m-1} e^{-t} = \frac{1}{(m-1)!} \int_0^1 da \ a^{m-1} e^{(1-a)x},$$

we can write each term (which is referred as a “path” in path-integral language) on the LHS of (3.61) as

$$\sum_{\{n_i\}} \frac{(-it)^L}{(L + \sum_{i=0}^L n_i)!} (-iH_1t)^{n_0}H_0(-iH_1t)^{n_1} \cdot H_0...(-iH_1t)^{n_{L-1}}H_0(-iH_1t)^{n_L}$$

$$= \frac{(-it)^L}{(L-1 + \sum_{i=1}^L n_i)!} \int_0^1 da_1 a_1^{L-1} e^{-ia_1H_1t}H_0 \sum_{n_1} (-ia_1H_1)^{n_1}H_0...$$

$$\cdot (-ia_1H_1t)^{n_{L-1}}H_0(-ia_1H_1t)^{n_L}$$

$$= \ldots...$$

$$= (-it)^L \left( \prod_{i=1}^{L+1} \int_{a_i=0}^1 da_i \right) \delta(\sum a_i - 1) e^{-ia_1H_1t}H_0 e^{-ia_2H_1t}H_0...$$

$$\cdot e^{-ia_LH_1t}H_0 e^{-ia_{L+1}H_1t}$$

$$= (-it)^L \int_{-\infty}^{+\infty} \frac{d\xi}{2\pi} e^{-i\xi\tilde{P}(\xi)}H_0\tilde{P}(\xi)...H_0\tilde{P}(\xi),$$

(3.63)
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Here we rewrite the Delta function as
\[ \delta\left(\sum a_i - 1\right) = \int_{-\infty}^{+\infty} \frac{d\xi}{2\pi} e^{-i\xi(\sum a_i - 1)} \]
so that the \( a_i \) integrals are independent with each other. We define the projection operator \( \tilde{P}(\xi) \) in the last line of (3.63) as
\[
\tilde{P}(\xi) = \sum_n f(M_n, \xi, t) |\phi_n\rangle \langle \phi_n|,
\] (3.64)
In our spin bath model, we take \( H_1 = \sum_k h_k \cdot \sigma_k \); its eigenstates \( |\phi_n\rangle \)s satisfy \( H_1 |\phi_n\rangle = M_n h |\phi_n\rangle \), where \( h \) represents the value of the field strength \( |h_k| \).

The function \( f(M, \xi, t) \) is defined as
\[
f(M, \xi, t) = \frac{e^{i(\xi - Mht)} - 1}{i(\xi - Mht)}. \quad (3.65)
\]
The function \( f(M_n, \xi) \) is centered at the point \( \xi = M_n t \). If \( M_n \neq M_m \), the integral \( \int_{-\infty}^{+\infty} \frac{d\xi}{2\pi} e^{-i\xi} \prod_n f(M_n, \xi) \) is inversely proportional to \( (M_n - M_m) \) (see Appendix C). If \( (M_m - M_n)ht \gg 1 \), we can neglect all paths in this summation except the ones with the same polarization all along the path, i.e. \( M_n = M, \forall n \) in the path. This implies that the paths which involve bath spins hopping between different polarization groups do not contribute significantly to the total time evolution. The “Orthogonal Blocking Approximation” is obtained by ignoring these terms in the path-integral by utilizing the following projection operator:
\[
P_M \equiv \delta(\sum_k h_k \cdot \sigma_k - Mh) = \int_{0}^{2\pi} \frac{d\xi}{2\pi} e^{i\xi(\sum_k h_k \cdot \sigma_k - Mh)}.
\] (3.66)
In OBA, we insert such a projection operator in place of the \( \tilde{P}(\xi) \) terms in the last line of (3.63) to enforce the restriction on bath spin flipping. The result is
\[
e^{-iHt} = \sum_M e^{-iMht} \sum_{L=0}^{\infty} \frac{(-it)^L}{L!} (P_M H_0 P_M)^L.
\] (3.67)
The summation over \( M \) is over all possible polarizations of bath spins. It is equivalent to replacing the Hamiltonian with
\[
H = H_0 + H_1 \rightarrow \sum_M P_M H_0 P_M + H_1
\] (3.68)
If \( h \rightarrow \infty \) this method is exact. This approximation is usually used when the external field strength \( h \), which determines the energy difference between different polarization groups, is much larger than other energy scales in the system, i.e. the high field limit. In our case, the high field limit is valid when \( |\alpha_{ij}^{ij} \Delta_{ij}| \ll |h_k| \) in (3.59).
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3.3.2 Perpendicular Coupling

We start with a Hamiltonian which only contains the perpendicular off-diagonal coupling. We will study the general case with both perpendicular and parallel couplings in section 3.3.4.

If we only allow the spins to couple to a single hopping amplitude, we can rotate all the $\alpha_{kij}$ to $x$-direction as well as keeping all $h_k$ at $z$-direction. The Hamiltonian can be written as

$$H = \Delta_o e^{i \sum_{(ij)} (\phi_{ij} + \sum_k \alpha_{kij}^z \sigma_k^z)} c_i^\dagger c_j + h.c. + \sum_k h_k \sigma_k^z. \quad (3.69)$$

To shorten the expressions, we again choose $\Delta_{\langle ij \rangle} = \Delta_o$. We can see later that this choice does not change the main result in this chapter.

The goal here is to calculate the reduced density matrix

$$\rho_{ij}(t) = \langle \sum_{k,l} G(i,k;t) G^\dagger(j,l;t) \rho_{kl}(t = 0) \rangle. \quad (3.70)$$

Here $\langle \ldots \rangle$ is the partial trace over the bath variables and $G(i,k;t) = \langle i|e^{iHt}|k\rangle$ is the propagator from site $i$ to site $k$ of the central particle.

We can write the Green’s functions in the path integral language:

$$G(i,k;t)\rho_{kl}(0)G^\dagger(j,l;t) = \langle \phi_i|e^{-iHt}|\phi_k\rangle \langle \phi_k|\rho(0)|\phi_l\rangle \langle \phi_l|e^{iHt}|\phi_j\rangle$$

$$= \langle \phi_i| \sum_{L=0}^\infty \frac{(-it)^L}{L!} H^L |\phi_k\rangle \langle \phi_k|\rho(0)|\phi_l\rangle \sum_{L=0}^\infty \frac{(it)^L}{L!} H^L |\phi_j\rangle$$

$$= \sum_{L,L',i_1,...,i_{L-1},j_1,...,j_{L'-1}} \frac{t^{L+L'} i^{L-1} j^{L'-1}}{L!L'!} \langle \phi_{i_1} | H | \phi_{i_{L-1}} \rangle \langle \phi_{i_{L-1}} | H | \phi_{i_{L-2}} \rangle \cdots \langle \phi_{i_1} | H | \phi_{i_0} \rangle \cdot \rho_{kl}(0) \langle \phi_{j_1} | H | \phi_{j_1} \rangle \cdots \langle \phi_{j_{L'-1}} | H | \phi_{j_{L'-1}} \rangle. \quad (3.71)$$

Here $L, (L')$ is the length of a path (conjugate path). The sequence $\{i_0,...,i_L\}$ ($\{i_0',...,i_{L'-1}'\}$) represents the sites passing by the central particle in this path, with $i_0,...,i_L$ being the indices of lattice sites. $i_0 = k, i_L = i$ ($i_0' = l, i_{L}' = j$) are the starting and ending sites of this path.

The summation over $L, L'$ and $i_1...i_{L-1}, i_1', i_{L-1}'$ is equivalent to the summation over all possible paths. So we can define the contribution function...
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$W$ of a pair of paths as

$$W_{i_0 \ldots i_L i'_{L'}} \equiv \frac{L^{L'}!}{L!L'^{L}!} \langle \phi_{i_0} | H | \phi_{i_{L-1}} \rangle \langle \phi_{i_L} | H | \phi_{i_{L-2}} \rangle \ldots \langle \phi_{i_1} | H | \phi_{i_0} \rangle$$

$$\cdot \langle \phi_{i'_{L'}} | H | \phi_{i'_{L'-1}} \rangle \langle \phi_{i'_{L'}} | H | \phi_{i'_{0}} \rangle,$$

(3.72)

and

$$G(i, k; t) \rho_{kl}(0) G^d(j, l; t) = \rho_{kl}(0) \sum_{\text{all possible paths}} W_{i_0 \ldots i_L i'_{L'} \ldots i'_0}.$$  (3.73)

The problem is now converted to calculating the path contribution function $W$.

At the first glance, we might want to treat the terms $\sum_k \alpha_{ik}^{ij} \sigma_k^x$ as a perturbation to the hopping amplitude $\Delta_o$. However, this picture is wrong since it ignores the dynamics of bath spin variables. The quantum spin is rotating around the field acting on it. In (3.69), the “effective” field acting on a bath spin is $\mathbf{h}_{\text{eff}} = \langle \sum_{ij} \Delta_o \hat{c}_i \hat{c}_j \sin \alpha_{ik}^{ij} + h.c. \rangle \hat{x} + h_k \hat{z}$. Because of the $\alpha_{ik}^{ij}$ term, this “effective” field keeps changing its amplitude and direction while the central particle is hopping from site to site. This cause the precession of bath spins. Since the interaction is through $\sigma_k^x$ terms, quantum mechanically, this precession of bath spins is equivalent to saying that some bath spins are flipped when the central particles hop from site to site.

Unfortunately, this behavior is not well described by the usual perturbative approach towards the central system. The dynamic of the bath variables are smeared out through the premature partial trace process and eventually lost in the Markovian approximation. On the other hand, OBA preserves the behavior and allows us to see this point clearly.
We can write down the contribution function $W$ using the OBA as

$$W_{i_0...i_{L'},...,i'_0} = \frac{(\Delta_0 t)^{L+L'-L-L'}}{L!L'!} \left( \delta \left( \sum_k h_k \sigma_k^z - M \right) e^{i \sum_k \alpha_k \hat{L} \sigma_k^x} \right) \cdot \delta \left( \sum_k h_k \sigma_k^z - M \right) e^{i \sum_k \alpha_k' \hat{L}' \sigma_k^x} \cdot \delta \left( \sum_k h_k \sigma_k^z - M \right) e^{i \sum_k \alpha_k' \hat{L}' \sigma_k^x} \cdot \delta \left( \sum_k h_k \sigma_k^z - M \right).$$

(3.74)

Here $\langle ... \rangle$ is the average over the spin bath variables. The operator $e^{i \sum_k \alpha_k \hat{L} \sigma_k^x}$ flips the bath spins. Suppose the initial polarization of bath spins is $M$; in this limit the bath spins cannot flip at all unless the total polarization $M$ is preserved. This is usually referred as a resonant transition in the literature. In the last line we again use (3.66) to expand the delta function, so that the initial and final state of a particular bath spin are related by the following transition operators:

$$T^k_L |\sigma_k^{in}\rangle = |\sigma_k^{out}\rangle.$$  

(3.75)

$$T^k_L = e^{i \xi_k h_k \sigma_k^z} e^{i \alpha_k \hat{L} \sigma_k^x} ... e^{i \xi_k h_k \sigma_k^z} e^{i \alpha_k' \hat{L}' \sigma_k^x} e^{i \xi_k h_k \sigma_k^z}.$$  

(3.76)

These transition operators describe the dynamics of the bath spins and preserve information about the precession of the bath spins.

The result will depend on the initial polarization $M$ of the bath spins. To make things as simple as possible we drop all degeneracy blocking effects, i.e., we make all $h_k$ the same. This is generally true if all bath spins have the same origin (e.g., nuclear spins of the same atoms, the same type of amino acid residue, etc.) In this case the bath can be separated into $2K+1$ different polarization groups with the degeneracy

$$p(M) = \frac{K!}{(K+M)!} \frac{1}{(K-M)!!2^K}.$$  

(3.77)

Here $M = \sum_k \sigma_k^z$ and $K$ is the total number of bath spins. One important comment is that the small $M \approx 0$ configurations have way larger phase space
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than the configurations with large \( M \). We could expand (3.77) as

\[
\log \frac{p(M)}{p(0)} \approx e^{-\frac{M^2}{2K}} + O(M^4).
\]  

The leading term away from the identity is proportional to \( \exp(-\frac{M^2}{2K}) \) for small \( M \). Henceforth, we can write the result as an expansion of the total polarization \( M \) as

\[
W_{i_0...i_{L'L',...i_0}} = \frac{(\Delta_0 t)^{L+L'}i_{L-L'}}{L!L'!} \left( \prod_n \int_0^{2\pi} d\xi_n \right) \left( \prod_n' \int_0^{2\pi} d\xi_n' \right) 
\]

\[
\cdot \frac{e^{-\frac{M^2}{2K}}}{\theta(K)} \sum_{M=-K}^{K} A_M(L, L').
\]  

(3.79)

Here \( \theta(K) = \sum_{M=-K}^{K} e^{-\frac{M^2}{2K}} \) is the normalization factor for this summation. The \( A_0(L, L') \) term represents the contribution from the \( M = 0 \) polarization group which is a major part of the total bath Hilbert space if the number of bath spins is large. The \( A_M(L, L') \) terms represent the contribution from other polarization groups. Actually, detailed calculations show that the contribution from the \( M = 0 \) polarization group is of \( O(\alpha^2) \) order while the contribution of the \( M = 1 \) polarization group is of order \( O(\alpha^4) \). Combined with the \( e^{-\frac{M^2}{2K}} \) factor, we can safely neglect all the \( M \neq 0 \) terms in (3.79).

The detailed calculations and expressions for the derivation of (3.79) can be found in Appendix C, as well as the calculations of both \( A_0(L, L') \) and \( A_1(L, L') \).

**Zero Polarization**

The term which contributes most is from the zero polarization group \( M = 0 \). If we ignore the non zero polarizations of the bath spins, we have the result (for details again check Appendix C):

\[
W_{i_0...i_{L'L',...i_0}}^0 = \frac{(i\Delta_0 t)^{L+L'}i_{L-L'}}{L!L!} \int_0^{\infty} \frac{z \, dz}{2\pi} e^{-\frac{1}{2}z^2}
\]

\[
\cdot \left( \prod_n J_0(\sum_k \alpha_k i_n^{i_n+1} z) \right) \left( \prod_n' J_0(\sum_k \alpha_k' i_n'^{i_n'+1} z) \right).
\]  

(3.80)

\( J_0(x) \) is the Bessel function of the first kind. Compared to the path integral of the bare system, we can see that \( J_0(\sum_k \alpha_k i_n^{i_n+1} z) \) can be absorbed
into $\Delta_0$. Actually, even if the system is not symmetric, this term can still be absorbed into $\Delta'_{\mu',\nu'}^{\mu',\nu'+1}$. This justifies the simplification we make by assuming all $\Delta_{ij} = \Delta_0$. As a result, we get a new Hamiltonian for the central particle as

$$H_0(z) = \sum_{\langle ij \rangle} \Delta_{ij} J_0(\sum_k \alpha_k^i z^j c_i^\dagger c_j). \quad (3.81)$$

And the density matrix evolution under such a Hamiltonian is

$$\tilde{\rho}_0(z; t) = e^{-iH(z)t} \rho_0 e^{iH(z)t}. \quad (3.82)$$

We can then write the reduced density matrix $\rho_{ij}(t)$ in the high field limit as

$$\rho(t) = \int_0^\infty z \, dz \, e^{-\frac{z^2}{2}} \rho_0(z; t). \quad (3.83)$$

Since $|J_0(\sum_k \alpha_k^i z)| \leq 1$, the renormalized Hamiltonian $H_0(z)$ is always more “localized” than the original one. The quenching factor

$$\kappa_{ij} = \left| \sum_k \alpha_k^i \right|^2, \quad (3.84)$$

makes the hopping terms small and the transfer between sites is suppressed. Therefore the excitations are more likely to be localized to their initial state. We can use $\kappa_{ij}$ as the control parameter of the decoherence in this high field region.

As a simple example, we consider the central system as a triangular lattice with three identical sites. The hopping amplitudes between three sites are $\Delta_{ij} = \Delta_0$. Without spin bath, the probability for the central particle to return to the original point after time $t$ is

$$P_{00}(t) = \frac{1}{9}(5 + 4 \cos(3\Delta_0 t)). \quad (3.85)$$

Then when we turn on the spin bath interactions, we have

$$\rho_{00}(t) = \int_0^\infty dz \, e^{-\frac{z^2}{2}} \frac{z}{9}[5 + 4 \cos(3\Delta_0 t J_0(\sum_k \alpha_k z))]. \quad (3.86)$$

Here we have assumed the symmetric case so $\kappa_{ij} = \kappa$.

We plot (3.86) for different $\kappa$ in Fig. 3.6. Since the OBA is mainly established to study the long time behavior of the system, it is interesting to check the asymptotic values as $t \to \infty$ for the reduced density matrix elements.
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Figure 3.6: Figures of $\rho_{00}(t)$ in (3.86) in high field limit. Different colors for different coupling strength parameter $\kappa = \kappa_{01} = \kappa_{12} = \kappa_{02}$ (3.84). Blue: $\kappa = 10^{-3}$; Red: $\kappa = 10^{-1}$; Green $\kappa = 10^2$;

There are two interesting things that need to be pointed out here. The first point concerns the asymptotic value of the diagonal elements. One might expect that as $t \to \infty$, the system will go to the thermal equilibrium state since spins are coupled to each site equally. For a 3-site symmetric system, this means $\rho_{00} \to \frac{1}{3}$. However,

$$\rho_{00}(t) \to \frac{5}{9} + \frac{4 \cos(3\Delta_o t + \theta(\kappa \Delta_o t))}{9\sqrt{1 + 9\kappa^2 \Delta_o^2 t^2}} \to \frac{5}{9}, \quad (3.87)$$

where $\theta(\kappa \Delta_o t)$ is a real integral function of $\kappa \Delta_o t$. This shows that in the high field limit, since the environmental spins are frozen in certain polarization subspaces, the dynamics of the central system is also “slaved” and is not susceptible to thermalization.

The second point concerns the off-diagonal terms in the reduced density matrix. The time evolution of off-diagonal elements gives the decoherence of the system. In the oscillator bath, these elements usually go to zero after a long time. But for this spin bath case, we have

$$\rho_{01}(1) \to \frac{1}{9}(-1 + \frac{e^{3i\Delta_o t}}{3i\Delta_o t \kappa + 1} - \frac{e^{-3i\Delta_o t}}{-3i\Delta_o t \kappa + 1}) \to \frac{-1}{9}. \quad (3.88)$$
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We can see that the coherence in the central system is “protected” by the bath spins. But this coherence protection phenomenon is not universal in all kinds of lattices. If we look at the general symmetric ring lattice with \( N \) identical sites we studies in the previous chapter, the density matrix after time \( t \) will be

\[
\rho_{jj'}^o(t) = \frac{1}{N^2} \sum_{n,n'=0}^{N-1} e^{-i(k_n j - k_{n'} j') + 4i\Delta_o t \sin[\phi - (k_n + k_{n'})/2] \sin[(k_n - k_{n'})/2]}, \tag{3.89}
\]

where \( k_n = \frac{2n\pi}{N} \) and \( \phi \) are the flux threading the ring. If there are no \( k_n \) and \( k_{n'} \) which satisfy \( \sin[\phi - (k_n + k_{n'})/2] = 0 \), then \( \rho_{jj'}(t) \to 0 \) for all off-diagonal terms \( j \neq j' \) as \( t \to \infty \). The long time asymptotic values for off-diagonal elements are non-zero only if we can find such \( k_n \) and \( k_{n'} \).

3.3.3 Spectral Function

The Fourier transform of the reduced density matrix element \( \rho_{00}(t) \) gives the spectral function. For a bare lattice

\[
S^o(\omega) = \frac{1}{2\pi} \int_{-\infty}^{+\infty} dt \rho_{00}(t)e^{i\omega t} = \frac{1}{N^2} \sum_{i,j} \delta(\omega - \varepsilon_i + \varepsilon_j), \tag{3.90}
\]

where \( \varepsilon_i \) are the energy eigenvalues. The spectrum is composed of several \( \delta \)-function peaks residing at all the resonant frequencies.

Again we take the \( N = 3 \) symmetric ring as an example; one then has

\[
S^o(\omega) = \frac{1}{9}[5\delta(\omega) + 2\delta(\omega - 3\Delta_o) + 2\delta(\omega + 3\Delta_o)]. \tag{3.91}
\]

There are three peaks at \( \omega = 0, \pm 3\Delta \). This basically reflects the band structure of this model.

In the previous sections, we studied both the pure phase decoherence limit with \( h_k = 0 \) and the high field limit with \( h_k \to \infty \). In this section we are going to study the spectrum of both cases. It helps us understanding the fundamental difference between these two types of environmental couplings.

**Pure phase decoherence** In the pure phase decoherence limit, we quote the result in the previous section for a 3-site systems, \( \text{viz.} \)

\[
\rho_{00}(t) = \frac{1}{3}(1 + 2J_0(2\sqrt{3}\Delta_o t) + 4 \sum_{p=1}^{\infty} J_{6p}(2\sqrt{3}\Delta_o t)F(6p)). \tag{3.92}
\]
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If we have a Gaussian distribution for the coupling $\alpha_k$, we can take $F(6p) = e^{-36\lambda p^2}$, with $\lambda = \frac{1}{2} \sum_k \alpha_k^2$. The Fourier transform of the Bessel functions is

$$\frac{1}{2\pi} \int_{-\infty}^{+\infty} J_n(at)e^{i\omega t} dt = \frac{e^{-i n \theta}}{2\pi \sqrt{a^2 - \omega^2}} \Theta(a^2 - \omega^2),$$

(3.93)

where $\Theta(x)$ is the Heaviside step function and $\theta = \arcsin \frac{\omega}{a}$. Notice that this expression is only nonzero when $\omega \in (-|a|, |a|)$. If $\omega^2 = a^2$, this function will diverge. However, this divergence is killed when $\lambda = 0$, i.e., for the bare ring case. The poles move to $\omega = 3\Delta$ due to the summation $\sum_{n=-\infty}^{+\infty} e^{in \arcsin \frac{\omega}{a}}$.

As a result, we have the spectral function in the pure phase decoherence limit,

$$S^p(\omega) = \frac{1}{3} [\delta(\omega) + \frac{2}{\pi \sqrt{12\Delta^2_0 - \omega^2}} \Theta(12\Delta^2_0 - \omega^2)] + 4 \sum_{p=1}^{\infty} \frac{\cos(6p \theta)}{\pi \sqrt{12\Delta^2_0 - \omega^2}} \Theta(12\Delta^2_0 - \omega^2) F(6p)].$$

(3.94)

Compared to the bare ring results, we can see that since we have a damping term in the series, the sum over $p$ converges. As a result, the poles move to $-2\sqrt{3}\Delta$ and $+2\sqrt{3}\Delta$. But there are still three divergent peaks in the spectrum, which means the system still preserve the band structure of the bare lattice qualitatively. And it is always true even when the interaction goes to infinity. For the limit when $\lambda \to \infty$, i.e., where there is an infinity number of bath spins, we still have three divergent peaks in the spectrum:

$$S^p(\omega) \to \frac{1}{3} [\delta(\omega) + \frac{2}{\pi \sqrt{12\Delta^2_0 - \omega^2}} \eta(12\Delta^2_0 - \omega^2)], \; \lambda \to \infty.$$  

(3.95)

**High Field Limit**  In the high field limit case, we have

$$\rho_{00}(t) = \int_0^\infty z \, dz \; e^{-\frac{z^2}{2}} \frac{1}{N^2} \sum_{i,j} e^{(\varepsilon_i - \varepsilon_j)j_0(\sum_k \alpha_k z)t}.$$  

(3.96)

Its Fourier transform is

$$S^h(\omega) = \frac{1}{N^2} \int_0^\infty z \, dz \; e^{-\frac{z^2}{2}} \sum_{i,j} \delta(\omega + (\varepsilon_i - \varepsilon_j)j_0(\sum_k \alpha_k z)).$$  

(3.97)
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We still consider the same three-site symmetric model. The spectral function is then

\[
S^h(\omega) = \frac{5}{9} \delta(\omega) + \frac{2}{9} \int_0^\infty z \, dz \, e^{-\frac{z^2}{2}} 
\cdot \left( \delta(\omega + 3\Delta_o J_0(\sum_k \alpha_k z)) + \delta(\omega - 3\Delta_o \prod_k J_0(\alpha_k z)) \right).
\]  

(3.98)

The first term is identical to the bare ring case, which indicates a \(\delta\)-peak at the origin. However, the two non-zero peaks are no longer divergent. Actually, for a frequency \(\omega\) which is close to the \(3\Delta_o\), the spectral function is

\[
S^h(\omega) \approx \frac{2}{27\Delta_o \kappa} e^{\frac{3\Delta_o - \omega}{3\Delta_o \kappa}}, \quad \omega \to 3\Delta_o.
\]  

(3.99)

In the weak coupling limit \(\kappa \to 0\), this function becomes a \(\delta\) function like the bare ring case. But it is no longer divergent for any nonzero \(\kappa\). In the strong coupling limit \(\kappa \to +\infty\) (for infinite numbers of bath spins), \(S^h(\omega)\) actually goes to zero for any nonzero \(\omega\). The whole spectrum becomes a single \(\delta\) function at the origin.

This means that unlike the pure phase decoherence case, the basic band structure of the central system is not preserved in the high field limit. The disappearance of non-zero peaks means these energy levels are no longer stable. Fig. 3.7 gives the plot of spectral functions in both cases.
3.3. High Field Region

Figure 3.7: Figures of spectral function for both the zero field limit (3.94) and the high field limit (3.98). Blue: zero field limit (the pure phase decoherence region); Red: High field limit. Each figure has different coupling strengths. The first row, left: $\kappa, \lambda = 0.001$; right: $\kappa, \lambda = 0.01$. The second row: left 0.05; right 0.1. The third row: left 0.5; right 1.0. The last row: 10.0.
3.3. High Field Region

3.3.4 General Coupling

Up to this point we have ignored the parallel coupling term \( \alpha_{ij}^\parallel \). To simplify the Hamiltonian, in the previous sections we also assumed that by rotating all of the \( h_k \) to the z direction, we can simultaneously align almost all the couplings \( \alpha_{ij}^\parallel \) to the x direction. We have established the method to deal with such systems and show the unique properties of this high field spin bath model. However, the restrictions on the directions of \( \alpha_{ij}^\parallel \) are not necessary and can be easily generalized to the most general case.

We start from equation (3.59) with \( h_k \) rotated to the z-direction:

\[
H = \sum_{<ij>} \Delta_o e^{i(\epsilon_{ij} + \sum_k \alpha_{ij}^k \sigma_k)} c_i^\dagger c_j + \sum_k h_k^z \sigma_k^z. \tag{3.100}
\]

Now \( \alpha_{ij}^k \) contains all three components \( \alpha_{ij}^{k,x} \), \( \alpha_{ij}^{k,y} \), \( \alpha_{ij}^{k,z} \). As long as \( h_k^z \) is still much larger than the other energy scales in this model, we can still use the OBA to study the result. The derivation is similar to the perpendicular coupling case but with a more complicated transition operator \( T_k^L \). Details can be found in Appendix C. The result can be written as

\[
W_{i_0...i_L}^{0...i_L} = \left( i \Delta_o \right)^{L+L'} e^{-\frac{1}{2} \sum_k \alpha_{ij}^{k,z} z} \left( \prod_n J_0(k_{ij}^n z) \right) \left( \prod_n' J_0(k_{ij}^n z) \right) \exp \left[ -\frac{1}{2} \sum_k \left( \sum_n \alpha_{ij}^{k,n} - \sum_n' \alpha_{ij}^{k,n'} \right)^2 \right]. \tag{3.101}
\]

Here \( \kappa_{ij}^g \) is a function associated with the perpendicular coupling \( \alpha_{ij}^{k,\perp} \), which is a direct generalization of (3.84), i.e.,

\[
\kappa_{ij}^g = \sqrt{\left( \sum_k \alpha_{ij}^{k,z} \right)^2 + \left( \sum_k \alpha_{ij}^{k,y} \right)^2} = \left| \sum_k \alpha_{ij}^{k,\perp} \right|^2. \tag{3.102}
\]

We also have an extra decoherence term, which depends on the parallel couplings \( \alpha_{ij}^{k,z} \). If the lattice is a symmetric ring, this term gives us a decoherence factor \( e^{-N(m-m')+j-j'} \lambda \) with \( \lambda = \frac{1}{2} \left( \sum_k \alpha_{ij}^{k,z} \right)^2 \). We immediately realize that this is exactly the decoherence factor we get in the pure phase decoherence case. Only the parallel coupling \( \alpha_{ij}^{k,\parallel} \) enters this decoherence factor, which is directly associated with the \( \lambda \) we introduced in (3.36).

Therefore, the parallel couplings \( \alpha_{ij}^{k,\parallel} \) and perpendicular couplings \( \alpha_{ij}^{k,\perp} \) have different effects. The former ones cause pure phase decoherence and the...
latter ones cause energy dissipation. We have already shown that these two have fundamentally different effects on the dynamics of the central system through their spectral. And this only relies on the angles between $h_k$ and $\alpha_k^{ij}$. Therefore, it allows us to manipulate the decoherence/dissipation properties of the system by changing the direction of fields $h_k$. If we know that $\alpha_k^{ij}$ are mostly lying in on plane, we could change the polarization field to the direction perpendicular to this plane, in order to protect the central system from phase decoherence and effectively localize the excitation hopping. On the other hand, if we want to protect the system from dissipation, we could rotate $h_k$ to reach a minimum $\kappa_k^{ij}$.

### 3.3.5 General Initial State of Spin Bath

Until now we have only considered the initial density matrix of the bath as an identity matrix. If the system is ergodic, it will eventually “forget” its initial state and the time average of the dynamics of the system will converge to a universal value. Therefore we could define an equilibrium state of the bath. But in previous sections, we have seen that the long term behaviour of the central system strongly depends on its initial state. It is worthwhile to explore the dependence of the bath behavior on its initial state.

In this section, we set the initial state to be $\rho_0 = \otimes \prod_k \rho_k(\hat{n})$, in which $\rho_k(\hat{n}) \equiv \frac{1}{2} I + \frac{1}{2} \hat{n} \cdot \sigma$, where $\hat{n}$ is the so called “Bloch vector” in 3-D space with $|\hat{n}| \leq 1$.

**Pure phase decoherence** Recall that the kernel of the influence functional in the pure phase decoherence region can be written as

$$F_0(\bar{p}) = \prod_k \cos(N\bar{p}|\alpha_k|),$$

where $\bar{p}$ is the winding number difference of the two path. This is derived based on an identity for the bath initial state. It is straight forward to evaluate the influence functional kernel in this new initial state:

$$F'_0(\bar{p}) = tr(\rho_0 e^{-i \sum_k N\bar{p} \alpha_k \cdot \sigma_k})$$

$$= \prod_k \langle \tilde{n}_k | e^{-i N\bar{p} \alpha_k \cdot \sigma_k} | \tilde{n}_k \rangle$$

$$= \prod_k \cos(N\bar{p} \alpha_k)(1 + i \hat{a}_k \cdot \hat{n} \tan(N\bar{p} \alpha_k))$$

$$= F_0(\bar{p}) \prod_k (1 + i \hat{a}_k \cdot \hat{n} \tan(N\bar{p} \alpha_k)).$$
3.3. High Field Region

The first term is just the original influence functional kernel. The correction term can be written as $e^{iN\hat{p}^k a_k \cdot \hat{n}}$ at the first order correction level. This basically gives a flux renormalization with the value $\Delta \Phi = \sum_k a_k \cdot \hat{n}$. It will not increase or reduce the decoherence time scale of the system, but change the Aharonov-Borm flux by a factor which is proportional to the inner product between the initial state vector $\hat{n}$ and the sum of the coupling vectors $\alpha_k$. Therefore, this initial state does not change the behavior of this system qualitatively.

For the high field limit, the expansion is more complicated. But we can still get some analytical results in some cases.

If $\hat{n}_k$ only has a z-component, which means the initial state is polarized in the same direction as the external field $\hat{h}_k$, the probability to find the system at a $\sum_k \sigma^z_k = M$ state is no longer proportional to $K!\left(\frac{M}{2}\right)^M\left(\frac{K-M}{2}\right)^{K-M}$. The effect of this term will be discussed next in the high order correction section. We can see the leading order is $O(\alpha^3_k)$. If $n_z^k = \pm 1$, then the system is completely frozen at an extreme state in which there is no freedom for the bath spins to flip. In this case, there is no decoherence of the central system. This bath only renormalizes the total flux of the central system as it does in the low field limit.

If $\hat{n}_k$ only has a y-component, which means the initial states are all polarized along the y-component, then we have similarly that

$$\rho_{ij}(t) = \int_0^\infty z \, dz \, J_0(n_y z) e^{-\frac{z^2 - n_y^2}{2}} \rho_{ij}^0(t; z). \quad (3.105)$$

The derivation of (3.105) can be found in Appendix C.6. There is an additional term $J_0(n_y z) e^{-\frac{n_y^2}{z^2}}$. This is a quenching term since it is always smaller than 1. In this case, dissipation effects are enhanced and the central system approaches its final states more quickly than the origin case.

We can see that the baths will have different decoherence effects depends on their different initial states. This is because when the $\hat{h}_k$ field is applied, the intrinsic dynamics of the bath itself matters. The memory effect of the bath can fundamentally change the decoherence or the dissipation rates of the central system, leading to various behaviors: from a pure phase decoherence ($n_x = n_y = 0, n_z \neq 0$) to a strong dissipation ($n_x \neq 0, n_y = n_z = 0$).

3.3.6 Finite $h_k$ Expansions

The orthogonal blocking approximation is only exact when the field $h \to \infty$. If $h$ is not sent to infinity but a finite large value, then the transitions between
3.3. High Field Region

different polarization group can happen and the result will be a series over \( \Delta_o/h \). The goal in this subsection is to calculate the next non-trivial order with a finite but large \( h \) and to show that we can systematically extend the OBA to any order of \( \Delta_o/h \).

To start, we go back to the original derivation of the OBA in 3.3.1. For a time-independent Hamiltonian \( H = H_0 + H_1 \), since \( I = \sum_M P_M \), we can insert this identity operator and rewrite the original Hamiltonian as

\[
H = \sum_{M,M'} P_M H_0 P_{M'} + H_1. \tag{3.106}
\]

From (3.63) we can write the propagator of this Hamiltonian as

\[
e^{iHt} = \sum_{L,M_0} (-it)^L g[t, \{M_j\}] P_{M_0} H_0 P_{M_1} H_0 ... P_{M_{L-1}} H_0 P_{M_L}. \tag{3.107}
\]

The function \( g \) is defined as

\[
g[t, \{M_j\}] = \int_0^\infty e^{i\xi} 2\pi d\xi \prod_{j=0}^L f(M_j, \xi, t), \tag{3.108}
\]

where \( f \) is defined in (3.65). In the OBA, we do not allow any transitions between different polarization groups. We only include the terms where \( M_0 = M_1 = ... = M_L = M \), and in this case \( g(t, \{M_j\}) = e^{iMht} / \sqrt{L!} \). This is equivalent to taking the following effective Hamiltonian:

\[
H = \sum_M P_M H_0 P_M + H_1, \tag{3.109}
\]

where \( P_M \) is the projection to polarization group \( M \). In the next leading order, we loosen the restrictions and allow the system to hop into another polarization group \( M' \) only once. That is we include paths which contain only one \( M_k = M' \) and another \( M_j (j \neq k) \) still equal to \( M \). The contribution to the propagator of such a path is

\[
(-it)^L g[t, \{M_j\}] P_{M_0} H_0 P_{M_1} ... H_0 P_{M_{L-1}} H_0 P_{M_L} P_M H_0 P_M, \tag{3.110}
\]

where

\[
g[t, \{M_j\}] = \sum_{a=1}^L \frac{-1}{(L-a)!} \frac{e^{-iMht}}{(i(M-M')ht)^a} + \frac{(-1)^L e^{-iM'ht}}{(i(M'-M)ht)^L}. \tag{3.111}
\]
Details of the calculation of $g$ can be found in Appendix C.1. We can see that now $g$ is a polynomial of $(i(M - M')\hbar t)^{-1}$. If we are only interested in the long time behavior of the system, we only need to keep the lowest order terms, which are proportional to $(i(M - M')\hbar t)^{-1}$, giving us

$$g[t, \{M_j\}] \approx -\frac{1}{(L-1)!}\frac{e^{-iM\hbar t}}{i(M - M')\hbar t} + O\left(\frac{1}{(i(M - M')\hbar t)^2}\right)$$  (3.112)

Then we can write the contribution of this path as

$$\frac{-1}{(L-1)!}\frac{(-it)^L}{(i(M - M')\hbar t)}e^{-iM\hbar t}P_M H_0...H_0 P_{M'} H_0...H_0 P_M$$

$$= \frac{(-it)^{L-1}}{(L-1)!}e^{-iM\hbar t}P_M H_0...H_0 P_{M'} H_0...H_0 P_M H_0...H_0 P_M$$  (3.113)

This is the same as the first order perturbation expansion of the following effective Hamiltonian:

$$H = \sum_M P_M \left( H_0 + \sum_{M' \neq M} \frac{H_0 P_{M'} H_0}{(M - M')\hbar} \right) P_M + H_1$$  (3.114)

Then we can follow the same procedure as in the OBA (Section 3.3.1) and write the path contribution function as

$$W_{i_0...i_L...i_0}^{i_L...i_L} = \frac{i^{L-L'}(\Delta_0 t)^{L+L'}}{L!L'!} \int_{-\infty}^{\infty} \prod_n \frac{\xi_n}{2\pi} \prod_{n'} \frac{\xi'_{n'}}{2\pi} \sum_{M'}$$

$$\langle e^{i\xi_0(\sum_k \sigma_k^z - M)} e^{i\sum_k \sigma_k^z} \rangle \langle e^{i\xi_{0'}(\sum_k \sigma_k^z - M')} e^{i\sum_k \sigma_k^z} \rangle$$  (3.115)

We can go through all the procedures in 3.3.2 before we summed over all possible $M'$ from $-K$ to $+K$. If the number of bath spins $K$ is very large, we can make the approximation that $K \to \infty$ and use the identity:

$$\sum_{M' = 1}^{\infty} \frac{\sin(M'\theta)}{M} = \frac{1}{2}(\pi - \theta), \text{ if } \theta \in (0, 2\pi).$$  (3.116)

Then the result of the next nontrivial order to the OBA can be written as:

$$\rho(t) = \int_0^\infty z dz \ e^{-z^2/2} e^{-iH(z)t} \rho(0) e^{iH(z)t}.$$  (3.117)
But $\tilde{H}_0(z)$ now becomes

$$\tilde{H}_0(z) = H_0(z) - \frac{\pi H_0^2(z)}{h},$$

(3.118)

with $H_0(z)$ defined by (3.81) as in the zeroth order OBA term.

We can systematically extend this method to higher orders by considering two or more different $M_j \neq M$ for each pair of paths. The standard procedure would be:

(i) calculate the integral $g[t, \{M_j\}]$ for the given number of allowed transitions;

(ii) discard terms higher than the given order of $((M - M')ht)^{-1}$. The coefficients in the expansion give the coefficients in the effective Hamiltonian;

(iii) follow the OBA procedure from Section 3.3.1 and sum over all possible polarization groups allowed.

At the end, we always get an expression similar to (3.117) but with a more complicated $\tilde{H}_0(z)$. 

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Chapter 4

Oscillatior Bath Model: Role of Vibrational Modes in Energy Transfer

The oscillator bath has been extensively studied, as reviewed in previous chapters. This problem is one of the fundamental topics in condensed matter physics as well as in other aspects of science. One can categorize different oscillator environments by their origins: i) acoustic phonons, the collective movements of the whole molecule: the coupling to the central system is long-range and weak for each single mode. ii) optical phonons: in the language of biology these are usually referred to the intra-molecular vibrational modes.

The former modes are usually weakly-coupled low energy modes whose numbers are enormous due to the huge number of degrees of freedom in biological complexes. They are associated with the low energy continuum in the spectrum. With these modes, decoherence goes hand-in-hand with dissipation\cite{18,19}. They have been extensively studied in the literature (see \cite{17,142} for a good summary). The latter ones, on the other hand, have localized microscopic origins (vibrations of chemical bonds, charged residues, etc.). These phonon modes can be observed as discrete peaks in the spectrum. Their numbers are fewer and their energy scale is higher, usually comparable to other relevant energy scales in the system. These modes also couple to the hopping amplitude of the excitons: excitons can hop down to other sites with lower site energies by exchanging energies with these vibrational phonons. The importance of these modes has been realized in resonant energy transfer processes in light harvesting molecules (see for example \cite{21}).

These vibrational modes couple not only to the on-site energies (which is known as the Holstein coupling in solid state physics\cite{23}), but also to the hopping amplitudes between the different pigments. The phonon-modulated transition was first mentioned by Peierls \cite{24} with regard to the Peierls transition. It was then studied in polyacetylene\cite{25,26} using the Su-Schrieffer-
4.1. Model of Resonant Energy Transfer into a Reaction Center

Heeger (SSH) model. It had already been realized that the SSH model can cause qualitatively different behaviors when compared with the Holstein model[27]. The Holstein couplings have been extensively studied in biological molecules, but these Peierls-type couplings have never been discussed in biological molecules. Experiments have already suggested that vibrational modes can directly couple to photon absorption[28]. It is natural to speculate that these modes also couple to the resonant energy transfer within molecules.

In this chapter, we investigate a dimer model for light harvesting molecules, which keeps the essential properties of a reaction-center-connected light harvesting complex. We try to address the role of phonons in resonant energy transfer by including phonon couplings of both Holstein type and Peierls type. We find that the two types of coupling affect the energy transfer rate in qualitatively different ways.

In this chapter we also study two-phonon interactions, i.e. the interaction terms which are proportional to $g_{kl}(a_k^\dagger + a_k)(a_l^\dagger + a_l)$. Two-phonon interactions are usually negligible for acoustic phonon modes in solid state physics because the coupling strength is usually much smaller than the linear interactions. There are arguments that for acoustic phonons interacting with electrons in a crystal, the lowest order in coupling strengths one can acquire from two-phonon couplings is an Ohmic spectral function which takes the form $J(\omega) \rightarrow \alpha \omega$[17]. This term can be absorbed into the one-phonon terms and is negligible since in general $\alpha \propto \frac{1}{N}$ for acoustic phonon modes[17]. However, this calculation only takes into account the second order cumulant and ignores higher order ones (which are not zero for the second order couplings). For optical phonons, on the other hand, there is little literature which considers the effect of the higher order couplings. In this chapter, we study two-phonon interactions between optical phonon modes with frequencies close to each other. We show that the two-phonon interaction can be mapped into a spin bath through path integral techniques.
4.1. Model of Resonant Energy Transfer into a Reaction Center

![Diagram of energy transfer in a reaction center](image)

Figure 4.1: An illustration of our whole system. In the top panel we show a schematic picture for our model. $c_1$ and $c_2$ are the two pigments in a molecule. The reaction center model in the hexagon is a Bethe lattice. Phonons couple to the system through $g_H$ (Holstein coupling) and $g_P$ (Peierls coupling). In the bottom panel, we show the energy difference in the model. $\Delta$ is the energy differences between $c_1$ and $c_2$. $2D$ is the bandwidth of the RC. $t_0$ is the hopping amplitude between $c_1$ and $c_2$.

4.1 Model of Resonant Energy Transfer into a Reaction Center

The model we will use to study the energy transfer into a reaction center is

$$H = H_0 + H_1 + H_2$$

(4.1)

$$H_0 = \varepsilon_2 c_2^\dagger c_2 + \varepsilon_1 c_1^\dagger c_1 + t_0 (c_2^\dagger c_1 + c_1^\dagger c_2) + t_1 (c_1^\dagger d_0 + d_0^\dagger c_1) + H_B$$

(4.2)

$$H_B = \sum_{\langle ij \rangle} V(d_i^\dagger d_j + h.c.) + \varepsilon$$

(4.3)

$$H_1 = \sum_{i=0,1} (g_H (a_i^\dagger + a_i) + \frac{g_H^2}{\Omega_i}) c_i^\dagger c_i$$

$$(g_P (a_2^\dagger + a_2) + \frac{g_P^2}{\Omega_2}) (c_2^\dagger c_1 + h.c.)$$

(4.4)

$$H_2 = \sum_{i=0,1,2} \Omega_i a_i^\dagger a_i$$

(4.5)
where $H_0$ is the bare molecular Hamiltonian without coupling to phonons, and $\{c_i^\dagger, c_i\}$ are the creation and annihilation operators of local excitons. We choose a dimer model in which there are only two pigments in a molecule. The exciton is first created at site $c_2$, which has the highest on-site energy $\varepsilon_2$ in the molecule. Let us define $\Delta \equiv \varepsilon_2 - \varepsilon_1$ is the energy difference between site $c_1$ and site $c_2$. Site $c_1$ is the pigment connected to the reaction center (RC). It couples to the RC through the term $t_1(c_1^\dagger d_0 + d_0^\dagger c_1)$. The center of the absorption spectrum of the RC is set at $\varepsilon = 0$ (an illustration of this model is shown in Fig. 4.1).

The interplay between RCs and photosynthetic antennae is complicated in vivo. Although the time scale for an RC to complete a chemical reaction circle is much longer than the exciton transfer time scale, the transfer time to the RC is actually close to the order of the intra-molecule transfer time (e.g. in purple bacteria, 20 ps for LH1-LH1 transfer, 56.8 - 130 ps for LH1-RC transfer, and 11.9 ps for RC-LH1 back transfer [153][67]; for smaller photosynthetic molecules the intra-molecule transfer rate is faster). The RC shuts down after receiving an exciton to complete the chemical reaction, but the transfer to the RC is still relevant under the relevant biological time scale. However, in most theoretical studies of the intra-molecule phonon-assisted transportation, the existence of RCs is either ignored or simply treated as a non-hermitian term in master equations for the dynamics. In the latter case, the effect of an RC is usually simplified into a single predetermined relaxation rate and the quantum-mechanical back transfer from the RC to the photosynthetic antennae is ignored. In this work we are going to study the effect of environmental phonons, not only on the transfer rate between two pigments within a single molecule, but also on the transfer rate to the RC. The transfer rate to the RC, as the most important measure of the biological functionality of this system, should not be predetermined. To avoid this, our phenomenological RC model should have a finite band width, and should be incorporated into the quantum model of the whole system.

In principle, many forms of lattice model which have finite band width could do the work. Here we choose a Bethe lattice (or Cayley tree) as our RC Hamiltonian $H_B$ in (4.1). A Bethe lattice is a lattice which has no closed loops and is completely characterized by the number of nearest neighbors $Z$. In Fig. 4.1 we show a portion of a Bethe lattice with $Z = 3$. In our calculations, we choose a lattice with infinite branching number $Z \rightarrow \infty$ but fixed bandwidth $D = 2V\sqrt{Z-1}$ to model the RC. In this case the propagator within the RC is known to be the Hubbard Green function $G_0^B(z) = \frac{2}{z+\sqrt{z^2-D^2}}$ [154]. In this chapter, we always set $D = 1$. There are
4.1. Model of Resonant Energy Transfer into a Reaction Center

several advantages to using this model: i) It does not contain any singularity within the spectrum, unlike the case of crystalline lattices. ii) The tree structure eliminates the possible emergent resonance between loop paths which would cause unnecessary complications. iii) It maintains analytic behavior near the band edges: the density of states is simply a semicircle. iv) It is exactly solvable and easy to study.

Without any phonon coupling, this RC model is equivalent to the Anderson-Fano model of impurity scattering. The exact solution is easily found [155]. The properties of this RC model are determined by both the energy difference $\varepsilon_1$ and coupling strength $t_1$. In the region $\varepsilon_1^2 + 4t_1^2 < D^2$, no localized state is formed and all excitons are eventually transferred to the RC (see D.2). This is the property we need for an RC, therefore we always work at $\varepsilon_1 = 0$ and $t_1 = 0.2D$ in this entire paper. A detailed description of our model for the RC can be found in Appendix D.2.

In (4.1), $H_2$ is the Hamiltonian of environmental vibrational modes. These modes couple to the central system through $H_1$. In (4.4), $g_H$ is the Holstein coupling which modulates the on-site energy of the system $\varepsilon_2, \varepsilon_1$; and $g_P$ is the Peierls coupling which modulates the hopping amplitude $t_0$ (see Fig. (4.1)). In this chapter, we only include the phonon modes whose frequency $\Omega$ is on resonance with the intra-molecular energy difference $\Delta$. The reason is that we are interested in the high energy vibrational modes, and various studies have already shown that these modes have the biggest effect in the resonant energy transfer process [21, 22, 156].

One comment we want to make is that Holstein couplings and Peierls couplings cannot be transformed into each other in our model, due to the existence of the RC. Without the RC, $g_H$ and $g_P$ can be transformed into each other by employing the canonical transformation $H \rightarrow e^S H e^{-S}$ with $S = \pi/4(c_0^\dagger c_1 - c_1^\dagger c_0)$. This transformation also changes the value $\Delta \rightarrow t_0$ and $t_0 \rightarrow -\Delta$. If there is a big difference between $\Delta$ and $t_0$, this transformation would change the basic physical features of the bare system. Among these light harvesting molecules which have been studied most (e.g. FMO, PE545), $\Delta$ is usually larger than $t_0$ by at least one order of magnitude [29, 157]. The addition of the RC also makes this transformation invalid, since the RC couples to the lattice.

The formal analytical solution of the bare system is easy to establish. The Green function of the whole Hamiltonian can be acquired by diagonalizing the bare Hamiltonian without the RC (for details see Appendix D.1). The numerical results we show in this thesis include 10 phonons in the whole system. The results already converge with fewer phonons. The transfer rate is defined as the probability of the exciton being transferred to the RC from
4.2 Holstein Coupling

the central system, i.e.

\[ \rho_{RC} = 1 - \rho_{22} - \rho_{11}, \tag{4.6} \]

where \( \rho_{22} \) and \( \rho_{11} \) are the elements of the reduced density matrix which represent the probability to find the exciton at site \( c_2 \) and site \( c_1 \) respectively. We also define the logarithmic fitting parameter \( \gamma \)

\[ (1 - \rho_{RC}) \propto e^{-\gamma t}. \tag{4.7} \]

The validity of this exponential relaxation approximation is discussed in Appendix D.3.

4.2 Holstein Coupling

In the pure Holstein coupling case \( g_P = 0 \), we start by confirming that the resonance condition \( \Omega_{0,1} = \Delta \) is important. We can see from Fig. 4.2(a) that even a little deviation from the resonant frequency has a significant impact on the transfer rate. We can see that there are multiple double peaks in the spectrum around \( \omega = n\Delta \) under the resonance condition (see Fig. 4.2(d)). The degenerate states associated with these peaks are the states in which either the exciton is at site \( c_1 \) with \( n \) phonons in the cloud, or the exciton is at site \( c_2 \) with \( n - 1 \) phonons in the cloud. These resonance states create extra channels for the exciton to move down to the lower energy sites. If we treat \( t_0 \) as a perturbation, the energy splitting of the lowest resonance states with energy \( E = \Omega = \Delta \) without the RC is

\[ \tilde{t}_0^H = \sqrt{2}\langle 0|c_2Hc_1^\dagger a_0^\dagger 0 \rangle = \sqrt{2}g_H \frac{t_0}{\Delta} e^{-g_H^2/\Omega^2}. \tag{4.8} \]

In the weak interaction limit \( g_H \ll \Omega \), this resonant transfer is the dominant mechanism for energy transfer, and \( \tilde{t}_0^H \) increases as \( g_H \) increases. This is the well known phonon-assisted transfer mechanism: the exciton leaves a phonon in the cloud to assist hopping to a low energy site [158]. We see that \( \tilde{t}_0^H \) starts to fall off when \( g_H \) is larger than \( \frac{\Omega}{\sqrt{2}} \). Fig. 4.4(a) is the illustration for the transfer rate \( \gamma \) as a function of coupling strength. We can see from that this property qualitatively holds for the pure Holstein case (the blue line in Fig. 4.4(a)): the coupling has an optimal value around \( g_H = 0.6 \) for the maximum transfer rate. This turning point has \( g_H \) smaller than \( \frac{\Omega}{\sqrt{2}} \). The reason is that distorted phonon clouds in the large coupling region also impede the transfer from site \( c_1 \) to the RC. The overlap between the distorted phonon cloud and free phonon cloud is \( \propto e^{-g_H^2/\Omega^2} \). In the strong
4.3 Peierls Coupling

Figure 4.2: Plots for the pure Holstein coupling case. For all plots, we choose the energy of site \( c_2 \) to be \( \varepsilon_2 = 2 \) and the energy of site \( c_1 \) to be \( \varepsilon = 0 \) (\( \Delta = 2 \)). The intra-molecules hopping amplitude is \( t_0 = 0 \). The RC has a bandwidth \( D = 1 \) and couples to the molecule by \( t_1 = 0.2 \). (a): Plot of the transfer rate when the phonon frequency is around the resonant point \( \Omega \approx \Delta = 2 \). From (b) to (d) the phonon frequency is set to be on resonance \( \Omega = \Delta = 2 \). (b): The transfer rate in the intermediate \( g_H \) region. (c): The reduced density matrix elements \( \rho_{11} \) (the population on site \( c_2 \)) and \( \rho_{00} \) (the population on site \( c_1 \)) when \( g_H = 1.5 \); the sub-panel is the transfer rate in the large \( g_H \) region. (d): Local spectra at site \( c_1 \).

interaction region, the exciton starts to oscillate within the molecule rather than propagating to the RC. The frequency of the oscillation is very close to the value of \( \tilde{t}_0^H \). We cannot observe such oscillation in the small \( g_H \) region (even though \( \tilde{t}_0^H \) could have the same value as in the strong interaction region), since the exciton will be promptly transferred to the reaction center once it reaches the \( c_1 \) site.

4.3 Peierls Coupling

In this section we study the Peierls type only coupling, i.e. \( g_H = 0 \). In a similar way to the previous case, the resonance condition \( \Omega \approx \Delta \) is again
4.3. Peierls Coupling

Figure 4.3: Plots for the pure Peierls coupling case. The values of the parameters in the Hamiltonian are the same as Fig. 4.2. Phonons couple to the hopping amplitude rather than the on-site energies. (a): Plot of transfer rate when the phonon frequency around the resonant point $\Omega \approx \Delta = 2$. From (b) to (d) the phonon frequency is set on resonance: $\Omega = \Delta = 2$. (b): the transfer rate in small $g_P$ region. (c): Plot of the reduced density matrix elements $\rho_{11}$ and $\rho_{00}$ when $g_P = 0.5$; the sub-panel is the transfer rate in intermediate $g_P$ region. (d): local spectra at site $c_1$.

important to the transfer rate (see in Fig. 4.3(a)). Under the resonance condition, the transfer rate is more sensitive to the size of the Peierls coupling $g_P$. We find that even when the Peierls coupling is so small that the change of the spectrum is almost invisible (see the $g_P = 0.06, g_P = 0.10$ spectra in Fig. 4.3(d)), the increase of the total transfer rate is already significant (Fig. 4.3(b)).

To understand this case, we again treat $t_0$ as a perturbation. The unperturbed Hamiltonian without the RC is a Jaynes Cummings Hamiltonian if we apply the Rotating Wave Approximation [159]. The unperturbed eigenvalues are

$$E_n = \Omega(n + \frac{1}{2}) \pm g_P\sqrt{n + 1}. \quad (4.9)$$

When $g_P$ is small, the energy states with the same $n$ are nearly degenerate with each other. The splitting of the lowest degenerate states with $n = 0$ is
4.3. Peierls Coupling

Figure 4.4: The plots obtained from fitting \((1 - \rho_{RC})\) as an exponential function of \(t\) for the pure Holstein case and the pure Peierls case. The parameters of the bare model are the same as the values in previous figures. The range of \(t\) is taken from 0 to 200. (a) The transfer rate \(\gamma\) as a function of \(g_H\) (blue circle) and \(g_P\) (red star); (b) The transfer rate \(\gamma\) as a function of \(\tilde{t}^H_0\) (blue circle) and \(\tilde{t}^P_0\) (red star); (c) The linear correlation coefficient between \(\log(1 - \rho_{RC})\) and \(t\); (d) the \(\log(1 - \rho_{RC})\) v.s. \(t\) plot in two transition regions: the lines within the dashed circle represent the region which the exponential model starts to fail; the line within the solid circle represent where the exponential behavior is restored.

simply

\[ \tilde{t}^P_0 = g_P. \]  

If we compare this with (4.8), we notice that the factor \(t_0/\Delta\) is missing in (4.10). This factor suppresses the energy splitting in the pure Holstein case. Under the condition \(t_0/\Delta \ll 1\), Peierls couplings are not negligible even when they are small compared with Holstein couplings. They have similar effects to the transfer rate as the Holstein couplings with much larger values. We can check whether the transfer rate agrees with each other when \(g_P\) and \(g_H\) are carefully chosen so that \(g_P = \sqrt{2g_H}\frac{t_0}{\Delta} e^{-g_H^2/\Omega^2}\). Actually we can see that both coupling agrees pretty well in Fig. 4.4(b) for the weak interaction region.

Fig. 4.4 is an illustration of the transfer rate \(\gamma\). In the weak interaction
4.3. Peierls Coupling

In this region, the transfer rate increases as $g_P$ increases, similar to the Holstein case (Fig. 4.4(a)). However, without the factor $t_0/\Delta$ in (4.10), the transfer rate is more sensitive to the Peierls coupling. It increases much faster for the pure Peierls coupling case under the condition $t_0/\Delta \ll 1$, which is the common situation in photosynthetic molecules. This indicates that Peierls couplings cannot be ignored even when they are much smaller than Holstein couplings. In this region, the perturbation theory works well for both cases and they agree with each other when we plot $\gamma$ as a function of $t_0$ in both cases (Fig. 4.4(b)). Even after the Holstein transfer rate starts to drop, the high transfer rate is still maintained in the Peierls case.

4.3.1 Jaynes-Cummings Model and Beyond

We can see from Fig. 4.4 that as we continue increasing the interactions ($g_P$ and $g_H$), the Peierls coupling shows a more interesting behavior. The spectrum is no longer qualitatively similar to the small interaction case, as shown in Fig. 4.3(d). The transfer speed $\gamma$ drops through different plateaus before it eventually reaches its final plateau when $g_P \geq 0.82$. In this subsection, we study the details of the transfer rate in the pure Peierls coupling case.

We first look at a simplified model, i.e. the Jaynes-Cummings Model (JCM) mentioned in the previous section. In this model, we omit the hopping term $t_0$ and the non-energy conserving term $a^\dagger c_2^\dagger c_1 + ac_2^\dagger c_1^\dagger$. The Hamiltonian becomes

\[
H = H_0 + H_1 + H_2 \tag{4.11}
\]

\[
H_0 = \varepsilon_2 c_2^\dagger c_2 + \varepsilon_1 c_1^\dagger c_1 + t_1 (c_1^\dagger d_0 + d_0^\dagger c_1) + H_B \tag{4.12}
\]

\[
H_1 = g_P (a^\dagger c_1^\dagger c_2 + ac_2^\dagger c_1) \tag{4.13}
\]

\[
H_2 = \Omega a^\dagger a \tag{4.14}
\]

with $H_B$ remaining the same (a Bethe Lattice with band width $D$). Under this approximation, the Hamiltonian can be solved analytically without the reaction center. In this section, we only consider the resonant case, i.e. $\Omega = \varepsilon_2$ and $\varepsilon_1 = 0$.

The energy levels of the JCM without the RC are

\[
E_n^\pm = \Omega (n + 1) \pm g_P \sqrt{n + 1}. \tag{4.15}
\]
4.3. Peierls Coupling

The eigenvectors associated with $E_0^\pm$ are

$$|n, +\rangle = \frac{\sqrt{2}}{2} (|1, n + 1\rangle + |2, n\rangle)$$

$$|n, -\rangle = \frac{\sqrt{2}}{2} (|1, n + 1\rangle - |2, n\rangle).$$

(4.16)

The state $|1, n + 1\rangle$ means the exciton is at site 1 and there are $n + 1$ phonons in the system. Using the equations in the Appendix [D.1], the resulting Green function $G_0(i,j;z)$ of the total system can be written as

$$[G_0^0(1,1; z)]_{pq} = \delta_{p,q} \frac{1}{2} \left( \frac{1}{z - p\Omega + g_P\sqrt{p}} + \frac{1}{z - p\Omega - g_P\sqrt{p}} \right).$$

(4.17)

Here $p$ and $q$ are the indices of phonon states and we are only interested in the case when $i = j = 1$. The poles of $G_0^0(1,1;z)$ are determined by the equation

$$t_1^2 \left( \frac{1}{z - p\Omega + \sqrt{(z - p\Omega)^2 - D^2}} \times \left( \frac{1}{z - p\Omega - g_P\sqrt{p}} + \frac{1}{z - p\Omega + g_P\sqrt{p}} \right) \right) = 1.$$  

(4.18)

This has two real solutions when $g_P \geq \sqrt{(1 - t_1^2)/p}$. For the lowest excitation space $|1, \pm\rangle$, we have $g_P \geq \sqrt{1 - t^2}$. If we start with the exciton sitting

Figure 4.5: The plot of the transfer rate $\gamma$ as a function of Peierls coupling $g_P$ for the JCM and the full Hamiltonian.
at site 2 and no phonon in the system initially, the two states associated with $E_1^\pm$ are actually the only relevant states in the system (since in the JCM we do not have terms which connect different $E_n$ subspaces). In Fig. 4.5 we can see that the JCM has a clear change of dynamics near $g_P = 1$. Beyond this point, there is a trapped region when two bound states are formed and the transfer rate towards the RC becomes small. On the other hand, in the weak interaction region $g_P < 0.1$, the JCM is also quite accurate compared with the full interaction cases. This shows that our perturbative description in the previous section is a good approximation in the weak $g_P$ region.

However, the pure JCM cannot recover the behavior between $0.1 < g_P < 1$. In particular, the decrease in the transfer rate near $g_P \approx 0.4$ is not captured. To recover this behavior, we add back the non-energy conserving term $a_c c_1^\dagger c_2 + a c_1 c_2^\dagger c_1$ so that the phonon interaction term becomes

$$H_1 = g_P(a_c a_c^\dagger + a c_1^\dagger c_2 + c_1 c_2^\dagger c_1)$$  \hspace{1cm} (4.19)$$

Now the system effectively becomes a Rabi Model without the RC. We can obtain the eigenstates and eigenvalues of the Rabi Model analytically, but this involves solving transcendental equations and there is no closed form for the results\[160]. Therefore we use only the numerical results here. In Fig. 4.6 we see the comparison between the results from JCM, Rabi and full Hamiltonians. We can see that Rabi Model agrees with the full Hamiltonian in the intermediate region $0.3 < g_P < 0.8$. In this region, we
4.3. Peierls Coupling

Figure 4.7: The first 11 energy levels as a function of Peierls coupling \( g_P \) for the JCM (top), the Rabi Model (middle), and the full Hamiltonian with \( t_0 = 0.1 \) (bottom).

notice that in the Rabi Mode, the transfer rate actually has several plateaus as it drops from 0.08 to 0.01. The most significant of these are the drop near \( g_P = 0.42 \) (first drop), \( g_P = 0.54 \) (second drop), and \( g_P = 0.82 \) (final drop). The final drop occurs earlier than in the JCM case \( (g_P = 1) \). This can be understood by comparing the eigenvalues of the Rabi Model and the JCM model (see Fig. 4.7). As we start with the state \( |2, 0\rangle \) (the particle at site 2, zero phonon), we expect that the eigenstates in this subspace are still dominant for the transfer even in the Rabi model. These states start as the green and red lines in Fig. 4.7(a). In the JCM, only these two states matter, and the final drop (which represents the formation of bound states) happens around the point where the energy level drops within the band range of the RC \((-1 < E < 1)\), which is around \( g_P = 1 \) (the intersection between the black dashed line \( E = 1 \) and the red line in Fig. 4.7(b)). In the Rabi case, however, the intersection point is at \( g_P = 0.833 \). This value is quite close to the final drop of the Rabi case at around \( g_P = 0.82 \). The extra terms in the Rabi Model introduce the interaction between the \( |1, \pm\rangle \) states with other \( |2n + 1, \pm\rangle \) states, so other states can also contribute to the total
4.4. The Full Hamiltonian

transfer rate. We can do a similar thing for the higher state subspace. The next subspaces are the two $|3, \pm\rangle$ states which starts at $E = 6$. We find the intersection point between the $E = 5$ line and the brown line in Fig. 4.7(b). This point turns out to be at $g_P = 0.53$, which is close to the value of $g_P$ at the second drop. We follow the same procedure for the $|5, \pm\rangle$ states and the result is $g_P = 0.43$ which is close to the value of the first drop. Based on this observation, we suggest that the multiple drops between $0.3 < g_P < 0.8$ can be understood as the shutdown of different transfer channels associated with the $|2n + 1, \pm\rangle$ subspaces. For higher states, the plateau is too small to be tracked in the calculation and we see a continuous decrease.

The last step is to restore the $t_0(c_2^\dagger c_1 + c_1^\dagger c_2)$ term in the Hamiltonian. In the weak interaction region, the parameter $t_0$ in the original Hamiltonian is not that important for the qualitative behavior. We can see in Fig. 4.5 that the transfer rate $\gamma$ is very robust against changes in $t_0$. The $t_0(c_2^\dagger c_1 + c_1^\dagger c_2)$ term does introduce an interaction between the $n = 1$ states and arbitrary $|n, \pm\rangle$, so there are more dips in the pattern. The overall behavior does not change qualitatively from $t_0 = 0.01$ to $t_0 = 0.2$, as shown in Fig. 4.5.

4.4 The Full Hamiltonian

In this section we study the full Hamiltonian (4.1) with both the Peierls coupling and the Holstein coupling. Due to the large parameter space we are not going to do a thorough exploration. We mainly focus on finding whether the previous results hold in this case. We find in Fig. 4.8(a) that the local spectrum is mainly determined by the Holstein coupling, but the transfer rate to the RC is very sensitive to changes in $g_H$ even when $g_P \ll g_H$ (Fig. 4.8(c,d)).

In a similar way to the Holstein coupling only case, there is an optimal value of the coupling $g_H$ when the transfer rate achieves the fastest transfer rate. (in Fig. 4.8(c), the optimal value is around $g_H = 0.6$ if $g_P$ is fixed). If $g_H$ is fixed, the system also behaves similarly to the Peierls-only case, as the transfer rate increases as $g_P$ increases (Fig. 4.8(d)). Comparing these two figures we confirm that the transfer rate to the RC is still very sensitive to $g_P$ even when a much larger $g_H$ exists, although Fig. 4.8(a) shows that the local spectrum is mainly determined by the Holstein coupling.

In the mixed case, if we follow the perturbation argument, the energy splitting of the lowest degenerate states is

$$t_0 = \sqrt{A^2 + B^2},$$

(4.20)
4.4. The Full Hamiltonian

Figure 4.8: Plots when both types of phonon couplings exist. The values of the parameters in the Hamiltonian are the same as for Fig.4.2. (a): The local spectra at site $c_1$ with various couplings. (b): The transfer rate when $\tilde{t}_0$ is fixed at 0.05, with $g_P$ determined by (4.20). (c): The transfer rate when $g_P$ is fixed at 0.06. (d) the transfer rate when $g_H$ is fixed at 0.7.

with $A = \sqrt{2}g_H \frac{\tilde{t}_0}{\Omega} e^{-\frac{g_H^2}{\Omega^2}}$ and $B = g_P e^{-\frac{g_H^2}{\Omega^2}}$. In Fig (4.8b), we keep $\tilde{t}_0$ fixed and vary $g_H$. We see that in the small $g_H$ region ($g_H = 0.1, 0.4, 0.7$), the curves agree with each other well. In the large $g_H$ case ($g_H = 1.0, 1.2$), the curves start to deviate since the phonon cloud coupled to site $c_1$ is too distorted to allow the exciton to move to the RC.

In Fig.4.9 (a), we fix $g_H$, and the behavior of $\gamma$ is qualitatively the same as for the pure Peierls case shown in Fig.4.3 (a). The plateau effect is barely noticeable due to the accuracy of the numeric calculation. The initial increase of the transfer rate to the RC is still rapid and sensitive to $g_P$, even when a relatively large $g_H$ exists. The result with $g_P$ fixed is shown in Fig.4.9 (b). The choice of $g_P$ is already large enough ($g_P = 0.05$ is already larger than the turning point of $\tilde{t}_H$ in the pure Holstein case, see Fig. 4.4(b)) for the transfer rate $\gamma$ to decrease monotonically as $g_H$ increases. In both cases, the existence of the Peirels coupling changes the behavior of the system qualitatively, even when its value is much smaller than the Holstein coupling.
4.5. Role of Off-Diagonal Couplings in Resonant Energy Transfer

In the previous sections, we investigated a dimer model of light harvesting molecules coupled to an RC and resonating environmental phonon modes. We included two different types of phonon couplings and we studied their effects on both the transfer rate to the RC and the local spectra. In the case of the pure Holstein coupling, we demonstrated the resonant phonon-assisted transfer mechanism: the coupling to phonons increases the transfer rate when it is small but eventually makes the exciton too heavy to propagate. We also showed that it can be described by degenerate perturbation calculations, in both the weak and strong coupling regions. In the case of the pure Peierls coupling, we found that in the weak coupling region \( g_P \ll \Omega \), if
4.6. Two-Phonon Interactions for Optical Phonons

$t_0/\Delta$ is small, a large Holstein coupling $g_H$ is equivalent to a small Peierls coupling $g_P = \sqrt{2} g_H t_0/\Delta^2 e^{-\sigma_H^2/\Omega^2}$. A small $g_P$ will have almost no effect on the local spectra, but still affects the transfer rate significantly. In the intermediate region $g_S \sim \Omega$, the Peierls couplings start to cause qualitatively different behavior compared with the Holstein couplings. The transfer rate is still high in this region. The spectrum contains complicated peaks located away from the resonant points, and the perturbation calculation starts to fail. We confirmed that our results in the two individual cases are still significant. The interesting properties of the Peierls couplings are not overshadowed by the existence of large Holstein couplings.

The excitation energy of the photosynthetic molecules (Bchls in the FMO case) changes due to the effect of the surrounding charges and solvent dielectricity, which is the major source of the Holstein coupling. Meanwhile, the hopping amplitude between Bchls is also modulated by the vibrational modes, since these modes change the wave function as well as the overlap integral between sites. This leads to the Peierls coupling term in the Hamiltonian. Most works only consider the former term and ignore the effect of the latter, since it is usually small and negligible in the spectrum. Our studies suggested that we cannot ignore the phonon-modulated hopping amplitude in the resonant energy transfer mechanism within biological molecules. The large $t_0/\Delta$ ratio in various light harvesting molecules makes Peierls couplings important even if they are negligible in the spectra.

In the next chapter, we are going to use a more realistic model of the light harvesting molecules, which contains more sites and more phonon modes compared with (3.1), to study the role of vibrational modes in these biological systems. It will be interesting to know whether or not the Peierls coupling plays a functionally important role in real-life photosynthetic processes. Our findings also show that Peierls couplings have qualitatively different dynamics beyond the small coupling region which requires new theoretical tools to describe. This might not be the case in photosynthetic molecules but is still interesting on its own from theoretical stand point, which could lead to interesting further research.

4.6 Two-Phonon Interactions for Optical Phonons

In this section we study the second-order phonon couplings for optical phonons. We start the section by studying two-phonon interaction terms added to the energy transfer model we have already studied in 4.2. In this simple
model, we neglect the linear couplings and find out that the cross interaction terms can be mapped into a spin bath if the frequency of the two interacting phonon modes are close to each other. The effect of this interaction is similar to the pure phase decoherence region in Section 3.2. In the second part of this section, we employ the path integral method to show that such a mapping is general for optical phonon modes when the linear terms are not zero.

In this section, we assume that the coupling is always to the spatial coordinate of the bath oscillators (i.e. $\hat{x} = a^\dagger + a$) for simplicity.

### 4.6.1 Two-Phonon Interaction in the Holstein model

First we consider two-phonon interactions added to the energy transfer model which has already been studied in previous sections. The Hamiltonian can now be written as

$$
H = H_0 + H_1 + H_2 \tag{4.21}
$$

$$
H_0 = \varepsilon_2 c_2^\dagger c_2 + \varepsilon_1 c_1^\dagger c_1 + t_0 (c_1^\dagger c_1 + c_2^\dagger c_2)
+ t_1 (c_1^\dagger d_0 + d_0^\dagger c_1) + H_B \tag{4.22}
$$

$$
H_B = \sum_{\langle ij \rangle} V (a_i^\dagger d_j + \text{h.c.}) \tag{4.23}
$$

$$
H_1 = \sum_{i=0,1} \left( g_i^{(1)} (a_i^\dagger + a_i) + g_i^{(2)} (a_i^\dagger + a_i)^2 + \frac{g_i^{(1)2}}{\Omega_i} \right) c_i^\dagger c_i \tag{4.24}
+ g_{ij}^{(2)} (a_i^\dagger + a_i) (a_j^\dagger + a_j) (c_i^\dagger c_j + c_j^\dagger c_i)
$$

$$
H_2 = \sum_{i=0,1,2} \Omega_i a_i^\dagger a_i. \tag{4.25}
$$

We see that there are two types of interaction being added to the system: the self interaction terms,

$$
g_i^{(2)} (a_i^\dagger + a_i)^2; \tag{4.26}
$$

and the cross terms,

$$
g_{ij}^{(2)} (a_i^\dagger + a_i) (a_j^\dagger + a_j). \tag{4.27}
$$

We still assume that $\Omega_i = \varepsilon_2 - \varepsilon_1 = \Omega$, which is the resonance condition. We also assume that there are only two phonon modes in the system; one couples to site-1 and another couples to site-2.
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Self Interaction Terms

If there are no cross interaction terms, i.e. \( g_{ij}^{(2)} = 0 \) \( \forall i \neq j \), then there are only self-interacting terms \( g_{ii}^{(2)}(a_i^\dagger + a_i)^2 \). We can follow the same perturbative argument as we did in Section 4.2. Without loss of generality, we assume \( g_{ii}^{(2)} = g^{(2)} \), \( \forall i \) and \( g_{ii}^{(1)} = g^{(1)} \), \( \forall i \).

The truncated Hamiltonian in the lowest degenerate energy subspace is

\[
H = \begin{pmatrix}
0 & A & B \\
A & 0 & 0 \\
B & 0 & \Delta \omega
\end{pmatrix}
\] (4.28)

where

\[
A = g^{(1)} \frac{2\Omega}{(\Omega + \Omega')^2} e^{-(2\Omega')^2 \Omega + \Omega'} \\
B = -g^{(1)} \sqrt{\frac{\Omega}{\Omega'}} \frac{2\Omega}{(\Omega + \Omega')^2} e^{-(2\Omega')^2 \Omega + \Omega'}.
\]

Here \( \Delta \omega = \Omega' - \Omega \). \( \Omega' = \sqrt{\Omega + g^{(2)}} \) is the detuned frequency caused by the second order coupling term \( g^{(2)} \). When \( g^{(2)} = 0 \), we have \( \Omega = \Omega' \), and (4.28) reduces to the result of the first order phonon couplings in Section 4.2. Compared to the previous result, we can see that the dependence on the first order coupling \( g^{(1)} \) is similar to what we found in previous sections and there is nothing qualitatively changed by the second order couplings. The self-interacting terms only reduce the effective transfer amplitude \( \tilde{t}_H \) by a certain amount in the weak interaction region. We find that the transfer rate decreases as we increases the second order coupling \( g^{(2)} \), although the amount it changes by is not very significant unless one increases the \( g^{(2)} \) beyond 0.1\( \Omega \), which is quite large compared to the first order couplings. This is what we expected since the self interacting terms effectively change the phonon frequency a little bit, and cause the system to deviate from the resonance condition, which results in the decrease of the energy transfer.

Cross Interaction Terms

On the other hand, the cross interaction terms \( g_{ij}^{(2)}(a_i^\dagger + a_i)(a_j^\dagger + a_j) \) are more interesting than the self interaction terms. We consider the case in which the two coupled modes \( \Omega_k \) and \( \Omega_l \) have similar energy \( \Omega_k \approx \Omega_l \). Including the cross interaction terms, we find the effective Hamiltonian matrix in the
resonance energy level subspace with $N$ phonons to be
\[
H_1 = \varepsilon + \begin{pmatrix}
N\Delta\omega & \sqrt{N}g_{ij}^{(2)} & 0 & \cdots & 0 \\
\sqrt{N}g_{ij}^{(2)} & (N-1)\Delta\omega & \sqrt{2(N-1)}g_{ij}^{(2)} & \cdots & 0 \\
0 & \sqrt{2(N-1)}g_{ij}^{(2)} & (N-2)\Delta\omega & \cdots & 0 \\
\vdots & \ddots & \ddots & \ddots & \ddots \\
0 & \cdots & \Delta\omega & \sqrt{N}g_{ij}^{(2)} & 0
\end{pmatrix},
\]
where $\Delta\omega = \Omega_i + 2g_{ij}^{(2)} - \Omega_j - 2g_{ ij}^{(2)}$. This can be directly mapped into a spin $N/2$ system
\[
H_1 = \varepsilon_N + \Delta\omega S^z_{N/2} + 2g_{ij}^{(2)}S^x_{N/2}.
\]
where the $S^x,y,z_{N/2}$ are spin operators of $N/2$ spins, and $\varepsilon_N = \varepsilon + \frac{N}{2}\Delta\omega + g_{ij}^{(2)} + g_{ij}^{(2)}$. The linear coupling couples the Hilbert space between different spin spaces which cannot be represented in the form of these spin operators.

This mapping can be easily verified in some simple models. As an example, we consider two identical phonon modes that couple to the off-diagonal terms of (4.21) with only the second order coupling. This problem, without the RC, is equivalent to the spin boson model:
\[
H = t\sigma^x + g_{12}^{(2)}(b_1^\dagger + b_1)(b_2^\dagger + b_2)\sigma^z + \Omega_0(b_1^\dagger b_1 + b_2^\dagger b_2).
\]
This can be further transformed into
\[
H = t\sigma^x + \frac{1}{2}(g_{12}^{(2)}(b_1^\dagger + b_1)^2 - g_{12}^{(2)}(b_2^\dagger + b_2)^2)\sigma^z + \Omega_0(b_1^\dagger b_1 + b_2^\dagger b_2).
\]
In the path integral picture, we marked the path of the central system by $\{t_n\}$, which satisfies $0 = t_0 < t_1 < ... t_{N-1} < t_N < t_{N+1} = T$. Any path of the central spin from $t = 0$ to $t = T$ which starts at $\sigma^z = -1$ can be described by a set of $\{t_n\}$ such that the path can be represented by
\[
\{t_n\} := -\frac{1}{2} + \sum_{n=1}^{n=N} \eta(t - t_n)(-1)^{n+1}.
\]
The propagator of a phonon mode which has a time dependent frequency $\Omega(t)$ can be written as
\[
\langle x|Te^{-i\int_0^T H(t')dt'}|y \rangle = \frac{1}{\sqrt{2\pi i \sin \Theta(t)}} e^{\frac{i}{2\sin \Theta(t)}((x^2+y^2)\cos \Theta(t) - 2xy)},
\]

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where \( \Theta(t) = \int_0^t \Omega(t) \, dt \). If the initial state is a thermal state with \( k_B T = \beta^{-1} \), the influence functional of a single phonon associated with these two paths \( \{t_n\}, \{t'_m\} \) can be represented by

\[
F_1(\{t_n\}, \{t'_m\}) = \frac{1}{Z} \sqrt{2\pi i} \sin(\Theta(t) - \Theta(t') - i\beta \Omega_0) \cdot \int_{-\infty}^{\infty} dx \exp \left( -\frac{i(1 - \cos(\Theta(t) - \Theta(t') - i\beta \Omega_0))}{\sin(\Theta(t) - \Theta(t') - i\beta \Omega_0)} x^2 \right) = \frac{\sinh \frac{1}{2} \beta \Omega_0}{i \sin \frac{1}{2}(\Theta(t) - \Theta(t') - i\beta \Omega_0)}.
\]

(4.35)

If one considers both phonons, then the total influence functional is the product of them

\[
F(\{t_n\}, \{t'_m\}) = F_1(\{t_n\}, \{t'_m\}) F_2(\{t_n\}, \{t'_m\}) \frac{1}{\sinh \frac{1}{2} \beta \Omega_0} \left( \frac{4 \sinh^2 \frac{1}{2} \beta \Omega_0}{e^{\beta \Omega_0} + e^{-\beta \Omega_0} - 2 \cos(\Theta_0(t) - \Theta_0(t'))} \right) = \frac{1}{1 + \frac{\sin^2 \frac{1}{2}(\Theta_0(t) - \Theta_0(t'))}{\sinh^2 \frac{1}{2} \beta \Omega_0}}.
\]

(4.36)

Notice that \( \Theta(t) \) and \( \Theta'(t) \) are generated by an identical central path with the opposite sign of coupling \( \pm B_{12} \). Therefore, we have the relation that \( \Theta(t) + \Theta'(t) = \frac{T}{2}(\Omega_+ + \Omega_-), \ \frac{1}{2}(\Theta(t) - \Theta'(t)) = \frac{1}{2}(\Omega_+ - \Omega_-) \sum_{n}(t_{n+1} - t_n)(-1)^n := \Theta_0(t) \). Based on this we can rewrite the denominator as \( \frac{1}{2}(\cos(\Theta_0(t) - \Theta_0(t')) - \cos(-i\beta \Omega_0)) \). Then for this spin boson model we have

\[
F(\{t_n\}, \{t'_m\}) = \frac{4 \sinh^2 \frac{1}{2} \beta \Omega_0}{e^{\beta \Omega_0} + e^{-\beta \Omega_0} - 2 \cos(\Theta_0(t) - \Theta_0(t'))} = \frac{1}{1 + \frac{\sin^2 \frac{1}{2}(\Theta_0(t) - \Theta_0(t'))}{\sinh^2 \frac{1}{2} \beta \Omega_0}}.
\]

(4.37)

On the other hand, if we start with the spin Hamiltonian as in (4.30), we
4.6. Two-Phonon Interactions for Optical Phonons

have the influence functional

\[ F(t_n, t'_m) = \sum_{N=0}^{\infty} \left( \frac{e^{-\beta N \Omega_0}}{Z} \sum_{S_N = -N/2}^{N/2} e^{2i g^{(2)}_{12} s_N(z)(\sum_n (t_{n+1} - t_n)(-1)^n - \sum_m (t'_{m+1} - t'_m)(-1)^m)} \right) \]

\[ = \sum_{N=0}^{\infty} \left( \frac{e^{-\beta N \Omega_0}}{Z} \frac{\sin(N + 1)(\tilde{\Theta}(t) - \tilde{\Theta}'(t))}{\sin(\Theta(t) - \Theta'(t))} \right) \]

\[ = \frac{1}{1 + \frac{\sin^2 \frac{1}{2}(\Theta(t) - \Theta'(t))}{\sinh^2(\frac{1}{2}\beta \Omega_0)}} \]  

(4.38)

where \( Z = \sum_{N=0}^{\infty} (N + 1)e^{-\beta N \Omega_0} = \frac{e^{-\beta \Omega_0}}{(1 - e^{-\beta \Omega_0})^2} \), and \( \tilde{\Theta}(t) = g^{(2)}_{12} \sum_n (t_{n+1} - t_n)(-1)^n \). In the small coupling region, \( \Omega_{\pm} = \sqrt{\Omega_0(\Omega_0 \pm 2g^{(2)}_{12})} \approx \Omega_0 \pm g^{(2)}_{12} \), and \( \tilde{\Theta}(t) \approx \Theta(t) \). Therefore these two expressions (4.37) and (4.38) agree with each other in this weak interaction regime.

For the light harvesting molecules problem, we realize that the optical phonon (the intra-molecule vibronic modes) has a very high excitation energy compared to room temperature (from 500 \( cm^{-1} \) to 1500 \( cm^{-1} \)), and also high compared to the hopping amplitude of the excitons (around 10 \( cm^{-1} \)). Therefore, in the case when \( 2\omega_{k,l} \gg T \), we can replace these two resonating energy levels as a two level system, i.e. an environmental spin. In (4.29), let us take \( N = 1 \). Then if \( \Delta \omega \ll |g^{(2)}_{12}| \), this is exactly the pure phase decoherence term described in the Section 3.2. The phase decoherence rate is governed by the parameter \( \kappa = \sum_i \text{Re}(g^{(2)}_{12})^2 \), which is not necessarily small after summation of all correlated energy levels.

4.6.2 A General Path Integral Formalism

In the previous subsection, we showed that the cross interaction terms of the two-phonon interactions can be mapped into a spin bath of the simplest spin boson model without first order phonon couplings. In this section we try to show that this mapping is still valid when we include the first order couplings, making it applicable to the most general models.

In this section, we use the path-integral formalism and the Lagrangian
of the system takes the form

\[ \mathcal{L} = \mathcal{L}_0 + \mathcal{L}_I + \mathcal{L}_B \]

\[ \mathcal{L}_0 = L_0(t, q(t), \dot{q}(t)) \]

\[ \mathcal{L}_B = \sum_{\alpha} \frac{1}{2} m_\alpha \dot{x}_\alpha^2 - \frac{1}{2} m_\alpha \omega_\alpha^2 x_\alpha^2 \]

\[ \mathcal{L}_I = \sum_{\alpha} g^{(1)}_\alpha x_\alpha q(t) + \sum_{\alpha, \beta} g^{(2)}_{\alpha \beta} x_\alpha x_\beta G[q(t)] \]

where \( \mathcal{L}_0 \) is the Lagrangian of the central system and \( q(t) \) is the generalized coordinate. The Lagrangian of the phonon bath is \( \mathcal{L}_B \), and \( \mathcal{L}_I \) is the interaction term. Without loss of generality we assume the phonons couple directly to \( q(t) \) to first order. The first order linear coupling is \( g^{(1)}_\alpha \), and \( g^{(2)}_{\alpha \beta} \) is the second order coupling.

For a product initial state, we can write the influence functional kernel (Feynman-Vernon kernel) as

\[ \mathcal{F}[q, q'] = \int dx_i dx'_i dx_f \rho_B(x_i, x'_i) F(q; x_i, x_f) F^*(q'; x'_i, x_f) \]

In which \( \rho_B(x_i, x'_i) \) is the initial density matrix of the phonon modes and

\[ F(q; x_i, x_f) = \int_{x(0)=x_i}^{x(T)=x_f} Dx \exp \left( i \int_0^T dt (\mathcal{L}_B(x) + \mathcal{L}_I(q(t), x)) \right) \]

Up to this point, these are all standard procedures. The next step is to evaluate the functional integral \( F(q; x_i, x_f) \). If one has only the first order coupling, the calculations are straightforward. Unfortunately, we now have second order terms in \( \mathcal{L}_I \). To reduce the second order terms to the first order terms, we introduce a set of auxiliary variables \( y(t) \) and use the identity

\[ \exp \left( i \int_0^T dt q(t) \sum_{\alpha, \beta} g^{(2)}_{\alpha \beta} x_\alpha x_\beta \right) \]

\[ = \frac{1}{Z_y} \int Dy \exp \left( -\frac{1}{4} \sum_{\alpha, \beta} \int_0^T dt y_\alpha [A^{-1}(t)]_{\alpha \beta} y_\beta + i \sum_\alpha \int_0^T dt y_\alpha(t) x_\alpha(t) \right) \]

where the matrix \( A(t) \) contains all the information about the two-phonon interactions:

\[ [A(t)]_{\alpha \beta} = -i G[q(t)] g^{(2)}_{\alpha \beta} \]

(4.46)
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Here $Z_y$ is the normalization factor, and $\log Z_y \propto \int dt \log \det A(t)$. Now the second order couplings are reduced to first order couplings: $g^{(1)}_\alpha x_\alpha q(t) \rightarrow (g^{(1)}_\alpha q(t) + y(t)) x_\alpha$. Therefore, we can use the result of the linear couplings for the influence functional kernel.

**Influence Functional Kernel**

If the initial phonon state is a thermal state, the influence functional kernel for the real time path integral can be written as

$$
\mathcal{F}[q, q'] = \int D\mathbf{y} \int D\mathbf{y}' \frac{1}{Z_y Z_{y'}} \exp \left[-\Phi(y, y', q, q')\right] \exp \left\{-\frac{1}{4} \sum_{\alpha, \beta} \int_0^T dt \left( [A^{-1}(t)]_{\alpha \beta} y_\alpha y_\beta + [A^{-1}(t)]_{\alpha \beta} y'_\alpha y'_\beta \right) \right\},
$$

(4.47)

Here we have

$$[A'(t)]_{\alpha \beta} = iG[q'(t)]^{(2)}_{\alpha \beta},
$$

(4.48)

$$\Phi(y, y', q, q') = \Phi_0(q, q') + \Phi_1(y, y', q, q') + \Phi_2(y, y'),
$$

(4.49)

$$
\Phi_0(q, q') = \sum_\alpha \int_0^T dt \int_0^t dt' \left\{ [q(t) - q'(t)] L_1^\alpha (t - t') [q(t') - q'(t')] \\
- i [q(t) - q'(t)] L_2^\alpha (t - t') [q(t') + q'(t')] \right\}
+ i \mu^\alpha \int_0^T dt \left[ q^2(t) - q'^2(t) \right],
$$

(4.50)

$$
\Phi_2(y, y') = \sum_\alpha \int_0^T dt \int_0^t dt' \left\{ [y_\alpha(t) - y'_\alpha(t)] \frac{L_1^\alpha (t - t')}{(g^{(1)}_\alpha)^2} [y_\alpha(t') - y'_\alpha(t')] \\
- i [y_\alpha(t) - y'_\alpha(t)] \frac{L_2^\alpha (t - t')}{(g^{(1)}_\alpha)^2} [y_\alpha(t') + y'_\alpha(t')] \right\}
+ i \frac{\mu^\alpha}{(g^{(1)}_\alpha)^2} \int_0^T dt \left[ y^2_\alpha(t) - y'^2_\alpha(t) \right],
$$

(4.51)
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\[ \Phi_1(y, y', q, q') = \sum_\alpha \int_0^T dt \int_0^T dt' \left\{ \left[ y_\alpha(t) - y'_\alpha(t) \right] \frac{L_1^\alpha(t-t')}{g_\alpha^{(1)}} \left[ q(t') - q'(t') \right] \right. \\
- i \left[ y_\alpha(t) - y'_\alpha(t) \right] \eta(t-t') \frac{L_2^\alpha(t-t')}{g_\alpha^{(1)}} \left[ q(t') + q'(t') \right] \\
+ i \left[ y_\alpha(t) + y'_\alpha(t) \right] \eta(t'-t) \frac{L_2^\alpha(t-t')}{g_\alpha^{(1)}} \left[ q(t') - q'(t') \right] \right\} \\
+ i \frac{2\mu_1^\alpha}{g_\alpha^{(1)}} \int_0^T dt \left[ y_\alpha(t)q(t) - y'_\alpha(t)q'(t) \right]. \tag{4.52} \]

In (4.50), \( \Phi_0(q, q') \) is the influence functional when there is no second order couplings and

\[ L_1^\alpha(t) = \frac{(g_\alpha^{(1)})^2}{m_\alpha \omega_\alpha} \coth \left( \frac{\beta \omega_\alpha}{2} \right) \cos \omega_\alpha t \tag{4.53} \]

\[ L_2^\alpha(t) = \frac{(g_\alpha^{(1)})^2}{m_\alpha \omega_\alpha} \coth \left( \frac{\beta \omega_\alpha}{2} \right) \sin \omega_\alpha t \tag{4.54} \]

\[ \mu_1^\alpha = \frac{(g_\alpha^{(1)})^2}{m_\alpha \omega_\alpha^2} \tag{4.55} \]

are the standard Feynman-Vernon kernels, which are quadratic functions of the first order couplings. The two-phonon interactions introduced the additional term \( \Phi_1(y, y', q, q') \). Its effects can be calculated by calculating the functional integral over \( y \) and \( y' \) in (4.47).

For a multidimensional Gaussian Integral, we have

\[ \int \text{d}x e^{-\frac{1}{2} \sum_{ij} x_i A_{ij} x_j + \sum_i B_i x_i} = \sqrt{\frac{(2\pi)^n}{\det A}} e^{-\frac{1}{2} B^T A^{-1} B}. \tag{4.56} \]

To use this formalism, we write all terms in \( \Phi_1(y, y', q, q') \) and \( \Phi_2(y, y') \) in matrix form. The basis of vectors \( y \) is chosen as

\[ y = \begin{pmatrix} y_1(t) \\ y'_1(t) \\ \vdots \\ y_\alpha(t) \\ y'_\alpha(t) \\ \vdots \end{pmatrix}. \tag{4.57} \]
As a result, \( \Phi_2(y, y') \) is quadratic over the variables \( y \) and can be written as

\[
\Phi_2(y, y') = \int_0^T dt \int_0^t dt' y^T(t) \begin{pmatrix}
Q_1(t-t') & 0 & \cdots \\
0 & Q_2(t-t') & \cdots \\
\vdots & \vdots & \ddots
\end{pmatrix} y(t')
\]

\[
= \int_0^T dt \int_0^t dt' y^T(t) \Delta A(t-t') y(t').
\]

(4.58)

This defines the kernel matrix \( \Delta A(t-t') \). Here \( Q_\alpha(t-t') \) is a two by two matrix which is independent of the first order coupling \( g^{(1)} \), i.e.,

\[
Q_\alpha(t-t') = \frac{1}{m_\alpha \omega_\alpha}
\]

\[
\times \begin{pmatrix}
\coth(\frac{\beta \omega_\alpha}{2}) e^{-i\omega_\alpha t + 2i\delta(t)/\omega_\alpha} & -\coth(\frac{\beta \omega_\alpha}{2}) e^{i\omega_\alpha t} \\
-\coth(\frac{\beta \omega_\alpha}{2}) e^{-i\omega_\alpha t} & \coth(\frac{\beta \omega_\alpha}{2}) e^{i\omega_\alpha t} - 2i\delta(t)/\omega_\alpha
\end{pmatrix}.
\]

(4.59)

On the other hand, \( \Phi_1(y, y', q, q') \) is linear in the first order coupling \( g^{(1)}_\alpha \). This term can be written as

\[
\Phi_1(y, y', q, q') = \int_0^T dt B_{1,\alpha}(t) y_\alpha(t) + B_{2,\alpha}(t) y'_\alpha(t)
\]

\[
= \int_0^T dt B(t) \cdot y(t),
\]

(4.60)

where

\[
B_{1,\alpha}(t) = \int_0^T dt' \frac{g^{(1)}_\alpha}{m_\alpha \omega_\alpha} \coth(\frac{\beta \omega_\alpha}{2}) \left( e^{-i\omega_\alpha |t-t'|} q(t') - e^{i\omega_\alpha (t-t')} q'(t') \right)
\]

\[
+ i \frac{2g^{(1)}_\alpha}{m_\alpha \omega_\alpha^2} q(t)
\]

(4.61)

\[
B_{2,\alpha}(t) = \int_0^T dt' \frac{g^{(1)}_\alpha}{m_\alpha \omega_\alpha} \coth(\frac{\beta \omega_\alpha}{2}) \left( e^{i\omega_\alpha |t-t'|} q'(t') - e^{-i\omega_\alpha (t-t')} q(t') \right)
\]

\[
- i \frac{2g^{(1)}_\alpha}{m_\alpha \omega_\alpha^2} q'(t)
\]

(4.62)

We also rewrite the non-interacting integral kernel in (4.47) as

\[
\exp \left( -\frac{1}{2} \int_0^T dt \int_0^T dt' y^T(t) A_0^{-1}(t-t') y(t') \right)
\]

(4.63)
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with

\[ A_0(t) = 2\delta(t - t') \]

\[
\begin{pmatrix}
-iG[q(t)]g^{(2)}_{11} & 0 & -iG[q(t)]g^{(2)}_{12} & 0 & \cdots \\
0 & iG[q'(t)]g^{(2)}_{11} & 0 & iG[q'(t)]g^{(2)}_{12} & \cdots \\
-iG[q(t)]g^{(2)}_{21} & 0 & -iG[q(t)]g^{(2)}_{22} & 0 & \cdots \\
0 & iG[q'(t)]g^{(2)}_{21} & 0 & iG[q'(t)]g^{(2)}_{22} & \cdots \\
\vdots & \vdots & \vdots & \vdots & \ddots
\end{pmatrix}
\]

\( \times \)

Therefore, the influence functional kernel can be formally written as

\[
F[q, q'] = e^{-\Phi_0(q, q')} \int D\mathbf{y} \, \frac{1}{Z_0 Z_{q'}} \exp \left\{ -\frac{1}{2} \int_0^T dt \int_0^T dt' \mathbf{y}^T(t) \right. \\
\cdot \left. (A_0^{-1}(t - t') - 2\Delta A(t - t')) \mathbf{y}(t') + \int_0^T dt \mathbf{B}(t) \cdot \mathbf{y}(t) \right\}
\]

\[
= e^{-\Phi_0(q, q')} \sqrt{\frac{\det A_0^{-1}}{\det (A_0^{-1} - 2\Delta A)}} \exp \left[ -\frac{1}{2} \mathbf{B}^T (A_0^{-1} - 2\Delta A)^{-1} \mathbf{B} \right],
\]

where \( e^{-\Phi_0(q, q')} \) is the influence functional kernel of the linear coupling terms. The rest of the terms are the effects of the two-phonon couplings. The terms in exponents, i.e. \( \mathbf{B}^T (A_0^{-1} - 2\Delta A)^{-1} \mathbf{B} \) are quadratic functions of \( q \) and \( q' \), which can be absorbed into the linear coupling kernel \( \Phi_0(q, q') \) as shown in (4.50). Considering that \( A_0 \propto g^{(2)}_{\alpha\beta} \) and \( \Delta A \propto \frac{1}{m_\omega \omega_\alpha} \), if the two-phonon interactions are small compared to the phonon frequency (which is usually true for optical phonons), this kernel is dominated by \( A_0^{-1} \). Since \( \mathbf{B} \propto \frac{g^{(1)}_{\alpha\beta}}{m_\omega \omega_\alpha} \), the exponents are proportional to \( \frac{(g^{(1)}_{\alpha\beta})^2 g^{(2)}_{\alpha\beta}}{m_\omega \omega_\alpha m_\omega \omega_\alpha} \) to lowest order in \( g^{(2)} \). We expect that in this situation, the extra dynamics introduced by the two-phonon interactions can be safely treated as a perturbation to the linear couplings without any intrinsic difference.

On the other hand, the factor \( \sqrt{\det A_0^{-1} / \det (A_0^{-1} - 2\Delta A)} \) cannot be absorbed into the first order dynamics. The factor \( \Delta A \) is completely independent of \( g^{(1)} \). To actually calculate this factor requires us to calculate the logarithm of the product of matrices. We can use the Baker - Campbell -
Hausdorff formula to write it formally as

\[
\sqrt[\text{det } A^{-1}_0 / \text{det } (A^{-1}_0 - 2\Delta A)] = \exp \left[ -tr \log (A^{-1}_0 - 2\Delta A) - tr \log A_0 \right]
\]

\[= \exp tr \left\{ -Y + \frac{1}{2}[X, Y] - \frac{1}{12} ([X, [X, Y]] - [Y, [Y, X]]) + ... \right\} \tag{4.66}\]

in which \(X = \log A_0\) and \(Y = \log(1 - 2A_0\Delta A)\). Unfortunately this procedure is too complicated to get a closed form for the general case. However, we notice that this term does not depend on the first order couplings. In the last section, we already calculated the pure two-phonon interaction kernel \((4.37)\), which is the \(g^{(1)}_{\alpha\beta} = 0\) case in \((4.65)\). Since the kernel \((4.37)\) is analogous to the coupling to the spin bath kernel \((4.38)\), so is the \(\sqrt{\text{det } A^{-1}_0 / \text{det } (A^{-1}_0 - 2\Delta A)}\) factor. Therefore, the mapping to a spin bath in the previous section is still valid after we turn on the linear coupling terms.
Chapter 5

Multi-Pathway Light Harvesting Molecules

In the last chapter we have explored the functional importance of Peierls polarons in energy transfer in two-site models. In this chapter we are going to expand the same technique to study the more complex light harvesting complexes. Due to the lack of knowledge of the actual parameters in real world biological molecules, we are not going to try to reproduce the details of experimental observations. Instead, we focus on exploring new mechanisms introduced by the Peierls polarons and the spin baths.

In the first section of this chapter, we write down the full Hamiltonian of vibrational modes coupled to energy transfer again. We summarize the methods we are using from the previous chapters to approach this Hamiltonian. In the next section, we apply the model to the FMO complex. To reduce complexity, our calculations are mainly based on a reduced 3-site model of FMO. Site-energies and hopping amplitudes are taken from [8, 29, 161]. The phonon frequencies are no longer in resonance with the energy gaps, in this simplified model we still find that the Peierls couplings introduce resonant peaks in the weak interaction region. The sensitivity to the coupling strength is qualitatively different from the Holstein coupling case. In the last subsection, we will study the path-selecting mechanism in several multiple-pathway models. We find that the effect of off-diagonal couplings strongly depends on the energy difference between the two sites it couples to. It can enhance the transfer rate as well as the coherence between the two sites. Although the two branches of biological molecules have the same chemical structure, the transfer rate through each of them can be due to different environmental phonons.
5.1 Approach to the Complete Hamiltonian for Energy Transfer

We again write down the complete Hamiltonian for an exciton coupling to vibrational modes of the environment in Chapter 1 as:

$$H = H_0 + H_1 + H_2$$

(5.1)

$$H_0 = \sum_i \varepsilon_i c_i^\dagger c_i + \sum_{\langle ij \rangle} (t_{ij} c_i^\dagger c_j + h.c.) + t_0 (c_1^\dagger d_0 + d_0^\dagger c_1) + H_B$$

(5.2)

$$H_B = \sum_{\langle ij \rangle} V (d_i^\dagger d_j + h.c.)$$

(5.3)

$$H_2 = \sum_k \Omega_k a_k^\dagger a_k.$$  

(5.4)

$$H_1 = \sum_i \left( \sum_k g_{H,i}^{(1)} (a_k^\dagger + a_k) + \sum_{k,k'} g_{H,k,k',i}^{(2)} (a_k^\dagger + a_k) (a_{k'}^\dagger + a_{k'}) \right) c_i^\dagger c_i$$

$$+ \sum_{\langle ij \rangle} \left( \sum_k g_{P,i,j}^{(1)} (a_k^\dagger + a_k) + \sum_{k,k'} g_{P,k,k',ij}^{(2)} (a_k^\dagger + a_k) (a_{k'}^\dagger + a_{k'}) \right) c_i^\dagger c_j$$

$$+ h.c.$$  

(5.5)

Based on our studies in previous sections, we can at first map several terms into spin bath models to simplify the expression, and help to understand the dynamics of the system.

There are two major sources of spin bath interactions in the system. One is from the direct truncation of the high energy phonon modes. For the phonons with energy $\Omega_k \gg k_B T$ (at room temperature $300K \approx 208cm^{-1}$), considering the weak interaction assumption $g^2/\Omega \ll t_{ij}, |\varepsilon_i - \varepsilon_j|$ (if the phonon energy is around $200cm^{-1}$, the criterion is $g \ll 100cm^{-1}$ which is quite reasonable in the FMO complex), we can safely assume that only their ground states and first excitation states are involved in the energy transfer. Therefore, we can truncate such phonon modes into two-level systems, a.k.a., spin $\frac{1}{2}$ modes. Replacing the $\{a_k, a_k^\dagger\}$ with $\{\sigma_k^+, \sigma_k^-\}$ and $(a_k^\dagger a_k - \frac{1}{2})$ with $\sigma_k^z$
5.1. Approach to the Complete Hamiltonian for Energy Transfer

, we can write down the mapped spin bath coupling terms as

\[ H_{hf} = \sum_{k,\langle ij \rangle} (g_{P,k,\langle ij \rangle}^{(1)} (a_k + a_k^\dagger) c_i^\dagger c_j + h.c.) + \sum_k \Omega_k a_k^\dagger a_k \]

\[ \rightarrow \sum_{k,\langle ij \rangle} (g_{P,k,\langle ij \rangle}^{(1)} \cdot \sigma_k^x c_i^\dagger c_j + h.c.) + \sum_k \Omega_k \sigma_k^z. \]

(5.6)

Due to the big energy difference \( \Omega_k \), this interaction falls into the high field regime which we have already studied in 3.3. The effects from the associated phonon modes dissipate the system and we can introduce the parameter \( \kappa_{ij} \) to describe the dissipation rate:

\[ \kappa_{ij} = \sum_k \left( \frac{g_{k,\langle ij \rangle}^{(1)}}{t_{ij}} \right)^2. \]

(5.7)

The resulting reduced density matrix can then be approximated as

\[ \rho(t_{ij}, t) = \int_0^\infty zdze^{-z^2/2} \rho_0(z, t), \]

(5.8)

where \( \rho_0(z, t) \) is the density matrix under the modified Hamiltonian \( t_{ij} \rightarrow t_{ij} e^{\kappa_{ij} z} \).

Another source of spin bath couplings is from the two-phonon cross-interactions \( g_{H,P,k,k'}^{(2)} \) when \( \Omega_k \approx \Omega_{k'} \). In Section 4.6, we have already shown that the only non-trivial effects from the two-phonon interactions come from the cross-interaction terms \( g_{k,k',\langle ij \rangle}^{(2)} (a_k + a_k^\dagger) (a_{k'} + a_{k'}^\dagger) \) when \( k \neq k' \). They can be mapped into the spin bath interaction \( (\Omega_k - \Omega_{k'}) \sigma_k^z + g_{k,k',\langle ij \rangle}^{(2)} \sigma_k^x \), in which the \( \sigma_k \)s are the operators of spin 1/2 systems. As a result, the cross-interaction terms can be written as

\[ H_{pf} = \sum_{k,\langle ij \rangle} (g_{P,k,k',\langle ij \rangle}^{(2)} (a_k + a_k^\dagger) (a_{k'} + a_{k'}^\dagger) c_i^\dagger c_j + h.c.) + \sum_k \Omega_k a_k^\dagger a_k \]

\[ \rightarrow \sum_{\langle kk' \rangle,\langle ij \rangle} (g_{k,k',\langle ij \rangle}^{(2)} \cdot \sigma_{k,k'}^x c_i^\dagger c_j + h.c.) + \sum_{\langle kk' \rangle} (\Omega_k - \Omega_{k'}) \sigma_{k,k'}^z. \]

(5.9)

This mapping is valid when i) the phonon frequency is much larger than the coupling strength , i.e., \( |\Omega_k|, |\Omega_{k'}| \gg g_{k,k',\langle ij \rangle}^{(2)} \); and ii) the phonon frequency difference is much smaller than the other relevant energy scales phonons couple to, i.e., \( |\Omega_k - \Omega_{k'}| \ll t_{ij}, |\epsilon_i - \epsilon_j|, g_{k,k',\langle ij \rangle}^{(2)} \). Noticing that the terms \( |\Omega_k - \Omega_{k'}| \) are equivalent to the local fields \( h_k \) acting on bath spins, we can
5.1. Approach to the Complete Hamiltonian for Energy Transfer

immediately recognize that the second criterion is exactly the condition of
pure phase decoherence regime of spin baths we discussed in Section 3.2.
From that section, we show that if $\Omega_k \approx \Omega_{k'}$, the couplings to bath spins in
this regime would only cause phase decoherence, with no energy dissipation.

The actual decoherence rate is determined by the topology of the central
lattice. In general, for a particular path of the exciton, the factor that
governs the decoherence rate is given by

$$
\lambda = \frac{1}{2} \sum_{k,\langle ij \rangle} \left( \frac{\langle t_{ij} \rangle}{g_{kk',ij}} \right)^2.
$$

(5.10)

Here the summation indices $\langle ij \rangle$ are taken along a particular path. For
this particular path, the decoherence rate is proportional to $e^{-\lambda t}$ (see 3.2).
Summing over all possible paths, we can get the dynamics of the off-diagonal
elements of the reduced density matrix.

If we know enough details of the phonon couplings to calculate $\kappa$ and $\lambda$,
we can use the aforementioned mappings to spin baths to isolate the effects
introduced by the high energy modes as well as the two-phonon interac-
tions. This procedure leaves us the coupling to the modes with energy $\Omega_k$
close to the energy scales of the central system, which are more likely to be
on resonance with certain energy gaps $|\epsilon_i - \epsilon_j|$ between different Bchls in
light harvesting molecules. In Chapter 4, we have already studied the case
when the phonon energy is on resonance exactly. Similar techniques will
be employed in this chapter to study the case when the phonon energy is
not on resonance. We shall see that most of our results in Chapter 4 are
still applicable with new parameters. Combining these results with the spin
bath mapping techniques, we can acquire a thorough understanding of the
Hamiltonian (5.1) to (5.5).

One may notice that we omit the diagonal couplings to the vibrational
phonon modes in the mapping to spin baths. Our argument is based on the
properties of Holstein couplings. In the parameter region of our problem,
Holstein couplings always show similar behavior: increasing the transfer rate
in the weak interaction region but decreasing the transfer rate when the
coupling strength is beyond a certain point (the optimal coupling strength).
The overall dependence on the coupling strength varies smoothly. There
is no rapid raise nor dropping for the energy transfer rate. We also find
that such dynamics are quite robust regardless of the details of the models.
This robustness can also be verified in later sections of this chapter when
the resonant condition is not satisfied. Therefore, including multiple sources
of Holstein couplings would only result in a renormalization of the optimal
5.2 Application to the FMO Complex

Figure 5.1: This is the energy pathway of a 8-site model from with on-site energies, as well as the scheme to reduce to a 3-site model. Site-3 is the site that connecting to the RC. Site-8 has the highest on-site energy and receives excitons from the baseplate directly. Reprinted with permission from [8]. Copyright (2011) American Chemical Society.

coupling strength as well as the energy spectrum. Practically, if we want to study the effect of multiple sources of Holstein couplings qualitatively, we could simply study them as a whole, as a single bath with a renormalized spectrum. Actually in experiments, we cannot distinguish the effects from different sources either. Obviously, this argument is not universal and only valid if the bare system is not in the localized regime. If the system is in a localized phase, the increasing of Holstein couplings could eventually destroy the localization and cause a phase transition. But in FMO complexes, we can clearly see a hierarchy of on-site energies so localization is not the case here. As a result, we do not have to map certain Holstein couplings into the spin bath model separately in the problems we are interested in this thesis.

5.2 Application to the FMO Complex

 Usually the energy transfer in the FMO complexes is considered as a two-pathway transfer. It was generally believed that there were two major pathways for FMO complexes: 1-2-3 and 5-6-7-4-3 (see for example [8, 30, 162]). The site numbers and on-site energies are illustrated in Figure 5.1. Site 3 is the site which is connected to the RC. Being the two pigments which are closest to the baseplate, site 1 and site 5 are believed to accept excitons
from the baseplate and start a two-pathway transfer towards site 3. Later on, however, the discovery of the 8th pigment changed this picture[3, 8, 161, 163]. The crystal structure indicates that the 8th pigment resides roughly midway between the baseplate and the Bchl at site 1. Based on the crystal structure and photoemission spectrum of FMO complexes, it was shown that the 8th pigment provides the most efficient pathway due to its position and orientation with respect to the surrounding chlorosome[8, 161, 164].

One of the most widely-used Hamiltonians for the 8-site FMO complex was worked out by Renger and his co-workers ([161]); in a site representation on e has

\[
H_0 = \begin{pmatrix}
310 & -98 & 6 & -6 & 7 & -12 & -10 & 38 \\
-98 & 230 & 30 & 7 & 2 & 12 & 5 & 8 \\
6 & 30 & 0 & -60 & -2 & -10 & 5 & 2 \\
-6 & 7 & -60 & 180 & -65 & -17 & -64 & -2 \\
7 & 2 & -2 & -65 & 405 & 89 & -6 & -2 \\
-12 & 11 & -10 & -18 & 89 & 320 & 32 & -10 \\
-10 & 5 & 5 & -64 & -6 & 32 & 270 & -11 \\
38 & 8 & 2 & -2 & 5 & -10 & -11 & 505
\end{pmatrix} \text{ cm}^{-1}. \tag{5.11}
\]

The parameters in (5.11) were calculated based on the traditional master equation method with Holstein couplings to acoustic phonons. Obviously these numbers can be problematic when we include Peierls couplings. However, since we expect that the Peierls coupling is smaller than the Holstein coupling and not significant in spectra, this is still among the most accurate Hamiltonians of the FMO complex we can have. If the exciton is initially created at site 8, numerical calculations show that the left pathway 8-1-2-3 becomes the dominant pathway in this model [161, 164]. The large energy gaps between the eighth pigment and the rest of the pigments, as well as the weak inter-path interactions, suppress the oscillations between the two primary pathways. The energy transfer process changes from an oscillation between two pathways into a ladder diffusion from site 8 to site 3. Considering the fact that site 1 and site 2 have close on-site energy and strongly coupled to each other, one can also treat them as a single site. In this way, we acquire a reduced 3-site effective model for the light harvesting molecules. Renger and his co-workers show that there is no qualitative difference for site-populations between the 8-site model and reduced 3-site model [161]. It is not clear that only taking into account of a subset of sites from the whole system would affect other functional properties of the whole system besides the site-populations. In this thesis, we mainly focus on the site-populations, as the energy (exciton) transfer is the major function of FMO complexes.
Therefore, we use the simplified 3-site model as our starting point.

The three site effective model based on the work of Schmidt et al[161] is (again in the site representation):

\[
H_0 = \begin{pmatrix}
505(3.70) & 38(0.282) & 0 \\
38 & 270(2.00) & 30(0.222) \\
0 & 30 & 0
\end{pmatrix} \text{ cm}^{-1}
\] (5.12)

The numbers in the brackets in (5.12) are the dimensionless renormalized site-energies for numerical purposes. The energy difference between the lowest two sites are renormalized to 2. In the following sections, the energy value of any dimensionless number \(a\) is \(a \times 135 \text{ cm}^{-1}\) (e.g., the numbers in the bracket in (5.12)).

The next step is to determine the vibrational phonon frequencies and their couplings. The possible frequencies for the vibrational phonon modes range from 20 cm\(^{-1}\) to > 1600 cm\(^{-1}\). Based on the previous studies, we can argue that only the phonons with frequencies close to the energy differences between sites are important, which are at the order of 10^2 cm\(^{-1}\). In [29], it was estimated that the typical vibrational phonon frequency \(\Omega = 180 \text{ cm}^{-1} = 1.33\) in our renormalized unit. The associated Huang-Rhys factor \(S \equiv \frac{g^2}{2\hbar} = 0.22\). The corresponding coupling strength \(g = 0.77\). Noticing that this is the Holstein coupling of the most dominant vibrational phonons; we cannot use the value for the Peierls couplings. In this section, we assume that such phonons also couple to the central system through Peierls couplings. Not knowing the actual size of Peierls couplings, we vary their coupling strength from 0 to 2 to see their effects on the overall dynamics.

The last step is to determine the parameters of the RC. Unfortunately, we do not have detailed knowledge of the interaction between FMO complexes and RCs in vivo. In most experiments on the FMO complexes, these complexes are separated from their natural biological environment and studied in laboratory solvents. All we know about the RC is based on spectroscopy. From the photoemission spectrum of the RC in purple bacteria, we can see that the energy difference of absorption peaks of the closes pigments between the FMO and the RC is about 580 cm\(^{-1}\) [6]. This is a huge energy gap which is larger than any on-site energy differences within the FMO. From its absorption spectrum, the bandwidth of RC is apparently 150 cm\(^{-1}\), which apparently does not overlap with the absorption spectrum of FMO[4]. However, it is not guaranteed that there is no intermediate Bchl pigment lost during distilling procedures, as with the 8th pigment of the FMO complexes. It is difficult to determine the actual parameter of the RC and the
5.2. Application to the FMO Complex

dynamic of the system actually heavily depends on the position of the RC absorption bands. Therefore, we also have to vary the parameters of RC to see the dynamics of the central system in different regimes. In most cases, we are going to face situations different from our toy models in the last chapter: the phonon frequency \( \Omega \) is no longer on resonance with the site energy differences and the site-energies do not necessarily overlap with the absorption band of RC.

5.2.1 Back to Two Level Model

Before we actually start calculating the reduced 3-site model, we go back to the two-site model, and tune the phonon frequency \( \Omega \) off resonance and change the position of the absorption band of RC. From this simple toy model we can obtain a qualitative understanding of the behavior of the system in this general case. We follow the same notations for variables in this section as in Chapter 4.

The model Hamiltonian can be written as

\[
H_0 = \sum_{\langle ij \rangle} \left( \Delta_{ij} + \sum_k b_{ij}^k (c_{ij}^\dagger + c_{ij}) \right) (|a_i\rangle\langle a_j| + \text{h.c.}) \\
+ \sum_i \epsilon_i |a_i\rangle\langle a_i| + \sum_{\langle ij \rangle} \Omega c_{ij}^\dagger c_{ij}.
\] (5.13)

We use the same site subscript \( \langle ij \rangle \) for phonon modes since we assume there is only one vibrational phonon coupling to each hopping amplitude.

At first, we set \( d = 0 \), which is the case we studied in 4: the bottom site sits at the center of the RC absorption spectrum. The dependence of transfer rate on the phonon frequency is illustrated in Fig. 5.2(a). We see that the overall transfer rate decreases as the phonon frequency is tuned away from resonance. The high-transfer-rate plateau gradually turns into a sharp transfer peak. The position of the peak can be understood by eigenvalue calculations: the maximum transfer happens when the lowest eigen-energy of the polaron drops into the band of the RC. The smaller the phonon frequencies are, the larger the coupling strength of the transfer peak is. For small phonon frequency \( \Omega = 1.0 \), we can even see another peak in the large coupling regime which is associated with the second lowest eigenenergy of the polaron.

In Fig. 5.2(b), we set the energy deviation \( d = \epsilon_1 - \epsilon_0 \) (the energy difference between site-1 of the lattice and site-0 in the RC model) to 1. Therefore, the bottom site is right outside the absorption spectrum of the
5.2. Application to the FMO Complex

RC. There is no energy overlap with the site and the absorption spectrum of the RC in this case. The dynamics is qualitatively different from the previous case in Fig. 5.2(a). First we can see that $\Omega \approx \epsilon_2 - \epsilon_1 = 2$ is no longer the resonance condition. The transfer rate drops rapidly when $\Omega = 2$ compared to the previous case. The energy of site 2 does not overlap with the RC band so the lowest polaron state $\epsilon \approx d \pm g_P$ is also outside the RC bandwidth. The actual resonance happens when the phonon frequency $\Omega$ comes close to the energy difference $d = 1$. Beyond $\Omega = 1$, if the phonon frequency increases, the height of the peak actually decreases.

From both cases, we can see that instead of the high-transfer plateau, transfer peaks become more common when the parameters are not fully on resonance. The location of these peaks are determined by whether a particular energy eigenstate of the polaron is on resonance with the RC band or not. Therefore, we can see a sudden increase or decrease of the transfer rate around these critical couplings. The transfer rate is sensitive to the change of coupling strength near these critical point couplings but remains almost constant in the rest of the parameter regime.

![Figure 5.2](image)

Figure 5.2: the plot of the transfer rate of the original two level system with different deviations $d$ and phonon frequencies $\Omega$, $D = 1, t_0 = 0.2$ a) the transfer rate with Deviation $d = 0$, different lines stands for different phono frequencies, b) the transfer rate with Deviation $d = 1.0$, different lines stands for different phono frequencies.

5.2.2 Reduced 3-Site Model for FMO complexes

Now we turn to the reduced 3-site model for FMO complexes (5.12) with the phonon frequency set to be $\Omega = 1.33(180 cm^{-1})$. The parameters we vary during the studies are: the phonon coupling strength $g$, the transfer
5.2. Application to the FMO Complex

Figure 5.3: a) The plot of transfer rate of Hamiltonian (5.12) with different types of phonon couplings, the reaction center parameters are chosen as $D = 1$, $t_0 = 0.2$, $d$ (deviation) = 1; b) the transfer rate of off-diagonal coupling with different $t_0$, $D = 1$, $d = 1$ c) the transfer rate of off-diagonal coupling with different $d$, $D = 1$, $t_0 = 0.2$; d) the transfer rate of off-diagonal coupling with different bandwidth $D$, $t_0 = 0.2$, $d = 1$.

amplitude to the RC $t_0$, the energy deviation of the RC $d$, and the half band width $D$ of the RC.

In Fig. 5.3(a), we examine the effects of three different types of phonon couplings: the Holstein coupling, the full Peierls coupling and the Rabi-type Peierls coupling. We set the band width $D$ of the RC as 1, $t_0$ as 0.2 and the deviation $d$ as 1. For the Holstein coupling case, we again see the phonon-assisted transfer which we have discussed multiple times before. This robustness against the change of parameters is a typical quality of Holstein couplings in this type of model. In contrast, there is a sharp peak in the transfer rate for both Peierls coupling cases. The peak is located around $g_P = 0.5$. The associated Huang-Rhys factor $g_P^2/2\pi \Omega = 0.07$, which is
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noticeably smaller than the reported value for the Holstein coupling model in [29]. The spectra and the time evolution of the site populations are plotted in Fig. 5.4. We can see that in the small interaction $g_P = 0.2$ case, the exciton is mainly oscillating between site-1 and site-2. The oscillation frequency is approximately the site energy difference $\epsilon_2 - \epsilon_1$. Near the transfer rate peak ($g_P = 0.5$), although there are still oscillations between 1-2, the transfer to site 3 is significantly increased. Actually it is similar to the transfer peak in the two-site case we just discussed in the previous part in Fig. 5.2(b). The resonance between the polaron state and the RC band significantly enhances the transfer between site-3 and the RC. For the large coupling $g_P = 0.8$, the exciton populations on site-1 and site-2 do not change compared to the $g_P = 0.5$ case. However, we can see a significant increase of the populations on site-3. Due to the big phonon couplings, the distorted phonon cloud prevents the further transfer into the RC. The back reaction from the RC becomes significant.

In the rest of the panels in Fig. 5.3, we change the parameters of the RC to see their effects on the exciton dynamics. Fig. 5.3(b) shows the dependence on the coupling strength $t_0$ between the system and the RC. The result is straightforward: increasing the coupling strength increases the transfer rate and the change of $t_0$ does not change the position of the transfer peak. Fig. 5.3(d) shows the dependence on the bandwidth $D$ of the RC. We can see that as long as the bandwidth $D$ does not exceed the phonon energy $\Omega$, i.e., only the zero-phonon polaron state on site-3 being in the range of the RC band, the change of bandwidth does not change the transfer rate peak. When the band width exceeds $\Omega = 1.33$ (the $D = 1.5$ line), another transfer peak appears, which is the result of the one-phonon polaron state is in the range of RC band. Fig. 5.3(c) shows the dependence on the energy difference $d$. Unlike the other cases, the position of the transfer peak changes for different $d$. This shows that the transfer peak is almost exclusively dependent on the energy difference between the RC and site-3.

Summary We find that the reduced 3-site model (5.12) with Peierls coupling qualitatively shows the same behavior as the two level system we studied in 5.2.1. The high transfer plateau is reduced to a transfer peak at a coupling strength which is still much smaller than the Holstein couplings. The sensitivity of the transfer rate near the transfer peak suggests that we cannot ignore Peierls couplings even if they are small. We show that only the energy difference between the RC band and the lowest energy site changes the position of such transfer peaks. Increasing the RC bandwidth would
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cause multiple transfer peaks. For the Holstein coupling case, however, the result is similar to what we studied before: increasing the Holstein phonon coupling gradually increases the transfer rate until it reaches the optimal value; further increasing the coupling will reduce the transfer rate due to the heavy phonon cloud.

The major obstacle preventing us from calculating the actual 8-site model (5.11) is the lack of knowledge of the actual coupling details of the light harvesting molecules. Most experiments on light harvesting molecules are photon-based. Photons create electronic excitations in the form of excitons but photons do not directly interact with phonons. It is the excitons that are directly observed. To get the phonon structure, we have to assume a particular theory of the phonon-exciton interactions and fit the parameters based on this pre-assumed theory [7, 29, 39, 40]. This has great success in low temperature physics since both the environment and the system are
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relatively “simple” and “clean”. Biological processes happen at room temperature and are usually more “messy”. This is the intrinsic problem of the current theoretical treatments in this field: the pre-assumed theory determines the values inferred for the parameters so there is no way to justify the theory itself. To overcome this difficulty, we need either i) a direct probe to the actual phonon structure such as neutron scattering experiments, rather than the current indirect photon probe, or ii) a first-principle calculation for the phonon couplings based on the structure of light harvesting molecules and the protein they are embedded in. Unfortunately, both methods are beyond the expertise of the authors. We cannot find similar researches on the detailed phonon structures in light harvesting molecules in the literature since quantum biology is a relatively new field for both physics and biology.

In the reduced 3-site model, although we do not know the details of the phonon spectra and RC parameters, we can vary these parameters to explore the dynamics in different parameter regions. However, if we go from the 3-site model to the full 8-site model, the number of hopping amplitudes between the 8 different sites is dramatically increased. There are 28 independent hopping amplitudes and associated phonon coupling spectra. Due to the lack of symmetry of their spatial distribution, it is not valid to assume the same coupling strength for each hopping amplitude. This leads to a much larger parameter space to explore. It is almost impossible for us to control variables in the way we do in the 3-site model. Also for the 8-site Hamiltonian, the dynamics are more sensitive to the hopping amplitudes as well as the coupling strengths in (5.11), due to its multiple-pathway nature. Any inaccuracy of the hopping amplitudes could give a completely different pathway scheme. The addition of the acoustic phonon continuum and Holstein couplings might also change the fitting results of the hopping amplitudes. Therefore, at this stage, we are mainly working on the reduced few-site models and trying to explore the new mechanism introduced by Peierls couplings, rather than actually fitting the experiment data.

5.3 Pathway Selecting Mechanism

The reduced 3-site model in the previous section is a straightforward ladder model: there is no direct interaction between site-2 and site-0. But as we mentioned before, it is not clear whether another pathway in FMO has functional importance. And the two pathway structure is not unique to the FMO complex; it is actually common among the light harvesting molecules. Another typical example is the reaction center of the purple bac-
5.3. Pathway Selecting Mechanism

terium \textit{Rhodobacter sphaeroides} (see Fig. 5.5). It has a pesudo two-fold symmetry, labelled by paths \textit{A} and \textit{B} in the Fig[5.5].

![Diagram of Rhodobacter sphaeroides reaction center](image)

Figure 5.5: This is the cofactors-only structure of the reaction center of \textit{Rhodobacter sphaeroides}. \textit{D}_A \textit{D}_B \text{ and } \textit{B}_A \textit{B}_B \text{ are four Bchl pigments with absorption peak at 870nm (P870).} \textit{H}_A \text{ and } \textit{H}_B \text{ are two bacteriapheophytins(BPh, basically the Bchl without the central Mg}^{2+}) \text{, and } \textit{Q}_A \text{ and } \textit{Q}_B \text{ are two quinones. At the bottom there is a metal ion Fe}^{2+}. \text{Reprinted with permission from [6].}

In the RC of \textit{Rhodobacter sphaeroides}, the top part (the part which is closest to FMO complex) is composed by two cofactors, each of which has a BChl-a \textit{P870} pigment, which is named after the absorption peak of its \textit{Q_y} band. Note that 870nm is approximately 11630cm$^{-1}$. The lowest excitation energy of the BChl in FMO complex is 12195cm$^{-1}$, which is 568cm$^{-1}$ higher than the absorption peak. The top \textit{P870} pigments absorbs an exciton to form an excited state \textit{P870}*. This state is unstable and it decays in 3 ps by donating an electron to the neighbour Bchl to form a radical pair \textit{P870}^{+} \textit{BChl}_A^{-}. This state decays to \textit{P870}^{+} \textit{BPh}_A^{-} radical pairs rapidly in 1ps. Eventually this electron is transferred to quinone \textit{Q_A} which makes it \textit{P870}^{+} \textit{Q}_A^{-}. This step takes a much longer time, which is around 200ps. \textit{Q}_A^{-}, \textit{Q}_B^{-} and other cytocrhomes form another chemical reaction circle which takes a much longer time to complete.

Although it has an apparent two-fold symmetry in the structure, the energy path-way is not symmetric. Estimates of the ratio for the electron transfer probability down the A branch compared with the B branch are about 100 : 1[6]. Neither the function of the other structure nor the reason
5.3. Pathway Selecting Mechanism

Figure 5.6: Illustration of the two-pathway models. (a) The ladder model: site-2 serves as the ladder between site-3 and site-1. (b) The symmetric Model: site-2 has the same energy as site-1. In both cases, the excitation is initially created at site-1 and eventually transferred into RC. (c) The symmetric 4-site model.

for this path-selecting phenomenon is clear at the present time.

It would be interesting to study how phonon couplings affect the transfer pattern in different pathways. In this section, we are trying to answer these questions and to gain some insight of the real biological world, by studying a couple of two-pathway models.

5.3.1 Ladder Model

The major difference between the two-site and three-site systems is that for the three-site system we actually have multiple pathways from the starting site to the sink. Here we will start with a three-site ladder model but with direct couplings between the top and the bottom site (see Fig 5.6(a)). In this case, we can really talk about the choice between multiple pathways and the interaction between them. The bare Hamiltonian of our first model is, in site representation:

$$H_0 = \begin{pmatrix} 4 & 0.1 & 0.2 \\ 0.1 & 2 & 0.1 \\ 0.2 & 0.1 & 0 \end{pmatrix}$$

Site-1 has the highest energy and the excitation is initially created on this site. Site-3 has the lowest energy and resides in the center of the RC band,
5.3. Pathway Selecting Mechanism

Figure 5.7: The transfer rate of the Hamiltonian (5.14). The phonon energy $\Omega = 2$. The parameters of the RC couplings are the same as Fig. 4.2. Different lines stand for different types of phonon couplings. For simplicity we assume the same coupling strength for all coupled phonon modes.

which has a width of 1. Site-2 serves as a “ladder” in between the other two sites (see Fig. 5.6(a)). In this model the excitation is created at site 1, which is similar to the eighth pigment of FMO complexes. To reach the RC, there are two major path ways, i.e. site-1→site-3, and site-1→site-2→site-3. This is intended to be an analogue to the FMO complexes with two different path ways. The bare system evolution can be found in Fig. 5.8(d). We can find that $\rho_{22}$ is almost zero throughout the time so that the exciton is directly transferred into site-3. The first pathway 1→3 dominate the excitation transfer.

Then we have phonons coupled to this model. We use the same numerical in Chapter 4. The phonon energy $\Omega = 2$ which matches the energy gap between the site 1-2 and 2-3. Fig. 5.7 is the general result of the transfer rate in this model with various types of phonon couplings. Fig 5.8 shows the time evolution for site populations for some particular choice of phonon couplings.

We can see that for the Holstein coupling case, the result does not change much from the two-site case in Chapter 4. There is an optimal transfer rate when $g_H \sim 1$. And we can see that Holstein coupling does not change the site population qualitatively either.

On the other hand, for the Peierls coupling case, the highest transfer rate is achieved when phonons only couple to the hopping amplitude 1-2 and 2-3. Similar to the two-site case studied in the last chapter, the transfer
5.3. Pathway Selecting Mechanism

Figure 5.8: The time evolution of the Hamiltonian (5.14) for the weak coupling case $g_P = 0.16$ (top panel) and strong coupling $g_P = 0.72$ (bottom panel). The parameters are the same as Fig. 5.7. Different colors indicate different site populations ($\rho_{11}, \rho_{22}, \rho_{33}$). a) phonons couple to all three off-diagonal hoppings, b) phonons couple to 1-2 and 2-3 hopping, c) phonons only couple to 1-3, d) no phonon coupling at all.
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rate increases rapidly in the weak interaction region and falls off when bound states are formed in the large interaction region. This is what we expect since the phonon energy is resonant with the energy difference between 1-2 and 2-3 so the phonon coupling to these branches has more impact on the total transfer rate. The full Peierls coupling shows the same behavior qualitatively but with a smaller transfer rate. This shows that in this case 1→2→3 becomes the dominant energy transfer pathway. We can confirm this by comparing the time evolution of $\rho_{22}$ and $\rho_{33}$ in both cases in Fig. 5.8. We can see that the behavior of the density matrix element is qualitatively the same. The population on site-3 follows the trend of the population on site-2 in both cases.

For other cases, we can see from Fig. 5.7 that the coupling between 1-2 or 2-3 alone has almost no effect on the transfer rate. The coupling on only one of the hopping amplitudes in the second path is not enough to improve the overall energy transfer.

For the couplings between site 1-3 only, we have effectively a phonon-assisted transfer but with no resonant condition. Overall, this does not change the transfer rate significantly. We can also see from Fig. 5.8(c) that
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the sole coupling to 1-3 qualitatively does not change compared to the bare system even in the large interaction region. On the other hand, we notice that there is a sudden change of transfer rate around the intermediate region $g_P \sim 1$. We can understand this behavior by looking at the eigenstates of the system without the RC. When $g_P < 1$, the drop is caused by the forming of bound states as we explained in 4.3.1. The reason for the sudden increase in the transfer rate afterwards is because around $g_P = 1$, the eigenenergy of the two-phonon plaron state starts to drop into the range of the RC spectrum. Since the energy difference between 1-3 is exactly two times the phonon energy, this state actually satisfies the resonant condition and affects the transfer rate more than the non-resonant one-phonon state.

We can also see the time evolution of the off-diagonal elements in Fig. 5.9. The trace of the reduced density matrix is not conserved here so we use the normalized density matrix element $|\rho_{ij}|$. Again we can confirm that the 1-2-3 pathway is dominant for the full Peierls coupling case since the behavior of the off-diagonal elements is almost the same for the full Peierls coupling case and the 1-2 2-3 coupling case. The decay of the oscillation of the off-diagonal elements is usually a signal of decoherence in spectroscopic experiments. We can see that for the $g_P = 0$ case we already have the decoherence due to the coupling to the bath. After we turn on the coupling, one of the interesting things here is that, even though the effect of the 1-3 only coupling does not effect the diagonal elements significantly, it does cause decoherence between site-1 and site-2. This suggest that the off-diagonal coupling can affect the decoherence rate, but at the same time does not affect the energy transfer rate.

5.3.2 Symmetric Model

In this section we study a symmetric model. The bare Hamiltonian in site representation of our second model is

$$H_0 = \begin{pmatrix} 2 & 0.2 & 0.1 \\ 0.2 & 2 & 0.1 \\ 0.1 & 0.1 & 0 \end{pmatrix}$$  \hspace{1cm} (5.15)

Here we change the energy of site-1 to the same energy as site-2 (see Fig. 5.6). We also set the hopping amplitude between site 1-2 to be the biggest amplitude. The time evolution of the bare Hamiltonian can be found in Fig. 5.10(d). The excitation is mainly oscillating between site 1 and site 2 as expected.
5.3. Pathway Selecting Mechanism

Figure 5.10: The time evolution of the Hamiltonian (5.15). Different colors indicate different site populations ($\rho_{11}$, $\rho_{22}$, $\rho_{33}$). The top four figures are for the weak interaction $g_P = 0.16$; and the bottom four figures are for the strong interaction $g_P = 0.72$. a) phonons couple to all three off-diagonal hoppings, b) phonons couple to 1-2 and 2-3 hopping, c) phonons only couple to 1-3, d) no phonon coupling at all. Top panels are small couplings $g_P = 0.16$. Bottom panels are large couplings $g_P = 0.72$. 

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Figure 5.11: The transfer rate of the Hamiltonian (5.15). The phonon energy \( \Omega = 2 \). The parameters of the RC couplings are the same as Fig. 4.2. Different lines stand for different types of phonon couplings. For simplicity we assume the same coupling strength for all coupled phonon modes.

As a function of phonon couplings, the transfer rate to the RC is illustrated in Fig. 5.11. If phonons only couple to the hopping amplitude 1-2 (the brown line in Fig. 5.11), it does not affect the transfer rate significantly. We can see from the time evolution in Fig. 5.10 that the effect of 1-2 coupling is mainly to change the oscillation frequency between site 1-2. Since there is no energy difference between 1-2, there is no emergent resonant effect either.

On the other hand, the coupling to the amplitude 1-3 and 2-3 has a more significant effect on the transfer rate, just the same as what we saw in the previous model.

5.3.3 Symmetric Pathways with a Single Entry

To better illustrate the path-selecting mechanism, instead of the 3-site model, we study a symmetric 4-site model in this section. The Model Hamiltonian is, in site representation:

\[
H_0 = \begin{pmatrix}
4 & 0.2 & 0.2 & 0 \\
0.2 & 2 & 0 & 0.2 \\
0.2 & 0 & 2 & 0.2 \\
0 & 0.2 & 0.2 & 0 \\
\end{pmatrix}.
\]  

(5.16)

The system has a single entry at site-1 and two symmetric paths: 1→3→4 and 1→2→4 (see Fig.5.6(c)).
5.3. Pathway Selecting Mechanism

Figure 5.12: The transfer rate of the 4 site model \((5.16)\). The transfer rate when phonons couples to different hopping amplitude. All couplings are either the same or zero.

Figure 5.13: The time evolution of a 4 site model \((5.16)\). Different colors indicate different site populations\(\rho_{11}, \rho_{22}, \rho_{33}, \rho_{44}\). a, b) Peierls phonons couple to the left branch of the molecules; c,d) Peierls phonons couple to both branches.
5.4 Summary and Future Researches

We study two cases: i) Peierls phonons coupled to both paths and 2) Peierls Phonon coupled to only one of the path (1→3→4). The time evolution of site-populations is illustrated in the dependence of transfer rate in Fig. 5.13. We can see the clear path selecting mechanism here. As for the both the weak interaction case \( g_P = 0.1 \) and the strong interaction case \( g_P = 1.0 \), the population on site-3 is significantly larger than the population on site-2. The pathway which couples to phonons (→3→4) has the dominant role in energy transfer. If the phonon couples to both pathways, however, the transfer rate is suppressed. The backwards transfers from site-4 to both site-2 and site-3 are both enhanced by phonon couplings and therefore impede the transfer to the RC. The excitons are more likely to be trapped compared with the single pathway case.

This can be confirmed with the dependence of transfer rate on coupling strength plots in Fig. 5.12. The transfer rate when the phonons only couple to a single branch is actually higher than the transfer rate when the phonons couple to both branches. We have already found similar behaviors in Fig. 5.7 and Fig. 5.11. This shows that for a multiple pathway model, it is actually more efficient to enhance the transfer rate along a particular pathway rather than several of them. It is interesting to see that the full Holstein coupling now has the higher transfer rate with the optimal value \( g_H \approx 0.75 \). However, the Peierls coupling still has a more significant effect on the transfer rate in the small interaction region.

5.4 Summary and Future Researches

In this chapter, we at first gave a complete description for the vibrational modes coupling in light harvesting molecules. The two-phonon interactions can be mapped into a spin bath model in the pure decoherence region, which introduce decoherence without dissipation. The high energy phonon modes can be mapped into a spin bath model in the high field region which has a Non-Markovian dissipative behavior. The intermediate vibrational modes can be treated with the method we developed in Chapter 4.

However, the lack of knowledge of the actual phonon couplings in the real system prevents us from studying the model thoroughly. Instead, we studied the reduced 3-site model of FMO complexes and explored different parameter regions of the unknown variables. In this case, the phonon energy is no longer on resonance. We find that the Holstein coupling still gives qualitatively the same effects as in Chapter 4. The Peierls coupling, on the other hand, gives a sharp transfer peak in the intermediate coupling.
5.4. Summary and Future Researches

region, instead of the high-transfer-rate plateau we found in Chapter 4. The optimal value of the coupling strength $g$ is robust against several parameters in the model, such as the coupling strength to the RC $t_0$, and to the RC bandwidth $D$. Only the energy deviation of the RC $d$ and phonon frequencies $\Omega$ can change the positions of the transfer peaks. The typical values of the Huang-Rhys factor associated with transfer-rate peaks ($\sim 0.07$) are still much smaller than the reported value for Holstein phonons ($\sim 0.22$).

In the last part of this chapter, we studied the path selecting mechanism for multiple-pathway models. Our models have two pathways to reach the RC. A Peierls coupling to phonons greatly enhances the site population on the coupled pathway. The transfer rate is also increased significantly if the phonon energy is close to the energy different between sites. We also find that it is more efficient for energy transfer if Peierls phonons only couple to a particular pathway in the system rather than couple to both of them. The competition between different pathways actually impedes the transfer into the RC. Therefore, beside the resonant transfer mechanism we introduced in Chapter 4 vibrational phonons can also help to increase the overall transfer rate by enhancing a particular path and suppressing the oscillation between pathways. This might explain the Nature’s preference for a particular pathway in an apparently symmetric structure.

In future researches, one can combine the numerical calculations of the acoustic phonon modes together with the vibrational modes discussed here. Master equation approaches are generally better for these acoustic phonon modes so one can combine such techniques with the methods we developed in this thesis. We have already shown the sensitivity of the transfer rate to the Peierls coupling and the robustness of Holstein couplings. It could be interesting to see how the acoustic phonon modes change the transfer peaks of the Peierls couplings.

To actually answer the questions about real world systems, one needs detailed information about the system. We have already shown that the sensitivity of the transfer rate to the Peierls phonon couplings even in the small interaction regime. Small Peierls couplings might have negligible effects on the local spectrum but can have a significant effect on the transfer rate. Current indirect experiments on the phonon couplings are not sufficient to fully understanding the physics in FMO complexes. A direct experiment on the actual phonon spectrum would be important in understanding the role of polaronic modes in light harvesting molecules. Also, first-principle studies based on the chemical structure of biological molecules would also be a good implement for further researches.
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Appendix A

Spin Chain Decoherence

A.1 Neglecting Commutator

In (2.79), we notice that $H'_n$ does not commute with each other, i.e.

$$[H_n, H'_n] = -\frac{2J^2}{N}(\gamma^\dagger_{kn} - \gamma_{kn})(\gamma^\dagger_{kn'} - \gamma_{kn'}).$$  \hspace{1cm} (A.1)

We can use the Zassenhaus formula [165] to get

$$e^{i \sum_n H_n t} = \prod_n e^{it H_n} \prod_{n_1 > n_2} e^{\frac{t^2}{2} [H_{n_1}, H_{n_2}]} \times \prod_{n_1 \geq n_2 \geq n_3} e^{-\frac{t^2}{6} ([H_{n_1}, [H_{n_2}, H_{n_3}]] + [[H_{n_1}, H_{n_2}], H_{n_3}]) + ...}.$$  \hspace{1cm} (A.2)

Although the Hamiltonian is not block diagonal in each $\{\gamma^\dagger_{kn}|0\rangle, |0\rangle\}$ subspace, if we restrict our model to the weak interaction region, i.e. $J \ll 1$, we can omit this commutator since it always comes into the final expression in higher order. For example, for the $\prod_{n_1, n_2} e^{\frac{t^2}{2} [H_{n_1}, H_{n_2}]}$ term, we could expand it in powers of $1/N$ and take expectation values

$$\text{tr}_b \left( \prod_{n_1 > n_2} e^{\frac{t^2}{2} [H_{n_1}^+, H_{n_2}^+]} \prod_{n_1, n_2} e^{\frac{t^2}{2} [H_{n_1}^-, H_{n_2}^-]} \right)$$

$$= \text{tr}_b \left( e^{-\frac{t^2}{6N} \sum_{n_1 > n_2} (\gamma^\dagger_{kn_1} - \gamma_{kn_1})(\gamma^\dagger_{kn_2} - \gamma_{kn_2})} \right)$$

$$\approx 1 - \frac{J^4 t^4}{N^2} N(N - 1).$$ \hspace{1cm} (A.3)

As we can see in the main text this already happens in the $J^2$ order. Therefore in the weakly interacting region, our calculation can be a good approximation to the exact result.
A.2 Adiabatic Decoupling

The goal is to solve the asymptotic solution to the following equation

\[ a(t) = \mp \sqrt{N} \dot{b}(t) \tag{A.4} \]

\[ \ddot{b}(t) - (iE_n + \frac{j(t)}{N}) \dot{b}(t) + \frac{J^2(t)}{N} b(t) = 0. \tag{A.5} \]

We first study the evolution of the state \((0,1)\). Actually, the state \((1,0)\) can be treated in the same way just with an opposite sign of \(J(t)\) and \(E_n\). Then we have the initial condition

\[ b(t_0) = 1 \tag{A.6} \]

\[ \dot{b}(t_0) = 0. \tag{A.7} \]

Define the following quantity for simplification, keeping in mind that \(\frac{J^2}{N}\) is very small

\[ \epsilon = \frac{J^2}{N}. \tag{A.8} \]

The general solution of the equation (2.95) is

\[ b(t) = C_1 e^{-iE_n t/2 - iE_n \sqrt{1 + 4\epsilon/E_n^2}/2} (1 + e^{kt})^{i\sqrt{\epsilon}/k} f_1(-e^{kt}) + C_2 e^{-iE_n t/2 + iE_n \sqrt{1 + 4\epsilon/E_n^2}/2} (1 + e^{kt})^{i\sqrt{\epsilon}/k} f_2(-e^{kt}). \tag{A.9} \]

Here

\[ f_1(x) = 2F_1\left( \left[ \begin{array}{c} \frac{iE_n}{2k} + \frac{i\sqrt{\epsilon}}{k} \right] \right) \left[ \begin{array}{c} \frac{iE_n}{2k} - \frac{i\sqrt{\epsilon}}{k} \sqrt{1 + \frac{4\epsilon}{E_n^2}}, 1 \end{array} \right] \left[ \begin{array}{c} \frac{iE_n}{2k} + \frac{i\sqrt{\epsilon}}{k} \sqrt{1 + \frac{4\epsilon}{E_n^2}} \end{array} \right] \right]. \tag{A.10} \]

\[ f_2(x) = 2F_1\left( \left[ \begin{array}{c} \frac{iE_n}{2k} + \frac{i\sqrt{\epsilon}}{k} \right] \right) \left[ \begin{array}{c} \frac{iE_n}{2k} - \frac{i\sqrt{\epsilon}}{k} \sqrt{1 + \frac{4\epsilon}{E_n^2}}, 1 \end{array} \right] \left[ \begin{array}{c} \frac{iE_n}{2k} + \frac{i\sqrt{\epsilon}}{k} \sqrt{1 + \frac{4\epsilon}{E_n^2}} \end{array} \right]. \tag{A.11} \]

We set our initial time \(t_0 \to -\infty\), then \(e^{kt} \to 0\) and

\[ f_{1,2}(-e^{kt}) \to 1. \tag{A.12} \]

Therefore

\[ b(t_0) = 1 \]

\[ = C_1 e^{-iE_n t_0/2 - iE_n t_0 \sqrt{1 + 4\epsilon/E_n^2}/2} + C_2 e^{-iE_n t_0/2 + iE_n t_0 \sqrt{1 + 4\epsilon/E_n^2}/2}; \tag{A.13} \]
A.2. Adiabatic Decoupling

\[ \dot{b}(t_0) = 1 \]

\[ = C_1(-iE_n/2 - iE_n\sqrt{1 + 4\epsilon/E_n^2 / 2})e^{-iE_n t_0/2 - iE_n t_0\sqrt{1 + 4\epsilon/E_n^2 / 2}} 
+ C_2(-iE_n/2 + iE_n\sqrt{1 + 4\epsilon/E_n^2 / 2})e^{-iE_n t_0/2 + iE_n t_0\sqrt{1 + 4\epsilon/E_n^2 / 2}}. \]  
(A.14)

Then we can get the constant \( C_1, C_2 \) as

\[ C_1 = \frac{1}{2} e^{iE_n t_0/2 + iE_n t_0\sqrt{1 + 4\epsilon/E_n^2 / 2}} (-1 + (1 + \frac{4\epsilon}{E_n^2})^{-\frac{1}{2}}) \]  
(A.15)

\[ C_2 = \frac{1}{2} e^{iE_n t_0/2 - iE_n t_0\sqrt{1 + 4\epsilon/E_n^2 / 2}} (1 + (1 + \frac{4\epsilon}{E_n^2})^{-\frac{1}{2}}). \]  
(A.16)

After we get the solution, we could study its behavior when \( t \to \infty \). We use the fact that when \( t \to \infty \)

\[ f_1(-e^{kt}) \to A e^{iE_n t/2 - i\sqrt{\epsilon t} + \sqrt{iE_n^2 / 2}} \]  
(A.17)

\[ f_2(-e^{kt}) \to B e^{iE_n t/2 - i\sqrt{\epsilon t} - \sqrt{iE_n^2 / 2}} \]  
(A.18)

with

\[ A = \frac{\Gamma(1 + \frac{iE_n}{k} - i\sqrt{\epsilon} - \sqrt{iE_n^2 / 2})}{\Gamma(1 + \frac{iE_n}{k} + i\sqrt{\epsilon} - \sqrt{iE_n^2 / 2})} \times \frac{1}{\Gamma(1 + \frac{iE_n}{k} + \sqrt{iE_n^2 / 2})} \]  
(A.19)

\[ B = \frac{\Gamma(1 + \frac{iE_n}{k} + i\sqrt{\epsilon} + \sqrt{iE_n^2 / 2})}{\Gamma(1 + \frac{iE_n}{k} - i\sqrt{\epsilon} + \sqrt{iE_n^2 / 2})} \times \frac{1}{\Gamma(1 + \frac{iE_n}{k} + i\sqrt{\epsilon} + \sqrt{iE_n^2 / 2})}. \]  
(A.20)

Recalling that \( \epsilon = \frac{j_0^2}{N} \) is a very small number, we can expand the solution according to the order of \( \epsilon \).

**Zeroth order** : if \( \epsilon = 0 \), then \( C_1 \to 0 \), \( C_2 \to 1 \), and

\[ B \to \frac{\gamma(1 + \frac{iE_n}{k})\gamma(1 + \frac{iE_n}{k})}{\gamma(1 + \frac{iE_n}{k})\gamma(1 + \frac{iE_n}{k})} \to 1. \]  
(A.21)

\[ \Rightarrow b(t) \to 1, \] which is exactly what we expected.
A.2. Adiabatic Decoupling

First order Since \( \sqrt{1 + \frac{4\epsilon}{E_n}} \approx 1 + \frac{2\epsilon}{E_n^2} \), we have

\[
C_1 \to e^{iE_nt_0} (1 + \frac{i\epsilon t}{E_n}) \left( -\frac{\epsilon}{E_n^2} \right) = -\frac{\epsilon}{E_n^2} e^{iE_nt_0} \tag{A.22}
\]

\[
C_2 \to e^{-i\epsilon t_0/E_n^2} (1 - \frac{\epsilon}{E_n}) = 1 - \frac{\epsilon}{E_n^2} - \frac{i\epsilon t}{E_n^2}. \tag{A.23}
\]

As a result

\[
A \to \Gamma(1 - \frac{iE_n}{k}) \Gamma(1 + \frac{iE_n}{k}) \times \left[ 1 - \frac{i\epsilon}{kE_n} \left( \frac{\Gamma'(1 - iE_n/k)}{\Gamma(1 - iE_n/k)} + i\Gamma'(1) \right) \right. \\
+ \frac{\epsilon}{E_n^2} (\Gamma'(1) - \Gamma''(1)) \right] \tag{A.24}
\]

\[
B \to 1 - \frac{\Gamma'^2(1 + \frac{iE_n}{k})}{\Gamma(1 + \frac{iE_n}{k})^2} \frac{\epsilon}{k^2} + \frac{\Gamma''(1 + \frac{iE_n}{k}) \epsilon}{\Gamma(1 + \frac{iE_n}{k}) k^2}; \tag{A.25}
\]

\[
\Rightarrow b(t) \to 1 - \frac{\epsilon}{k^2} e^{iE_nt_0} \Gamma(1 - \frac{iE_n}{k}) \Gamma(1 + \frac{iE_n}{k}) - \frac{\epsilon}{E_n^2} \frac{i\epsilon t}{E_n^2} - \frac{\epsilon}{k^2} \frac{\Gamma'^2(1 + \frac{iE_n}{k})}{\Gamma(1 + \frac{iE_n}{k})^2} + \frac{\epsilon}{k^2} \frac{\Gamma''(1 + \frac{iE_n}{k})}{\Gamma(1 + \frac{iE_n}{k})} + O(\epsilon^2). \tag{A.26}
\]

Then the trace of \( \text{tr}(e^{iH_n^+t} e^{iH_n^-t}) \) is \( |b(t)|^2 - |a(t)|^2 \). Since \( |b(t)|^2 - |a(t)|^2 = 1 \), \( \text{tr}(e^{iH_n^+t} e^{iH_n^-t}) = 2|b(t)|^2 - 1 \). For adiabatic decoupling we mentioned in the main text, we take \( k \to 0 \), then \( \frac{d}{dt} J(t) \to 0 \). The system is slowly decoupled from the bath. We use the fact that when \( |z| \to \infty \)

\[
(\ln \Gamma(z))' = \ln z + \frac{z - \frac{1}{2}}{z} + O(z^{-2}) \tag{A.27}
\]

\[
(\ln \Gamma(z))'' = \frac{\Gamma''(z)}{\Gamma(z)} - \left( \frac{\Gamma'(z)}{\Gamma(z)} \right)^2 \tag{A.28}
\]

\[
(\ln \Gamma(z))''' = \frac{1}{z} + \frac{1}{2z^2} + O(z^{-3}) \tag{A.29}
\]

\[
\text{We can get the factor } b(t) \text{ as well as the decoherence factor } \kappa_n \text{ for this subspace as}
\]

\[
|b(t)|^2 \to 2(1 - \frac{\epsilon}{E_n^2}) \tag{A.31}
\]

\[
\kappa_n(t) = \text{tr}(e^{iH_n^+t} e^{iH_n^-t}) \to 1 - \frac{2J_0^2}{NE_n^2} \tag{A.32}
\]
Appendix B

Pure Phase Decoherence

B.1 Free Particle

We consider first the free particle for the $N$-site symmetric ring, with Hamiltonian

$$H_o = \sum_{<ij>} \left[ \Delta_o c_i^\dagger c_j e^{iA_{ij}} + H.c. \right]. \quad (B.1)$$

and band dispersion $\epsilon_{k_n} = 2\Delta_o \cos(k_n - \Phi/N)$.

For this free particle the dynamics is entirely described in terms of the bare 1-particle Green function

$$G_{jj'}^o(t) \equiv \langle j|G^o(t)|j'\rangle \equiv \langle j|e^{-iH_o t}|j'\rangle = \frac{1}{N} \sum_n e^{-i2\Delta_0 t \cos(k_n - \Phi/N)} e^{ik_n(j' - j)}. \quad (B.2)$$

which gives the amplitude for the particle to propagate from site $j'$ at time zero to site $j$ at time $t$. This can be written as a sum over winding numbers $m$, viz.,

$$G_{jj'}(t) = \frac{1}{N} \sum_{k_n} e^{-i2\Delta_0 t \cos(k_n - \Phi/N)} e^{ik_n(j' - j)}$$

$$= \sum_{\ell=0}^{\infty} \sum_{m=0}^{\ell} \frac{(-i\Delta_0 t)^\ell}{m!(\ell - m)!} e^{i\Phi/N(\ell - 2m)}$$

$$\times \frac{1}{N} \sum_{n=0}^{N-1} e^{-i2\pi n(\ell - 2m - j + j')} \quad (B.3)$$

This sum may be evaluated in various forms, the most useful being in terms
B.1. Free Particle

of Bessel functions:

\[ G^{0}_{jj'}(t) = \frac{1}{N} \sum_{n=0}^{N-1} \sum_{m=-\infty}^{+\infty} J_{m}(2\Delta_{o}t)(-i)^{m} e^{im(k_{n}-\Phi/N)+ik_{n}(j-j')} + \sum_{m=-\infty}^{+\infty} J_{m}(2\Delta_{o}t)(-i)^{m} e^{-im\Phi/N} \delta_{Np,m+j-j'} \]

\[ = \sum_{m=-\infty}^{+\infty} J_{Np+j'-j}(2\Delta_{o}t)e^{-i(Np+j'-j)(\Phi/N+\pi/2)} \]

which can also be written as

\[ G^{0}_{jj'}(t) = \sum_{p} e^{i(p\Phi+j\Phi/N}(j-j')I_{Np+j-j'}(-2i\Delta_{o}t) , \] (B.5)

where we use the hyperbolic Bessel function \( I_{\alpha}(x) \), defined as \( I_{\alpha}(x) = (i)^{-\alpha}J_{\alpha}(ix) \), and we drop the modulus signs for the hyperbolic Bessel functions \( I_{\alpha} \), since \( I_{-\alpha} = i^{\alpha}J_{\alpha} = i^{\alpha}(-1)^{\alpha}J_{\alpha} = i^{-\alpha}J_{\alpha} = I_{\alpha} \) as long as \( \alpha \in \mathbb{Z} \).

Consider now the free particle density matrix. As discussed in the main text, we have in general some initial density matrix \( \rho_{o,l,l'} = \langle l|\rho(t=0)|l'\rangle \) at time \( t = 0 \) (where \( l \) and \( l' \) are site indices), so at a later time \( t \) we have

\[ \rho_{o,jj'}^{0}(t) = \sum_{l,l'} \rho_{l,l'} G_{jl}^{0}(t)G_{l'l'}^{0}(t)\dagger . \] (B.6)

Now the most obvious way of evaluating this is by using the result for the Green function, to produce a double sum over winding numbers:

\[ \rho_{o,jj'}^{0}(t) = \sum_{l,l'} \rho_{l,l'} \sum_{pp'} e^{i(p-p')\Phi} e^{i\Phi(j-j'+l-l')/N} (-i)^{|Np+j-l|} \langle i|Np'+j'-l'| \]

\[ J_{|Np+j-l|}(2\Delta_{o}t)J_{|Np'+j'-l'|}(2\Delta_{o}t) \]

\[ = \sum_{l,l'} \rho_{l,l'} \sum_{pp'} e^{i(p-p')\Phi} e^{i\Phi(j-j'+l-l')/N} \]

\[ I_{|Np+j-l|}(-2i\Delta_{o}t)I_{|Np'+j'-l'|}(-2i\Delta_{o}t) \] . (B.7)

However this expression is somewhat unwieldy, particularly for numerical evaluation, because of the sum over pairs of Bessel functions. It is then useful to notice that we can also derive the answer as a single sum over
winding numbers, as follows:

\[
\langle j | \rho(t) | j' \rangle = \frac{1}{N^2} \sum_{l,l'=0}^{N-1} \sum_{n,n'=0}^{N-1} \rho_{l,l'} \rho_{n,n'} e^{-i(k_n(j-l)-k_{n'}(j'-l'))+4i\Delta_o t \sin[\phi-(k_n+k_{n'})/2] \sin[(k_n-k_{n'})/2]}
\]

\[
= \frac{1}{N^2} \sum_{n,m=0}^{N-1} \sum_{l,l'=0}^{N-1} \sum_{p=-\infty}^{\infty} \rho_{l,l'} J_p[4\Delta_o t \sin(k_m/2)]
\]

\[
\times e^{ip(\phi-k_m/2)-ik_n(j-l)+i(k_n-k_{n'})(j'-l')}
\]

\[
= \sum_{l,l'=1}^{N} \frac{\rho_{l,l'}}{N} \sum_{p=-\infty}^{\infty} \sum_{m=0}^{N-1} (J_{Np'+j'-l-l'}[4\Delta_o t \sin(k_m/2)]e^{ik_m(l=l'-j'+Np')/2})
\]

\[
\times e^{i\phi(Np'+j'-j-l-l')}
\].

(B.8)

In the second step we replaced \(n' = m - n\). In the third step we also used the identity \(\sum_{n'=0}^{N-1} e^{ik_n n'} = \sum_{p=-\infty}^{\infty} \sum_{\ell=0}^{N-1} N \delta_{\ell,Np}\). If we start with \(\rho(0) = |0\rangle \langle 0|\), the expression is shortened to

\[
\rho_{jj'} = \frac{1}{N} \sum_{m=0}^{N-1} \sum_{\ell=-\infty}^{\infty} J_{Np'+j'-j} J_{\mu} J_{\mu} e^{i\phi(Np'+j'-j-Np')/2}
\]

(B.9)

It is useful and important to show that these two expressions ((B.7)) and ((B.8)) are equivalent to each other. To do this we use Graf's summation theorem for Bessel functions

\[
J_\nu(2x \sin \frac{\theta}{2})(-e^{-i\theta})^\nu = \sum_{\mu=-\infty}^{+\infty} J_{\nu+\mu}(x)J_\mu(x)e^{i\mu \theta}.
\]

(B.10)

We set \(\theta = 0, \frac{2\pi}{N}, \frac{2\pi m}{N}, \ldots, \frac{2\pi(N-1)}{N}\), which is the \(k_m\) in (B.8) and multiply \(e^{-ij\theta}\) on each side. We then have

\[
J_\nu(2x \sin \frac{k_m}{2})e^{-i(k_m+\pi)\nu} e^{-ik_m}
\]

\[
= \sum_{\mu=-\infty}^{+\infty} J_{\nu+\mu}(x)J_\mu(x)e^{i(\mu-j)k_m}.
\]

(B.11)

Noticing then that

\[
\sum_{m=0}^{N-1} e^{ik_m n} = \sum_{p} \delta_{Np,n},
\]

(B.12)
B.2 Including Phase Decoherence

we do the sum over \( m \); only \( \mu - j = Np \) survives, and thus

\[
\frac{1}{N} \sum_{m=0}^{N-1} J_\nu(2x \sin \frac{k_m}{2}) e^{-i(k_m+\pi)\frac{\nu}{2}} e^{-i(jk_m)}
\]

\[
= \frac{1}{N} \sum_p J_{Np+j+\nu}(x) J_{Np+j}(x). \quad (B.13)
\]

Setting \( \nu = Np' + j' - Np - j, x = 2\Delta_o t \), we then substitute back into \( (B.7) \), to get

\[
\rho_{jj'}^o(t) = \sum_{pp'} e^{i(\Phi/N + \pi/2)(Np' - Np + j' - j)} J_{Np+j}(2\Delta_o t) J_{Np'+j'}(2\Delta_o t)
\]

\[
= \frac{1}{N} \sum_p e^{i(Np+j')-j)(\frac{\Phi}{N} + \frac{\pi}{2})} \sum_{m=0}^{N-1} J_{Np+j'-j}(4\Delta_o t \sin \frac{k_m}{2})
\]

\[
e^{-i(k_m+\pi)\frac{Np+j'}{2}} e^{-i(jk_m)}
\]

\[
= \frac{1}{N} \sum_{p} \sum_{m=0}^{N-1} J_{Np+j'-j}(4\Delta_o t \sin \frac{k_m}{2}) e^{i(Np+j'-j)(\frac{\Phi}{N} - ik_m(j+j'+Np)/2)/2}. \quad (B.14)
\]

The density matrix \( \rho \) is Hermitian, i.e., \( \rho_{jj'} = \rho_{j'j}^* \); setting \( p' = -p \), we then have

\[
\rho_{jj'}^o(t) = \frac{1}{N} \sum_{p} \sum_{m=0}^{N-1} J_{-Np'+j-j'}(4\Delta_o t \sin \frac{k_m}{2}) e^{-i(-Np'+j-j')\frac{\Phi}{N} + ik_m(j+j'-Np')/2}
\]

\[
= \frac{1}{N} \sum_{m=0}^{N-1} \sum_{p'=-\infty}^\infty J_{Np'+j-j'}(4\Delta_o t \sin(k_m/2)) e^{i\Phi(Np'+j'-j)-ik_m(j+j'-Np')/2}. \quad (B.15)
\]

where in the last line, we use set \( k_m \rightarrow -k_m \), and use the fact that for integer order \( n \), \( J_n(-x) = J_{-n}(x) \). Thus we have demonstrated the equivalence of the single and double sum forms for the density matrix.

B.2 Including Phase Decoherence

To calculate the reduced density matrix for the particle in the presence of the spin bath, we need to average over the spin bath degrees of freedom.
We will do this in a path integral technique, adapting the usual Feynman-Vernon [14] theory for oscillator baths to a spin bath; the following is a generalization of the method discussed previously [1]. We can parametrize a path for the angular coordinate \( \Theta(t) \) which includes \( m \) transitions between sites in the form

\[
\Theta_{(m)}(t) = \Theta(t=0) + \sum_{i=1}^{m} \sum_{q_i=\pm} q_i \theta(t-t_i), \tag{B.16}
\]

where \( \theta(x) \) is the step-function; we have transitions either clockwise (with \( q_j = +1 \)) or anticlockwise (with \( q_j = -1 \)) at times \( t_1, t_2, \ldots, t_m \). The propagator \( K(1,2) \) for the particle reduced density matrix between times \( \tau_1 \) and \( \tau_2 \) is then

\[
K(1,2) = \int_{\Theta_1}^{\Theta_2} \int_{\Theta_1'}^{\Theta_2'} d\Theta d\Theta' e^{-\frac{i}{\hbar} (S_o[\Theta] - S_o[\Theta'])} F[\Theta, \Theta'], \tag{B.17}
\]

where \( S_o[\Theta] \) is the free particle action, and \( F[\Theta, \Theta'] \) is the “influence functional” [14], defined by

\[
F[\Theta, \Theta'] = \prod_k \langle \hat{U}_k(\Theta, t) \hat{U}_k^\dagger(\Theta', t) \rangle. \tag{B.18}
\]

Here the unitary operator \( \hat{U}_k(\Theta, t) \) describes the evolution of the \( k \)-th environmental mode, given that the central system follows the path \( \Theta(t) \) on its “outward” voyage, and \( \Theta'(t) \) on its “return” voyage. Thus \( F[\Theta, \Theta'] \) acts as a weighting function, over different possible paths \( (\Theta(t), \Theta'(t)) \). The average \( \langle ... \rangle \) is performed over environmental modes - its form depends on what constraints we apply to the initial full density matrix. In what follows we will assume an initial product state for the full particle/environment density matrix.

For the general Hamiltonian in eqtns. (3.1)-(3.12), the environmental average is a generalisation of the form that appears when we average over a spin bath for a central 2-level system, or “qubit” (see ref. (II), and also ref. ([97])). The essential result is that we can calculate the reduced density matrix for a central system by performing a set of averages over the bare density matrix. For a spin bath these can be reduced to phase averages and energy averages; and for the present case it reduces to a simple phase average.

Let us write the “bare” free particle density matrix in the form of a double sum over winding numbers

\[
\rho^0_{jj'}(t) = \sum_{pp'} \rho^0_{jj'}(p, p'; t). \tag{B.19}
\]
Including Phase Decoherence

Then the key result is that in the presence of phase coupling to the spin bath, the reduced density matrix takes the form

$$\rho_{jj'}(t) = \sum_{pp'} \sum_{ll'} \rho_{0j}^{p} \rho_{l,j'}^{l'}(p,p';t) F_{j,j'}^{l,l'}(p,p') \rho_{l'l}, \quad (B.20)$$

where the influence functional, initially over the entire pair of paths for the reduced density matrix, has now reduced to a much simpler weighting function $F_{i,j'}^{l,l'}(p,p')$ over winding numbers. We can do this because the effect of the pure phase coupling to the spin bath is to accumulate an simple additional phase in the path integral each time the particle hops. Just as for the free particle, we can then classify the paths by winding number; for a path with winding number $p$ which starts at site $l$ (the initial state) and ends at site $j$, the additional phase factor can then be written as

$$\exp\{-ip \sum_{k} \left( \sum_{(mn) = (01)}^{(N0)} - i \sum_{(mn) = (l,l+1)}^{(j-1,j)} (\alpha_{mn}^{k} \cdot \sigma_{k}) \right)\} \quad (B.21)$$

and for fixed initial and final sites, this additional phase only depends on the winding number. The weighting function $F_{i,j'}^{l,l'}(p,p')$ is just the influence functional, but now it is an ordinary function, which we will henceforth call the “influence function”. In the same way as the original influence functional, it depends in general on the initial state $\rho_{l,l'}$ of the density matrix at time $t = 0$. Performing the sums over the two paths as before, but now including the phase factors (B.21), we get:

$$F_{i,j'}^{l,l'}(p,p') = \rho_{0j}^{p} \rho_{l,j'}^{l'}(p,p') \frac{e^{-i(p-n')}}{e^{-i((j-1,j') + (l-1,l'))}} \frac{\alpha_{mn}^{k} \cdot \sigma_{k}}{\alpha_{k}^{j}, \sigma_{k}} \quad (B.22)$$

for the case of general phase couplings $\alpha_{ij}^{k}$ to the bath.

In the purely symmetric case where $\alpha_{ij}^{k} \rightarrow \alpha_{k}$ for every link, the influence function reduces to the much simpler result

$$F_{i,j'}^{l,l'}(p,p') = e^{-i[N(p-n')+(j-j'+l-l')]} \sum_{k} \alpha_{k} \sigma_{k} \quad (B.23)$$

which for a particle being launched from the origin gives the result (B.23) quoted in the main text.
Now consider the current $I_{j,j+1}(t)$, which is given in general by:

$$I_{j,j+1} = -i(\tilde{\Delta}_{j,j+1} \rho_{j+1,j} - \Delta_{j+1,j} \rho_{j,j+1}), \tag{B.24}$$

where we define

$$\tilde{\Delta}_{j,j+1} = \Delta_o e^{i\Phi/N} e^i \sum_k \alpha_{k,j+1}^j \sigma_k. \tag{B.25}$$

Using the results derived above for the density matrix, we can derive expressions for $I_{j,j+1}(t)$ in both single and double winding number forms. The double Bessel function form is

$$I_{j,j+1} = -2\Delta_o \sum_{pp'} J_{Np+j-l}(2\Delta_o t) J_{Np'+j+1-l'}(2\Delta_o t)$$

$$\times \text{Re} \langle \rho_{p,l} e^{i(N(p-p')+\frac{1}{N})\Phi} e^{-i(p-p') \sum_k \sum_{(mn)=(01)} (N^0)} \alpha_k^m \sigma_k \rangle \times \sum_k \sum_{(mn)=(j',j+1)} \alpha_{k,j+1}^j \sigma_k. \tag{B.26}$$

Again, we make the assumption of a completely ring-symmetric bath, so that $\alpha_{ij}^k \rightarrow \alpha_k$. Then we get

$$I_{j+1,j} = 2\Delta_o \sum_{pp'} \sum_{l,l'} J_{Np+j-l}(2\Delta_o t) J_{Np'+j+1-l'}(2\Delta_o t) F_{l,l'}(p',p)$$

$$\times \text{Re} \langle \rho_{p,l} e^{i(N(p'-p)+(l-l')/N)} \rangle \tag{B.27}$$

From this we can derive the single Bessel Function summation form as follows. Using the equation

$$\sum_p J_{Np+n-l}(x) J_{Np+n-l+v}(x) = \frac{1}{N} \sum_{m=0}^{N-1} J_k(2x \sin \frac{k_m}{2}) e^{-i(n-l)k_m - i(k_m - \pi/2)} \tag{B.28}$$

which is another form of Graf’s identity[166], we set $\nu = N(p' - p) + 1 + l - l'$, $x = 2\Delta_o t$; then

$$I_{j+1,j} = \frac{2\Delta_o}{N} \sum_{m=0}^{N-1} \sum_p \sum_{l,l'} J_{Np+1+l-l'}(4\Delta_o t \sin \frac{k_m}{2}) e^{-i(k_m - \frac{Np+1}{2} + n-(l+l')/2]}$$

$$\times \cdot i^{Np+1+l-l'} F_{l,l'}(p) \text{Re} \langle \rho_{p,l} e^{i[N(p'-p)+(l-l')/N]} \rangle \tag{B.29}$$

where we define $F_{l,l'}(p,0) \equiv F_{l,l'}(p)$. 

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If we make the assumption that the particle starts at the origin, these results simplify considerably; one gets

\[
I_{j+1,j} = 2\Delta_o \sum_{p} J_{Np+j} (2\Delta_o t) J_{Np'+j+1} (2\Delta_o t) F_0(p', p) \cos[(\frac{\pi}{2} N + \Phi)(p' - p)]
\]

\[
= \frac{2\Delta_o}{N} \sum_{m=0}^{N-1} \sum_{p} J_{Np+1} (4\Delta_o t \sin \frac{k_m}{2}) e^{-ik_m \frac{(Np+1) + j}{2} \frac{iNp+1}{N} N} F_0(p) \cos[(\frac{\pi}{2} N + \Phi)p]
\]

(B.30)

for the double and single sums over winding numbers, respectively; and \( F_0(p) \equiv F_{j,j}(p, 0) \). The latter expression is used in the text for practical analysis.
Appendix C

Orthogonal Blocking Approximation

C.1 A Useful Integral

In this section we are going to evaluate the integral

\[ I(t) = \int_{-\infty}^{\infty} \frac{e^{-i\xi}}{2\pi} d\xi \prod_{j=0}^{L} \left( \frac{e^{i(\xi - M_j ht)} - 1}{i(\xi - M_j ht)} \right). \]  

(C.1)

When \( L \geq 2 \), this integral does converge. So we are free to choose any principal value and get the same result. We replacing \( i\xi \) with \( z \) and shift the denominator by an infinitesimal \( -\eta < 0 \):

\[ I(t) = \int_{-i\infty}^{i\infty} \frac{e^{-z}}{2\pi i} dz \prod_{j=0}^{L} \left( \frac{e^{z - iM_j ht} - 1}{z - iM_j ht - \eta} \right). \]  

(C.2)

This function now has poles at \( z = iM_j ht + \eta \). If on expands the numerator one gets a polynomial of \( e^{z} \) with only one negative power term \( e^{-z}(-1)^{L+1} \). We use the residue theorem to evaluate the integral. The contour we choose goes along the imaginary axis. But whether it encloses the left or right half of the complex plane depends on the power of \( e^{z} \). Noticing that the poles are all in the right half plane, only the negative power term requires the contour being closed in the right half plane. We only need to consider the \( e^{-z} \) term in this choice. If \( M_j \neq M_k, \forall k \neq j \), the integral equals

\[ I(t) = (-1)^{L} \sum_{k=0}^{L} \prod_{j \neq k}^{L} \frac{e^{-iM_k ht}}{i(M_k - M_j)ht}, \]  

(C.3)

which is inversely proportional to \( (M_k - M_j) \). If all the \( M_j \) are equal to each other, \( M_j = M, \forall j \), we have

\[ I(t) = \frac{e^{-iMht}}{L!}. \]  

(C.4)
The residue calculation when not all the $M_j$ are the same is tedious but can be complicated. In the main part of the thesis we use the result when $M_j$ can only take two values: either $M$ or $M'$. In this case, the integral turns out to be:

$$\int_{-\infty}^{\infty} \frac{e^{-i\xi}}{2\pi} d\xi \prod_{j=0}^{n+m-1} \left( \frac{e^{i(\xi-Mht)}-1}{i(\xi-Mht)} \right)^n \left( \frac{e^{i(\xi-M'h)t}-1}{i(\xi-M'h)t} \right)^m$$

$$= \sum_{a=0}^{n-1} \frac{(-1)^m(m+a-1)!}{(n-1-a)!(m-1)!a!} \frac{e^{-iMht}}{(i(M-M')ht)^{m+a}}$$

$$+ \sum_{a=0}^{m-1} \frac{(-1)^n(n+a-1)!}{(m-1-a)!(n-1)!a!} \frac{e^{-iM'h}t}{i(M'-M)ht}^{n+a},$$

here $n, m > 0$ and $n + m = L + 1$.

C.2 OBA Expansion of the System

To evaluate this quantity, we define the operator

$$T_L \equiv \delta(\sum_k \sigma^z_k - M)e^{i\sum_k \alpha_k^{iL} \sigma^z_k}...\delta(\sum_k \sigma^z_k - M)e^{i\sum_k \alpha_k^{iL} \sigma^z_k}.$$  \hspace{1cm} (C.6)

We then substitute (3.66) into (C.6). We can decompose $T_L$ into

$$T_L = (\prod_k T^k_L)e^{-iM_{\sum_{n=0}^{L}} \xi_n}$$  \hspace{1cm} (C.7)

$$T^k_L = e^{i\xi_k \sigma^z_k} e^{i\alpha_k^{iL-1} \sigma^z_k} ... e^{i\xi_1 \sigma^z_k} e^{i\alpha_k^{iL} \sigma^z_k} e^{i\xi_0 \sigma^z_k}.$$  \hspace{1cm} (C.8)

Afterwards, we replace $\alpha_k^{iL} \sigma^z_k$ by $\sigma_k^{iL}$, since this does not cause confusion within a single path. Thereafter, we do a Taylor expansion to second order
C.2. OBA Expansion of the System

in $\alpha_k$:

\[ T^k_L \uparrow \rangle = e^{i \sum_{n=0}^{L} \xi_n} \{ \uparrow \} + i \sum_{n=1}^{L} \alpha^i_k e^{-2i \sum_{m=n}^{L} \xi_n} \downarrow \rangle \]

\[ - \left( \frac{1}{2} \sum_{n=1}^{L} (\alpha^i_k)^{2} + \sum_{m<n} \alpha^i_k \alpha^m_k e^{-2i \sum_{j=m}^{n-1} \xi_j} \right) \}

\[ T^k_L \downarrow \rangle = e^{-i \sum_{n=0}^{L} \xi_n} \{ \downarrow \} + i \sum_{n=1}^{L} \alpha^i_k e^{2i \sum_{m=n}^{L} \xi_n} \uparrow \rangle \]

\[ - \left( \frac{1}{2} \sum_{n=1}^{L} (\alpha^i_k)^{2} + \sum_{m<n} \alpha^i_k \alpha^m_k e^{2i \sum_{j=m}^{n-1} \xi_j} \right) \}

(C.9)

Here we still assume equally distributed initial states, i.e., the initial density matrix of the spin bath itself is an identity matrix. Given a certain total polarization $M$, all configurations with $\frac{K+M}{2}$ spin-ups and $\frac{K-M}{2}$ spin-downs compose the $\sum_k \sigma^z_k = M$ subspace. The weight of these configurations are

\[ p(M) = \frac{K!}{\left( \frac{K+M}{2} \right)! \left( \frac{K-M}{2} \right)! 2^K}. \]

(C.10)

The average amplitude within this subspace is defined in the following way:

\[ A^\pm_{k,M} (L, L') \equiv \langle \uparrow (\downarrow) | T^k_L T^{\dagger k}_{L'} | \uparrow (\downarrow) \rangle. \]

(C.11)
Therefore, $A_k$ can be written as

$$A_k^{\pm}(L, L') = e^{\pm i(\sum_{n=0}^{L} \xi_n - \sum_{n'=0}^{L'} \xi'_{n'})} \left[ 1 - \frac{1}{2} \sum_{n=1}^{L} (\alpha_k^{i_n})^2 - \frac{1}{2} \sum_{n=1}^{L'} (\alpha_k^{i'_n})^2 \right]$$

$$- \sum_{m<n}^{L} \alpha_k^{i_n} \alpha_k^{i_m} e^{\mp 2i \sum_{j=m}^{n-1} \xi_j} - \sum_{m<n}^{L'} \alpha_k^{i'_n} \alpha_k^{i'_m} e^{\mp 2i \sum_{j=m}^{n'-1} \xi'_{j}}$$

$$+ \sum_{n=1}^{L} \sum_{n'=1}^{L'} \alpha_k^{i_n} \alpha_k^{i'_{n'}} e^{\mp 2i(\sum_{m=0}^{n-1} \xi_m - \sum_{m'=0}^{n'-1} \xi'_{m'})}.$$

(C.12)

Here $A_k^+$ is for spin-up $\uparrow$ at $k$th spin; $A_k^-$ is for spin-down $\downarrow$ at $k$th spin. Then the product over all environment spins is

$$A_M(L, L') = \prod_k A_k^{\pm} e^{-iM(\sum_{n=0}^{L} \xi_n - \sum_{n'=0}^{L'} \xi'_{n'})}. \quad (C.13)$$

This product is for a certain configuration of environment spins with polarization $M$. The configuration determines the plus minus sign of $A_k^{\pm}$. We can see that the overall phase factor $e^{-iM(\sum_{n=0}^{L} \xi_n - \sum_{n'=0}^{L'} \xi'_{n'})}$ is canceled by the collective contribution from terms $e^{\pm i(\sum_{n=0}^{L} \xi_n - \sum_{n'=0}^{L'} \xi'_{n'})}$ acting on this configuration.

The next step is to take the average of this product in the $\sum_k \sigma_k^z = M$ subspace. This product is for a particular arrangement of spins. Notice that small $M$ configurations have a way larger phase space, which allows more possible configurations. We could expand (C.10), according to the standard method in the large $K$ case as

$$\log \frac{p(M)}{p(0)} = \log \frac{(K^2)!}{(K+M)!} \approx -\frac{M^2}{2K}. \quad (C.14)$$

The leading order is of order $-M^2/K^2$. We will then expand the result into a power series in $M/K. Within the \frac{M}{K} \approx 0$ region, we can find a complex
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conjugate of almost every \( A_k \). Actually, we can find \( K^\pm M \) plus sign terms and \( K^\mp M \) minus sign terms. To zeroth order in \( \frac{M}{K} \) we get

\[
A_0(L, L') = \exp\{-\sum_{n=1}^{L} \sum_{m<n} \frac{1}{2} \left( \alpha_k^{i_n} \right)^2 + \sum_{m<n} \alpha_k^{i_n} \alpha_k^{i_m} \cos(2 \sum_{j=m}^{n-1} \xi_j) \}
\]

\[
\sum_{n=1}^{L'} \sum_{m<n} \frac{1}{2} \left( \alpha_k'^{i_n} \right)^2 + \sum_{m<n} \alpha_k'^{i_n} \alpha_k'^{i_m} \cos(2 \sum_{j=m}^{n-1} \xi'_j) \}
\]

\[
+ \sum_{n=1}^{L} \sum_{n'=1}^{L'} \sum_{k} \alpha_k^{i_n} \alpha_k'^{i_{n'}} \cos(2 \sum_{j=0}^{n-1} \xi_j - 2 \sum_{j'=0}^{n'-1} \xi'_{j'}) \}
\]

The first order term is

\[
A_1(L, L') = \exp\{+iM \sum_{k} \sum_{n=1}^{L} \sum_{m<n} \alpha_k^{i_n} \alpha_k^{i_m} \sin(2 \sum_{j=m}^{n-1} \xi_j) \}
\]

\[
- \sum_{n=1}^{L'} \sum_{m<n} \alpha_k'^{i_n} \alpha_k'^{i_m} \sin(2 \sum_{j=m}^{n-1} \xi'_j) \}
\]

\[
+ \sum_{n=1}^{L} \sum_{n'=1}^{L'} \sum_{k} \alpha_k^{i_n} \alpha_k'^{i_{n'}} \sin(2 \sum_{j=0}^{n-1} \xi_j - 2 \sum_{j'=0}^{n'-1} \xi'_{j'}) \}
\]

The contribution of all polarization M configurations to first order is

\[
\bar{A}(L, L') = p(0) A_0(L, L') \cdot A_1(L, L') e^{-\frac{M^2}{2K}}
\]

Summing over all possible M, we have the result

\[
W_{i_0...i_L'...i_0'} = e^{i \Phi} \left( \frac{(\Delta t)^L}{L!} \right) e^{-\frac{M^2}{2K}} \sum_{M=-K}^{K} e^{-\frac{M^2}{2K}} \bar{A}_M(L, L').
\]

Here \( \theta(K) = \sum_{M=-K}^{K} e^{-\frac{M^2}{2K}} \) is the normalization factor for this summation. To evaluate an exact quantity, we make the following variable transforma-
C.2. OBA Expansion of the System

\[ \chi_n = 2^{n-1} \sum_{p=0}^{n-1} \xi_p ; \]
\[ \chi'_n = 2^{n'}-1 \sum_{p=0}^{n'-1} \xi'_p ; \]
\[ s^n_k = \alpha^{i_n}_k (\cos \chi_n, \sin \chi_n) ; \]
\[ s'^n_k = \alpha^{i'_n}_k (\cos \chi'_n, \sin \chi'_n) . \]

The transformation of integrations is
\[ \prod_{n} \int_{0}^{2\pi} \frac{d\xi_n}{2\pi} = \prod_{n} \int_{\chi_n+1}^{\chi_n+1+2\pi} \frac{d\chi_n}{2\pi} = \prod_{n} \int_{0}^{2\pi} \frac{d\chi_n}{2\pi} \] (C.20)

Here \( \chi_n \) does not need to have a particular order. Another thing we should notice here is that this transformation is only valid when \( \alpha^{i_n}_k \neq 0 \). If \( \alpha_k = 0 \) for some \( k \), then \( A_k \) is simply equal to 1. All the following calculations are based on the fact that \( \alpha^{i_n}_k \neq 0, \forall k, i_n \).

Defining
\[ S = \sum_{n,k} s^n_k - \sum_{n,k} s'^n_k, \] (C.21)
then we can rewrite \( A \)'s in the form
\[ A_0(L, L') = \int dS \delta^2(S - \sum_{n,k} s^n_k - \sum_{n,k} s'^n_k) e^{-\frac{1}{2}|S|^2} \] (C.22)
\[ A_1(L, L') = 1 + i\frac{M}{K} \sum_k \left( \sum_{n=1}^{L} \sum_{m<n} (s^n_k \times s^m_k) - \sum_{n=1}^{L'} \sum_{m<n} (s'^n_k \times s'^m_k) \right) \]
\[ - \sum_{n=1}^{L} \sum_{n'=1}^{L'} (s^n_k \times s'^n_{k'}) \right) \right) \] (C.23)

Here we include a constraint
\[ \delta^2(S - \sum_{n,k} s^n_k + \sum_{n',k} s'^n_k) = \int \frac{d^2z}{4\pi^2} e^{iz(S - \sum_{n,k} s^n_k + \sum_{n',k} s'^n_k)} \] (C.24)
C.3 Zero Polarization

In this section we will only deal with the lowest order in $\frac{M}{K}$, i.e. the $A_0(L, L')$ term. We will see that actually the higher order correction from $A_M(L, L')$ is proportional to $\alpha^4$, which is higher than the order of Taylor expansion we did in (C.9). Therefore we can simply neglect $A_M(L, L')$ and evaluate the whole density matrix explicitly.

\[
(\prod_n \int_0^{2\pi} \frac{d\xi_n}{2\pi})(\prod_{n'} \int_0^{2\pi} \frac{d\xi'_{n'}}{2\pi}) A_0(L, L') = (\prod_n \int_0^{2\pi} \frac{d\chi_n}{2\pi})(\prod_{n'} \int_0^{2\pi} \frac{d\chi'_{n'}}{2\pi}) \cdot \int d^2S \int d^2z e^{i\mathbf{S} \cdot (\sum_{n,k} \alpha_{i_n} z^k + \sum_{n',k} \alpha'_{i'_{n'}} z^k)} e^{-\frac{1}{2}|\mathbf{S}|^2}
\]

\[
= \int d^2S \int d^2z \left( \prod_n J_0(\sum_k \alpha_{i_n} z^k) \right) \left( \prod_{n'} J_0(\sum_{k'} \alpha'_{i'_{n'}} z^k) \right) e^{i\mathbf{S} \cdot z - \frac{1}{2}|\mathbf{S}|^2} - \frac{1}{2} z^2.
\]

(C.25)

Here we use the integral presentation of Bessel functions

\[
J_n(x) = \frac{1}{2\pi} \int_{-\pi}^{\pi} e^{-i(n\tau - x\sin \tau)} d\tau
\]

(C.26)

Then substituting back to (C.18), we have the result of each path to zeroth order in $\frac{M}{K}$,

\[
W_{i_0...i_L...i_0}^0 = \frac{(i\Delta_0 t)^{L+L'} L!L'!}{L!L'!} \int_0^{\infty} \frac{dz}{2\pi} \left( \prod_n J_0(\sum_k \alpha_{i_n} z^k) \right) \left( \prod_{n'} J_0(\sum_{k'} \alpha'_{i'_{n'}} z^k) \right) e^{-\frac{1}{2} z^2}.
\]

(C.27)

If we assume the perfectly symmetric case $\alpha_{k+1} = \alpha_k$ for every site, the zeroth order result becomes

\[
W_{i_0...i_L...i_0}^0 = \frac{(\Delta_0 t)^{L+L'} L!L'!}{L!L'!} \int_0^{\infty} \frac{dz}{2\pi} J_0(\sum_k \alpha z^k) e^{(L+L')/2} e^{-\frac{1}{2} z^2}.
\]

(C.28)
C.4 \( M = 1 \) Polarization

In this section we would like to deal with the \( A_1(L, L') \) terms in (3.79). We will verify our statement in (3.3.2) that the contribution from the \( M = 1 \) polarization group is of \( O(\alpha^4) \) order and therefore can be safely neglected. Higher polarization groups can be dealt in the same way but are more complicated.

At first we use the expansion of \( A_1(L, L') \) derived in the previous section to second order in \( \frac{M}{K} \), i.e.

\[
\overline{A}_1(L, L') = 1 + \frac{iM}{K} \sum_k \left( \sum_{n=1}^{L} \sum_{m<n} (s^m_k \times s^n_k) - \sum_{n=1}^{L'} \sum_{m<n} (s^m_k \times s^n_k) \right) - \sum_{n=1}^{L'} \sum_{m<n} (s^m_k \times s^n_k) \]

\[
- \frac{M^2}{2K^2} \left\{ \sum_k \left( \sum_{n=1}^{L} \sum_{m<n} (s^m_k \times s^n_k) \right)^2 \right\}.
\]

The cross product here simply means the value of its z-component, since the \( s^m_k \) are all 2-D vectors. To evaluate the correction of \( \overline{A}_M(L, L') \), which is

\[
(\prod_n \int_0^{2\pi} \frac{d\xi_n}{2\pi})(\prod_{n'} \int_0^{2\pi} \frac{d\xi_{n'}}{2\pi}) e^{-i\langle\sum_{n,k} s^n_k - \sum_{n',k} s'^{n'}_k \rangle} A_M(L, L'),
\]

we need the following relations:

\[
\langle s_n \rangle = \left( \int \frac{d\chi}{2\pi} e^{-i\chi s_n} \right) / \left( \int \frac{d\chi}{2\pi} e^{-i\chi s} \right) = i \frac{s J'_0(sz) z_n}{z J_0(sz)}
\]

\[
\langle s_m s'_n \rangle = - \frac{s J'_0(sz) z_m s' J'_0(s'z) z_n}{z J_0(sz) z J_0(s'z)} = \frac{ss' z_m z_n J'_0(sz) J'_0(s'z)}{z^2 J_0(sz) J_0(s'z)}
\]

\[
\langle s_m s_n \rangle = i \frac{\partial^2}{J_0(sz) \partial z_m \partial z_n} J_0(sz)
\]

\[
= \frac{s J'_0(sz)}{z^2 J_0(sz)} (z_n z_m - \delta_{m,n} z^2) - \frac{s^2 J''_0(sz)}{J_0(sz)} \frac{z_m z_n}{z^2}.
\]

Here \( z = (z_1, z_2), s = (s_1, s_2) = s(\cos \chi, \sin \chi), m, n = 1, 2 \). Then we can easily see that \( \langle s \times s' \rangle = \langle s_1 s'_2 - s_2 s'_1 \rangle = 0 \). Therefore the first order term does not contribute. To calculate the second term, we need to evaluate...
C.4. $M = 1$ Polarization

terms like $\langle (s_n \times s_m)(s_{n'} \times s_{m'}) \rangle$, with $n > m, n' > m'$.

If $n = n', m = m'$,

$$\langle (s_n \times s_m)(s_{n'} \times s_{m'}) \rangle = \frac{s_n s_m}{z J_0(s_m z) J_0(s_n z)} (s_m J''_0(s_n z) J'_0(s_m z) + s_n J''_0(s_m z) J'_0(s_m z)).$$

(C.34)

If $n = n', m \neq m'$,

$$\langle (s_n \times s_m)(s_{n'} \times s_{m'}) \rangle = \frac{s_n s_m s_{n'} s_{m'} J''_0(s_n z) J'_0(s_m z) J''_0(s_{n'} z) J'_0(s_{m'} z)}{z J_0(s_n z) J_0(s_m z) J_0(s_{n'} z) J_0(s_{m'} z)}.$$

(C.35)

If none of the $n, n', m, m'$ is identical to another, then

$$\langle (s_n \times s_m)(s_{n'} \times s_{m'}) \rangle = 0$$

(C.36)

Then we can deal with the second order terms. Before we go to the calculation details, we introduce a new sequence $w_n^k, n = 1, 2, ..., L, L + 1, ..., L + L'$ based on $s_n^k, s_{n'}^k$:

$$w_n^k = s_n^k, \quad 1 \leq n \leq L;$$

(C.37)

$$w_n^k = s_{L+1-n}^k, \quad L + 1 \leq n \leq L + L';$$

(C.38)

$$w_n^k = \sum_k w_n^k$$

(C.39)

$$u_n^k = \sum_k \alpha_n^k, \quad 1 \leq n \leq L;$$

(C.40)

$$u_n^k = \sum_k \alpha_{L+1-n}^k, \quad L + 1 \leq n \leq L + L';$$

(C.41)

In this notation,

$$\sum_{n=1}^{L+L'} \sum_{m<n} (w_n^k \times w_m^k)$$

(C.42)

$$= \sum_{n=1}^{L} \sum_{m<n} (s_n^k \times s_m^k) - \sum_{n=1}^{L'} \sum_{m<n} (s_{n'}^k \times s_m^k) - \sum_{n=1}^{L} \sum_{n'=1}^{L'} (s_n^k \times s_{n'}^k).$$
Then it is easy to calculate the correction \( \sim \frac{M^2}{K^2} \), for the \( n = n', m = m', k = k' \) case, the contributions are equal to

\[
\sum_k \sum_{n=1}^{L+L'} \sum_{m<n} \frac{1}{z} \frac{1}{z} \left( \frac{w^m_k w^n_k}{w^m_k w^n_k} \right)^2 \frac{J_0'(w^m_z) J_0'(w^n_z)}{J_0'(w^m_z) J_0'(w^n_z)} + \frac{w^m_k w^n_k}{w^m_k w^n_k} \frac{J_0'(w^n_z) J_0'(w^m_z)}{J_0'(w^n_z) J_0'(w^m_z)}
\]

\[
= \sum_k \frac{1}{z} \left( \sum_{l<n} \sum_{m<n} \frac{w^m_k w^n_k}{w^m_k w^n_k} \frac{J_0'(w^m_z) J_0'(w^n_z)}{J_0'(w^m_z) J_0'(w^n_z)} \right)(C.43)
\]

For the \( n = n', m \neq m', k = k' \) case; the contributions are

\[
\sum_k \sum_{l<m<n} 2 \frac{1}{z} \left( \frac{(w^l_k)^2 w^n_k w^n_k}{w^l_k w^n_k} \frac{J_0'(w^l z) J_0'(w^n z)}{J_0'(w^l z) J_0'(w^n z)} \right. \]

\[
\left. + 2 \sum_{l<m<n} \frac{(w^l_k)^2 w^n_k w^n_k}{w^l_k w^n_k} \frac{J_0'(w^l z) J_0'(w^n z)}{J_0'(w^n z) J_0'(w^n z)} \right). (C.44)
\]

Therefore \( W_{i_0 \ldots i_p} \ldots \) to the second order is

\[
W_{i_0 \ldots i_p} \ldots = W_{i_0 \ldots i_p} \ldots \times \sum_k^K \frac{e^{-\frac{\hat{s}}{2}}}{\theta(K)} \{ 1 - \frac{M^2}{zK^2} \} \sum_k \sum_{m \neq n} \frac{(w^m_k w^n_k)^2}{w^m_k w^n_k} \frac{J_0'(w^m z) J_0'(w^n z)}{J_0'(w^m z) J_0'(w^n z)}
\]

\[
+ 2 \sum_{l<m<n} \frac{(w^l_k)^2 w^n_k w^n_k}{w^l_k w^n_k} \frac{J_0'(w^l z) J_0'(w^n z)}{J_0'(w^n z) J_0'(w^n z)} \}. (C.45)
\]

As a result, the correction due to the \( M \neq 0 \) part is

\[
W_{i_0 \ldots i_p} \ldots \approx W_{i_0 \ldots i_p} \ldots \sqrt{\frac{1}{1 + a(z, L + L')}}. \quad (C.46)
\]

If we take the prefect symmetric case \( |w^n_k| = \alpha/K, \forall k, n \), noticing that our expression is an even function of \( \omega^m_k \), we get

\[
a(z, L + L') = \frac{2\alpha^3 J_0'(\alpha z)}{zK^3 J_0'(\alpha z)}(L + L')(L + L' - 1)[J_0'(\alpha z) J_0(\alpha z)
\]

\[
+ \frac{1}{3} J_0'(\alpha z)^2 (L + L' - 2)]. \quad (C.47)
\]

We can shorten the expression into the following form up to first order:

\[
\rho_{ij}(t) = \int_0^\infty z \ dz \ e^{-\frac{\hat{s}}{2}} (\rho_{ij}(\sum_k \alpha_k z)) - \kappa t^2 \frac{\partial^2}{\partial t^2} J_0(\sum_k \alpha_k z)). \quad (C.48)
\]

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Here we have another parameter for this term as $\kappa = \sum_k \alpha_k^4$ which is of $O(\alpha^4)$ order. This justifies our statement at the beginning of this section.

**C.5 General Coupling**

Before we start calculating the problem with couplings in arbitrary directions, we change our definition of notation a little bit:

\[
\alpha_{i n}^k = \sqrt{(\alpha_{n k}^i)^2 + (\alpha_{k y}^i)^2}\]  \hfill (C.49)

\[
\alpha_{k x}^{i n} = \alpha_{n k}^i + i \alpha_{k y}^i \]  \hfill (C.50)

\[
\alpha_{k y}^{i n} = \alpha_{k x}^i - i \alpha_{k y}^i . \]  \hfill (C.51)

Then, we can write the $T_k^L$ operators as

\[
T_k^L | \uparrow \rangle = e^{i \sum_{n=0}^L \xi_n} \{ | \uparrow \rangle + i \sum_{n=1}^L \alpha_{k x}^{i n} e^{-2i \sum_{m=n}^L \xi_m} | \downarrow \rangle \} - \left( \frac{1}{2} \sum_{n=1}^L \left((\alpha_{k x}^{i n})^2 \right) + (\alpha_{k x}^{i n})^2 + 2i \alpha_{k x}^{i n} \right) \left| \uparrow \rangle \right\}

+ \left( \frac{1}{2} \sum_{m<n} \left((\alpha_{k x}^{i n})^2 \right) + 2i \alpha_{k x}^{i n} \right) \left| \downarrow \rangle \right\}.
\]  \hfill (C.52)

Here we ignore the second order correction to the flipping terms, since it will only enter third order corrections of our final expression. Following the
same procedure, we get

\[ A_k^\pm (L, L') \approx e^{\pm i \sum_{n=1}^L \xi_n - \sum_{n'=1}^{L'} \xi'_n} \exp \left[ - \frac{1}{2} \sum_{n=1}^L \alpha_{k,n}^i \alpha_{k,-n}^i - \frac{1}{2} \sum_{n=1}^{L'} \alpha_{k,n}^{i'} \alpha_{k,-n}^{i'} \right. \]

\[ - \sum_{m<n} \alpha_{k,n}^i \alpha_{k,m}^{i'} e^{\mp 2i \sum_{j=m}^{n-1} \xi_j} - \sum_{m<n} \alpha_{k,n}^{i'} \alpha_{k,m}^i e^{\pm 2i \sum_{j=m'}^{n'-1} \xi'_j} \]

\[ + \sum_{n=1}^L \sum_{n'=1}^{L'} \alpha_{k,n}^i \alpha_{k,n'}^{i'} e^{\mp 2i (\sum_{m=0}^{n-1} \xi_m - \sum_{m'=0}^{n'-1} \xi'_m)} \]

\[ - \frac{1}{2} \left( \sum_{n=1}^L \alpha_{k,n}^i - \sum_{n=1}^{L'} \alpha_{k,n}^{i'} \right) \left( \sum_{n=1}^L \alpha_{k,n}^i - \sum_{n=1}^{L'} \alpha_{k,n}^{i'} \mp 2i \right) \].

(C.53)

We use the same tricks by defining

\[ \theta_{n,k} = \text{arg}(\alpha_{k,n}^i); \]

\[ \theta_{n,k}' = \text{arg}(\alpha_{k,n}^{i'}); \]

\[ \chi_n = 2 \sum_{p=0}^{n-1} \xi_p ; \]

\[ \chi'_n = 2 \sum_{p=0}^{n'-1} \xi'_p + \theta_{n,k}' ; \]

\[ s_{k,n} = \alpha_{k,n}^i (\cos(\chi_n + \theta_{n,k}), \sin(\chi_n + \theta_{n,k})); \]

\[ s_{k,n}' = \alpha_{k,n}^{i'} (\cos(\chi'_n + \theta_{n,k}'), \sin(\chi'_n + \theta_{n,k}')). \]

We can write our zeroth order correction as

\[ \overline{A}_0(L, L') = e^{-\frac{1}{2} \sum_k (\sum_{n=1}^L \alpha_{k,n}^i - \sum_{n=1}^{L'} \alpha_{k,n}^{i'} \right)^2} \int dS \delta^2(S - \sum_{n,k} s_{k,n} - \sum_{n,k} s_{k,n}' ) e^{-\frac{1}{2} |S|^2} , \]

(C.55)

\[ W_{i_0 ... i_L i'_L ... i'_0}^{0} = e^{i \Phi \left( \frac{L+L'}{L!L'!} \right)} \int_0^\infty \frac{dz}{2\pi} \left( \prod_n J_0(f_{i,n+1} z) \right) \]

\[ \times \left( \prod_{n'} J_0(f_{i',n'+1} z) \right) e^{-\frac{1}{2} z^2} e^{-\frac{1}{2} \sum_k (\sum_{n=1}^L \alpha_{k,n}^i - \sum_{n=1}^{L'} \alpha_{k,n}^{i'} \right)^2} . \]

(C.56)
Here $f_{ij}$ is a function associated with the z-direction coupling on each hopping term. In terms of $\alpha_{in}^k$, this function is

$$f_{in_{i+1}} = \sqrt{\left(\sum_k \alpha_{in}^k \cos \theta_{n,k}\right)^2 + \left(\sum_k \alpha_{in}^k \sin \theta_{n,k}\right)^2}$$

(C.57)

The value of this function depends on the inhomogenity of $\alpha_{in}^k$ and $\theta_{n,k}$. The maximum value is $\sum_k \alpha_{in}^k$ and the minimum value is determined by the average value of $|\alpha_{in}^k - \alpha_{in}^k'|$. We can also define the inhomogenity decoherence quantity as

$$\kappa = \langle f_{in_{i+1}} \rangle.$$  

(C.58)

This is basically a generalization of the previous $\kappa$ in (3.84).

### C.6 General Initial State in the High Field Limit

For general initial state $\rho_o = \otimes \prod_k \rho_k(\hat{n})$, in which $|\rho_k(\hat{n})\rangle \equiv \frac{1}{2}I + \frac{1}{2} \hat{n} \cdot \sigma$.

Then as before, we can write down the expression for $\tilde{A}_0(L, L')$ as

$$\tilde{A}_0(L, L') = \prod_k tr(T_L^k (\frac{1}{2}I + \frac{1}{2} \hat{n}_k \cdot \sigma_k)T_{L'}^k).$$

(C.59)

Define

$$T_L^k = \begin{pmatrix} 1 - a_k & i b_k \\ i b_k^* & 1 - a_k^* \end{pmatrix}$$

(C.60)

with

$$a_k = \frac{1}{2} \sum_n (\alpha_{in}^n)^2 + \sum_{m<n} \alpha_{in}^k \alpha_{im}^k e^{-2i \sum_{j=m}^{n-1} \xi_j}$$

(C.61)

and

$$b_k = \sum_n \alpha_{in}^n e^{-2i \sum_{m=n}^{L} \xi_m}.$$  

(C.62)
Then up to second order, we have

\[
tr(T_{L'}^{L}I T_{L'}^{L}) = tr \left( \begin{pmatrix} 1 - a_{k}^{*} & -ib_{k}^{*} \\ -ib_{k} & 1 - a_{k} \end{pmatrix} \begin{pmatrix} 1 - a_{k} & ib_{k} \\ ib_{k}^{*} & 1 - a_{k}^{*} \end{pmatrix} \right) \\
\approx 2 - a_{k} + a_{k} - a_{k}^{*} + b_{k} b_{k}^{*} + b_{k}^{*} b_{k} \quad \text{(C.63)}
\]

\[
tr(T_{L'}^{L} \sigma_x T_{L'}^{L}) = tr \left( \begin{pmatrix} 1 - a_{k}^{*} & -ib_{k}^{*} \\ -ib_{k} & 1 - a_{k} \end{pmatrix} \sigma_x \begin{pmatrix} 1 - a_{k} & ib_{k} \\ ib_{k}^{*} & 1 - a_{k}^{*} \end{pmatrix} \right) \\
\approx i(b_{k}^{*} - b_{k}^{*} - b_{k}) \quad \text{(C.64)}
\]

\[
tr(T_{L'}^{L} \sigma_y T_{L'}^{L}) = tr \left( \begin{pmatrix} 1 - a_{k}^{*} & -ib_{k}^{*} \\ -ib_{k} & 1 - a_{k} \end{pmatrix} \sigma_y \begin{pmatrix} 1 - a_{k} & ib_{k} \\ ib_{k}^{*} & 1 - a_{k}^{*} \end{pmatrix} \right) \\
\approx b_{k}^{*} - b_{k} + b_{k}^{*} - b_{k} \quad \text{(C.65)}
\]

\[
tr(T_{L'}^{L} \sigma_z T_{L'}^{L}) = tr \left( \begin{pmatrix} 1 - a_{k}^{*} & -ib_{k}^{*} \\ -ib_{k} & 1 - a_{k} \end{pmatrix} \sigma_z \begin{pmatrix} 1 - a_{k} & ib_{k} \\ ib_{k}^{*} & 1 - a_{k}^{*} \end{pmatrix} \right) \\
\approx -a_{k} + a_{k}^{*} + a_{k}^{*} - b_{k} b_{k}^{*} + b_{k}^{*} b_{k} \quad \text{(C.66)}
\]

This expression is really hard to solve, but we could separate each term to see its effect individually.

For the pure \( n_y \) case, by doing the same trick as in previous sections, we can deduce that

\[
\left( \prod_{n} \int_{0}^{2\pi} \frac{d\xi_{n}}{2\pi} \right) \prod_{n'} \int_{0}^{2\pi} \frac{d\xi_{n'}}{2\pi} \mathcal{A}_{0}(L, L')
\]

\[
= \left( \prod_{n} \int_{0}^{2\pi} \frac{d\alpha_{n}}{2\pi} \right) \prod_{n'} \int_{0}^{2\pi} \frac{d\alpha_{n'}}{2\pi} \int dS \int_{4\pi} \frac{dz}{2\pi}
\]

\[
\times e^{i(z \cdot (S - \sum_{n,k} s_{n,k}^{0} + \sum_{n',k} s_{n',k}^{0}))} e^{-\frac{1}{2} |S - \bar{n}_{y}|^2 + \frac{1}{2} n_{y}^2}
\]

\[
= \int dS \int_{4\pi} \frac{dz}{2\pi} \left( \prod_{n} J_{0}(\sum_{k} a_{k}^{n,z}) \right) \left( \prod_{n'} J_{0}(\sum_{k} a_{k'}^{n',z}) \right) e^{i(z \cdot S - \frac{1}{2} |S - \bar{n}_{y}|^2 + \frac{1}{2} n_{y}^2}
\]

\[
= \int_{0}^{\infty} z \\int_{0}^{\infty} dJ_{0}(n_{y} z) \left( \prod_{n} J_{0}(\sum_{k} a_{k}^{n,z}) \right) \left( \prod_{n'} J_{0}(\sum_{k} a_{k'}^{n',z}) \right) e^{-\frac{1}{2} z^2 + \frac{1}{2} n_{y}^2}.
\]

\[
\text{(C.67)}
\]

In this expression the zeroth order correction will be the \( (3.105) \) in the main text:

\[
\rho_{ij}(t) = \int_{0}^{\infty} z \\int_{0}^{\infty} dJ_{0}(n_{y} z) e^{-\frac{z^2 - n_{y}^2}{2}} \rho_{ij}^{0}(t J_{0}(\sum_{k} \alpha_{k} z)) \quad \text{(C.68)}
\]
Here \( n_y \) acts like an extra decoherence coefficient which quenches the value of this integral for longer path, since \( J_0(n_y z) \) is a larger quenching term than the boost \( e^{i n_y z} \).
Appendix D

Oscillator Bath model: Role of Peierls Coupling in Energy Transfer

D.1 Green Function

In this section, we show the derivation of Green functions for the whole Hamiltonian (4.1) in both the frequency and time domain. At first we rewrite the Hamiltonian as $H = H_o + H_I + H_B$. Here $H_B$ is the Bethe lattice Hamiltonian in (4.1), and $H_I = t_1(c_1^d d_0^l + d_0^d c_1)$. The rest of the terms in the Hamiltonian go to $H_o$. In the following derivation, we use $p, q, r$ to label different phonon states. At first we use Dyson’s equation for the Green function

$$G = G^0 + GH^0$$

with $G(z) = \frac{1}{z - H}$, and $G^0(z) = \frac{1}{z - H_o - H_B}$. In the one exciton subspace, we have

$$\langle p|c_i G(z) c_j^T |q\rangle$$

$$= \langle p|c_i G^0(z) c_j^T |q\rangle$$

$$+ \sum_r t_1 \langle p|c_i G(z) d_0^l |r\rangle \langle r|c_1^T G^0(z) c_j^T |a_j, q\rangle$$

$$= \langle p|c_i G^0(z) c_j^T |q\rangle$$

$$+ \sum_r t_1^2 \langle p|c_i G(z) c_1^T |r\rangle \langle r|c_1 G^0(z) c_j^T |q\rangle G^0_B(z, r)$$.  

Here $G^0_B(z, r) = G^0_B(z - E(r))$. $E(r)$ is the total phonon energy of the phonon state $r$ and $G^0_B(z) = \frac{2}{z + \sqrt{z^2 - D^2}}$ is the Hubbard Green function. In the last line of (D.2), we use the fact that

$$\langle p|c_i G(z) d_0^l |r\rangle = t_1 \langle p|c_i G(z) c_1^T |r\rangle \langle r|d_0 G^0_B(z) d_0^l |r\rangle$$

$$= t_1 \langle p|c_i G(z) c_1^T |r\rangle G^0_B(z - E(r))$$.  

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D.1. Green Function

By setting \( j = 1 \), we get

\[
\langle p | c_i G(z) c_1^\dagger | q \rangle = \langle p | c_i G^0(z) c_1^\dagger | q \rangle + \sum_r t_1 \langle p | c_i G(z) c_1^\dagger | r \rangle \langle r | c_i G^0(z) c_1^\dagger | q \rangle.
\] (D.4)

By defining matrices

\[
[G(i, j; z)]_{pq} = \langle p | c_i G(z) c_j^\dagger | a_j, q \rangle \quad (D.5)
\]
\[
[G^0(i, j; z)]_{pq} = \langle p | c_i G^0(z) c_j^\dagger | q \rangle \quad (D.6)
\]
\[
[A(z)]_{pq} = \delta_{pq} G_B^0(z, p), \quad (D.7)
\]
we can write the solution of (D.4) as

\[
G(i, 1; z) = G^0(i, 1; z) \frac{1}{1 - t_1^2 A(z) G^0(1, 1; z)}. \quad (D.8)
\]

Substituting (D.8) back to (D.2) gives us the general expression of Green function matrices, viz.,

\[
G(i, j; z) = G^0(i, j; z) + G^0(i, 1; z) \frac{t_1^2}{1 - t_1^2 A(z) G^0(1, 1; z)} A(z) G^0(1, j; z). \quad (D.9)
\]

If we know the Green’s function of a bare system \( H_o \) with phonon coupling, we can calculate the Green function for the whole system. Since there are not many phonon modes in this system, we diagonalize the \( H_o \) Hamiltonian exactly up to a maximum of 10 phonons in the system. Various tests show that results already converge around 5 phonons due to the large phonon energy. The time domain evolution can be acquired by the Fourier transformation:

\[
G(\tau) = \frac{i}{2\pi} \int_{-\infty}^{\infty} e^{-i\omega\tau} d\omega \ G(\omega + i\eta)
\]
\[
= \frac{1}{\pi} \int_{-\infty}^{\infty} e^{-i\omega\tau} d\omega \ \text{Im} G(\omega + i\eta). \quad (D.10)
\]

The spectral function is \( S(\omega) = -\text{Im} G(\omega + i\eta) \). The actual results for \( G(\tau) \) and \( S(\omega) \) are acquired by tracing over all the phonon modes in \( G(\tau) \) and \( S(\omega) \).
D.2 Bethe Lattice Reaction Center

In this section, we describe in detail how the reaction center model works in the main paper. To avoid unnecessary complexities, we consider the simplest case where there is only one site coupled to the reaction center. The Hamiltonian is now

\[ H_0 = \varepsilon_1 c_1^\dagger c_1 + t_1(c_1^\dagger d_0 + d_0^\dagger c_1) + H_B \]  

(D.11)

with \( H_B = \sum_{\langle ij \rangle} V(d_i^\dagger d_j + \text{h.c.}) \) being the Hamiltonian of a Bethe lattice with branching number \( Z \to \infty \). Without phonon, the matrix defined in (D.5) is a number,i.e.

\[ G(1, 1; z) = G^0(1, 1; z) \frac{1}{1 - t_1^2 A(z) G^0(1, 1; z)} \]  

(D.12)

with \( G^0 = \frac{1}{z + i\eta - \varepsilon_1} \) and \( A(z) = \frac{2}{z \pm \sqrt{z^2 - D^2}} \). The ± sign is determined by the real part of \( z \). \( D = 2V\sqrt{Z-1} \) is half the bandwidth of the RC. The time domain propagator is calculated through (D.10):

\[ G(1, 1; t) = \frac{i}{2\pi} \int_{-\infty}^{\infty} e^{-i\omega \tau} d\omega \frac{1}{\omega - \varepsilon_1 - \frac{2t_1^2}{\omega \pm \sqrt{\omega^2 - D^2}}} \]  

(D.13)

The contour of the right-handed integral is chosen to be the half circle in the lower half of the complex plane. The denominator has a branch cut from \((-D, +D)\) and up to two possible poles on the real axis. The integral around the branch cut is

\[ -\frac{1}{2\pi i} \int_{-D}^{+D} d\omega e^{-i\omega \tau} \left( \frac{1}{\omega - \varepsilon_1 - \frac{2t_1^2}{\omega + i\sqrt{D^2 - \omega^2}}} - \frac{1}{\omega - \varepsilon_1 - \frac{2t_1^2}{\omega - i\sqrt{D^2 - \omega^2}}} \right) \]

\[ = \frac{2t_1^2}{\pi} \int_{-D}^{+D} d\omega e^{-i\omega \tau} \frac{\sqrt{D^2 - \omega^2}}{4\omega(\omega - \varepsilon_1)t_1^2 + 4t_1^4 + (w - \varepsilon_1)^2 D^2} \]

\[ = \frac{1}{2\pi} \int_{-1}^{+1} dx \frac{\cos(xD\tau) \sqrt{1 - x^2}}{(x - \varepsilon_1)(x + t_1^2(x - \varepsilon_1)) + t_1^2} \]  

(D.14)

when \( \tau \to \infty \), the integral \( \to 0 \) according to the Riemann-Lebesgue lemma. Therefore, this part is a decaying part which eventually goes to zero.
The remaining part of the integral is determined by the poles at the lower half of the complex plane. i.e., the solutions of equation

\[
z - \varepsilon_1 - \frac{2t_1^2}{z + \sqrt{z^2 - D^2}} = 0
\]

with non-positive imaginary parts. We can prove that this equation does not have any real roots which coincide with the previous branch-cut. When \( \varepsilon_1^2 + 4t_1^2 < D^2 \), there are no roots for this equation. The transfer rate is solely determined by the branch cut integral (D.14). When \( \varepsilon_1^2 + 4t_1^2 > D^2 \), there are real roots of the equation (D.15). If \( \varepsilon_1 \geq D - \frac{2t_1^2}{D} \), the root

\[
z_1 = \frac{\varepsilon_1(t_1^2 - \frac{D^2}{2}) + \sqrt{\Box}}{2(t_1^2 - \frac{D^2}{4})}
\]

is a real root of (D.15). Here \( \Box = t_1^4 \varepsilon_1 + 4t_1^6 - D^2 t_1^4 \). If \( \varepsilon_1 \leq \frac{2t_1^2}{D} - D \), then the root

\[
z_2 = \frac{\varepsilon_1(t_1^2 - \frac{D^2}{2}) - \sqrt{\Box}}{2(t_1^2 - \frac{D^2}{4})}
\]

is a real root of (D.15).

Figure D.1: Illustration of phase diagram of single site system. The grey zone indicates there is no real root of (D.15). In this zone the exciton would be transferred into the sink completely. In the green zone there is one real root of (D.15). There are two real roots of (D.15) in the rest of the area.

Fig. D.1 is an illustration of the phase diagram of our single site system coupled to an RC. In the grey zone, with small coupling \( t_1 \) and small deviation \( \varepsilon_1 \), the site \( c_1 \) is on resonance with the RC and there is no localized
D.3 Logarithm Fitting

In this section, the transfer speed $\gamma$ is a quantity acquired by fitting $\log(1 - \rho_{RC})$ as a linear function of time $t$, i.e. we assume the exponential transfer from the molecule to the RC:

$$ (1 - \rho_{RC}) \propto e^{-\gamma t}. \quad (D.18) $$

Fig[D.2] is the result when the phonon frequency is near the resonant point $\Omega \approx \Delta$. The quantity $\gamma$ represents how fast the exciton transfers into the state formed around that site $c_1$. Any exciton would be transferred into the RC eventually. In the green zone, the deviation becomes stronger and there is a local state formed around site $c_1$. The probability to stay at site $c_1$ goes to a finite value when $t \to \infty$. In the rest area, $t_1$ becomes so strong that two local states are formed around the site $c_1$ and site $d_0$. In this region, the probability to find the exciton as that site will oscillate at a frequency

$$ f \approx \frac{\sqrt{\epsilon_1^2 + 4t_1^2 - D^2}}{1 - \frac{D^2}{4t_1^2}}. $$

The transfer efficiency of LHC, i.e. the ratio between the amount of photons transported to RC and the amount of photons absorbed by the antennae, is fantastically high, almost 100% efficient[4]. We also require that our RC model has a very high transfer rate. Therefore, in this paper, we always work in the grey region.
D.3. Logarithm Fitting

RC. We can see the huge increase of the transfer rate near the resonant point. The linear correlation coefficient has a dip near the resonant point too, but still better than 0.998. The results of the pure Holstein case and

Figure D.3: The plots of fitting \((1 - \rho_{RC})\) as a exponential function of \(t\) for the pure Holstein case and the pure Peierls case. The parameters of the bare model is same as the values in previous figures. The range of \(t\) is taken from 0 to 200. (a) the decay rate \(F\) as a function of \(g_H\) (blue circle) and \(g_P\) (red star); (b) the decay rate \(F\) as a function of \(\tilde{t}_H\) (blue circle) and \(\tilde{t}_P\) (red star); (c) the linear correlation coefficient between \(\log(1 - \rho_{RC})\) and \(t\); (d) the \(\log(1 - \rho_{RC})\) v.s. \(t\) plot in two transition regions: the lines within the dashed circle represent the region where the exponential model start to fail; the line within the solid circle represent where the exponential behavior is restored.

the pure Peierls case are illustrated in Fig.D.3. We can see from the linear correlation coefficient Fig.D.3(c) that \((4.7)\) is a good approximation in the weak interaction for both type of couplings. It is also a good approximation in the pure Holstein case in the intermediate to large coupling region. In the intermediate coupling region of the Peierls coupling case (0.7 > \(g_P\) > 0.4), the linearity drops down. We can see from Fig.D.3(d) how the behavior of \((1 - \rho_{RC})\) deviates from the exponential decay at the beginning and the end of this parameter region. For the initial drop, I think the reason is that
D.3. Logarithm Fitting

the branch cut integral in (D.13) \[ \frac{1}{2\pi} \int_{-1}^{+1} dx \frac{\cos(xD\tau)\sqrt{1-x^2}}{(x-\epsilon_0)(x+D^2(t_1^2(x-\epsilon_0))^{1/2})} \]
decays at a rate between \( \tau^{-1} \) to \( \tau^{-2} \) in certain parameter region. Therefore, after a sufficient long time this part would become dominant. However, the resonant energy transfer process happens fast in the light harvesting molecules (no more than a few pico seconds, which is equivalent to the order of \( 10^2 \) in our model. ) Therefore we believe \((4.7)\) is still a good approximation in the short time region.

When the coupling goes beyond 0.7, the transfer rate decreases and the linearity is restored. The reason for this is probably due to the fact that in the large coupling case, the spectrum of the whole interacting system is so different from the bare system that the resonance condition no longer holds.

In both cases, the correlation coefficient is still larger than 0.998, which makes the approximation in \((4.7)\) still a good measure of the transfer speed of the model.