# Decoherence in Photosynthetic Energy Transfer 

Based on a Spin Bath Model

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## Abstract

In this thesis we study the coherent energy transfer in photosynthetic systems. This resonant energy transfer has proven to be a coherent transfer in some light harvest complexes. The model which we suggest to describe this mechanism is an exciton hopping on an N -site ring coupled to a spin bath. Analytic results are found for both the dynamics of the influence functional and of the reduced density matrix of the excitons. We also give results for the dynamics of the current as a function of time. By setting states splitting initially into 2 separate wave-packets moving at different velocities, we reproduce the coherent beating phenomenon in experiments.

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## Chapter 1

## Introduction

The biosystems on Earth are not perpetual motion machines. It is through photosynthesis that they can harvest energy from sunlight to maintain their daily metabolic activities. Photosynthetic organisms, aka photoautotrophs, exist in plants, algae, and many species of bacteria. The colors of such plants and creatures are determined by their photosynthesis absorption frequencies. Most plants are green because they have a maximum absorption red-peak ranged from 680 Hz to 700 Hz which is why these photosynthetic molecules are called "chlorophyll". Chlorophyll varies in absorption spectra among different kinds of organisms and yield different colors, such as the bacteriachlorophyll in purple bacteria and carotenoid in yellow flowers.

In the 1930s, Robert Emerson and William Arnold discovered that light reaction productivity varied under different wavelengths of light.[1] They used three light sources: a neon-tube, a normal 40 watt lamp and a mercuryvapor lamp. More precise measurement confirmed their discovery with two reaction peaks: one absorbing up to 600 nm wavelengths, the other up to 700. Later people learned that the former one contains only chlorophyll$a$, the later one contains primarily chlorophyll- $a$ with most of the available chlorophyll- $b$, among other pigment. In addition, they also found that it takes 2480 chlorophylls to absorb enough energy to fix one molecule of carbon dioxide. This result implied that most chlorophylls are not directly engaged in the carbon fixation process[2]. They serve as light-harvesting antennae capturing the sunlight and funnelling the electronic excitation toward the few reaction centers ( RC ) located on the photosynthetic membranes. The existence of surrounding antennae is essential to maintain the high efficiency of the RCs and increase the cross section of photon absorption. In certain bacterial systems light harvesting efficiency is indeed above $99 \%$ [2].

In photosystems, chlorophyll molecules are specifically arranged in and around pigment protein complexes which are embedded in the thylakoid membranes of chloroplasts. In these complexes, chlorophylls serve two primary functions. One of the functions is to construct the RCs to host the photosynthetic reactions. The other function, which comprises most of the
chlorophylls (up to several hundreds of molecules per photosystem) is to absorb light and transfer the light energy to the RCs. The transfer takes only a few tens of picoseconds and is performed with extraordinarily high efficiency: most of the absorbed photons give rise to a charge separation event. Remarkably, recent experiments have shown that there is a long coherent time in this energy transfer process. [3, 4]

To understand the role of decoherence in this photosynthetic system, we propose a model which involves pure phase decoherence coming from spin bath. This model simulates a exciton propagating around a ring of N discrete sites(in the case of photosynthesis, there are usually 16 or 32 chlorophylls in a ring), while coupled to a spin bath. The general Hamiltonian we will study is
$H=\sum_{j} \sum_{<i j>}\left\{t_{i j} c_{i}^{\dagger} c_{j} \exp \left[i A_{i j}^{0}+i \sum_{k}\left(\phi_{k}^{i j}+\boldsymbol{\alpha}_{k}^{i j} \cdot \boldsymbol{\sigma}_{k}\right)\right]+H . c.\right\}+\sum_{k} \mathbf{h}_{k} \cdot \boldsymbol{\sigma}_{k}$
This thesis is organized as follows. In Chapter 2, we describe the structures of two well-known light-harvesting complexes, and review some remarkable experiments involving them. In Chapter 3, we provide several theories found in previous literature which were applied to this problem and discuss the advantages and disadvantages of these approaches. In Chapter 4, we introduce the influence functional theory to establish a theoretical framework in which to study the open system energy transfer. In Chapter 5, we propose a spin bath model to study the energy transfer in light harvesting complexes. We argue the necessities of a spin bath model in this problem. We show the derivation of our model Hamiltonian and the approximations we make in order to simplify calculations. Analytic results are found for the dynamics of the influence functional and of the reduced density matrix of the particle, both for initial single wave-packet states, and for states split initially into 2 separate wave-packets moving at different velocities. We also give results for the dynamics of the current from site to site as a function of time.

## Chapter 2

## Experiments on Light Harvesting Molecules

Light harvesting molecules have been studied for almost a century. Their structures have been thoroughly explored in late 1990s. Until early this century, the mechanism of energy transfer through multichromophore complexes was generally assumed to involve incoherent hoppings. There was nothing inherently quantum mechanical or wave-like in the process itself. These notions were challenged by new experimental evidences in 2007[3, 4].

In this chapter, we begin by introducing the structure of three commonly studied light harvesting complexes, the light harvesting complex type I and II in Rhodopseudomonas acidophila, and Fenna-Matthew-Olson (FMO) complex of Prosthecochloris aestuarii. Their structures are described and basic absorption spectrum is provided. We then introduce the experimental evidences about coherent quantum beating in light harvesting molecules. Such effect was observed in both FMO complexes and reaction centers of light harvesting complex type I.

### 2.1 Structures of Light Harvesting Molecules

There are two ways to look into the structures of light harvesting molecules. 1)Fluorescense detections. It has been, for a long time, the standard way to determine the distance between molecules. The fluorescence detections are highly sensitive. In Förster theory[5], emission spectrums are determined by overlap integrals of wave functions on different sites, and this value is inversely proportional to sixth power of distance. Hence, we are able to determine the distance between molecules. 2)X-ray crystallography. In this method, photosynthetic organisms are distracted from the membranes and crystalized in laboratory condition. Although this method depicts a direct observation on complexes' structures, the results were restricted by low resolution until late 1990s. [6] Compared with the plant chromophores, bacterial chromophores are easier to extract and purify. Late in the 20th century,
people found that in most purple bacteria, the photosynthetic membranes contain two types of light-harvesting complexes, light-harvesting complex I (LH1) and light-harvesting complex II (LH2).[7] LH1 is found surrounding directly the reaction centers $(\mathrm{RCs})$, where the energy from the photons is finally stored. LH2 is not directly associated with the reaction centers but transfers energy as antennae towards LH1 and thus RCs[2, 8].

In 1995, the crystal structure of peripheral light-harvesting complex type II (LH2) in a purple bacterium Rhodopseudomonas acidophila was resolved by x-ray diffraction[9]. One year later, the crystal structure of LH2 of Rhodospirillum molischianum was also determined to a resolution of 2.4 $\AA[10]$. This complex consists of 24 bacteriochlorophylls(BChls). Crystallized chlorophylls were distilled and grown under 293K [11]. These BChls have a C 8 global symmetry. 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).[2]. The diameter of the B850 ring is $23 \AA$ and that of the B800 ring it is $28 \AA$. Whereas the electronic interaction between neighboring B850 pigments is quite strong and gives rise to excitonic behavior [12], the interaction between adjacent BChl- $a$ in the outer B800 ring is much smaller than the inhomogeneous broadening of the B800 band [13], although the B800 ring are relatively larger and thus closer in space. B800 rings act rather like "antenna rings", which collect energy and transfer into the B850 ring of the same complex. B850 rings act like "storage rings", where the excitation delocalizes rapidly over a broad area.[9] The strong coupling between different B800 rings makes it a network throughout the organism. One interesting property of this complex is that excitions can always find a pathway towards the rare LH1 in the large network, extremely swiftly ( $3-5 \mathrm{ps}$ ) almost without energy loss.

In the same year, 1995, the structure of LH1 of $R b$. sphaeroides was shown as an electron density projection map in agreement with the $8.5 \AA$ resolution [14]. The preparation of crystals is same as of LH2's. The complex contains a ring of 32 BChls which is responsible for the 875 nm absorption band. The overall diameter of LH1 is $118 \AA[8]$. LH1 surrounds a reaction center (RC) which is the destination of incoming photons. The large LH1 ring lies in the center of the process of photosynthesis. They absorb excitations from LH2 networks and send it into the RCs. The details of interplay between LH1 and RC are not clear yet. The time scale for LH1 $\rightarrow$ RC transfer is around 35 ps , which is the longest stage in photosynthesis[2]. RC contains a BChls dimer in the center, two accessory BChls flanking on each side and
a bacteriopheophytin (BPhy) adjacent to each flanking BChl. These units make an individual RC itself a small exciton transfer network, in which couplings between them lead to a multi-band spectrum. The whole structures of both LH1 and LH2 are shown in [8].

Another popular photosynthesis units are the Fenna-Matthew-Olson (FMO) complex of Prosthecochloris(P.) aestuarii. In 1997, it became the first pigment-protein complex whose structure was solved by X-ray crystallography[15, 16]. It showed a global C 3 symmetry with an arrangement of three identical subunits. Each subunit contains seven BChls with the nearest neighbor distance of 11.3 to $14.4 \AA$, while the distance between nearest neighbors in different subunits of the trimer is about $24 \AA$ [17]. Actually, it has been shown that the optical spectrum of the FMO complex is mainly determined by the interactions within a single subunit[15]. They are almost not interacting with other monomers. Its structure is shown in [18]. The fundamental difference between FMO and LH1, 2 is that there is no spatial symmetry in FMO complex. Couplings between the seven BChls in single subunit are all different. Numeric simulations based on experiment spectrums show that the excitation band in single subunit are all localized near one or two BChls.[17] In LH1 and LH2, however, the excitation bands are spread all around the ring.

### 2.2 Coherent Quantum Beating Phenomenon

In 1932, Emerson and Arnold exposed the chlorophylls to various flashing light sources, with different intensity and wavelength. They measured the carbon dioxide reduced to determine the responses of chlorophylls after each flashing. Until the 1990's, due to the spectroscopy techniques, people can even directly track an individual chlorophyll on molecular level. However, if we not only want to study long term asymptotic behavior of multichromophores, but also wish to see their dynamics in first several moments, the fluorescence detection is not enough. Such single signal spectroscopy will only give us information about the band level and exciton energy levels[19, 20]. For example, a given complex composed by N chromophores, it has N one-exciton states that are given by linear combinations of N single-site wave function. Therefore, in principle the line shape of the absorption spectrum contains information of the N electronic transitions between the electronic ground and N one-exciton states. Since the N transition probabilities independently add up to produce the absorption spectrum, the spatiotemporal dynamics between different one-exciton states cannot be
studied by using conventional linear spectroscopic techniques.[20] The difficulty was overcome by nonlinear spectroscopies developed at the end of last century.[17]. The nonlinear pathways are results of four field-matter interactions, which create cross peaks between different states[21]. It contains generally $N^{2}$ peaks which are sufficient to describe $N$ on-site energy plus $\frac{N(N-1)}{2}$ couplings. This method allows us to directly see the wave-like process in transfer.

In 2007, Engel et al studied decoherence in FMO complexes under 77K through a 2D femtosecond nonlinear spectroscopy. They found that the coherence time is unexpectedly longer than most of the previous theoretical calculations ( $>660 \mathrm{fs}$ )[3]. This method involves 4 pulses sequentially applied into the system. The first two pulses are coherent(their relative phase is locked) and thus create coherence signals propagating in the system. Then they allowed the systems to freely dephase for a time $T$ then added the two probing signals. Fourier transform of the time intervals between the first two signals and the last two signals are called the excitation frequency and the detect frequency respectively, and T is called the dephasing time. They varied $T$ from 0 to 660 fs and found the spectrum peak oscillations always existed. It was a direct observation of decoherence in photosynthetic units, though the condition of samples is not natural. 77 K is still high compared with the normal low temperature physics requirement, but low enough to change the aggregate structures of biological molecules. To prevent the denaturing in low temperature, they mixed the sample with glycerol which created a glassy background in low T. But after all, it is still a remarkable evidence suggested that FMO complex might itself be structured to dampen fluctuations that would induce decoherence of the electronic excitation.

A few months later, Hohjai Lee et al found similar coherent effects in the RCs of Rhodobacter sphaeroides[4]. They used a two-color electronic coherence photon echo experiment (2CECPE) which involves two signals with different wavelengths to excite coherence between two exciton bands in RCs. They measured the oscillating echo signals after time T to study coherence effects. They did the experiment in both 77 K and 180 K and found that the coherent beating pattern survived at least 400 fs in both case. This evidence supported the previous one that the long coherent time is not unique to FMO complexes and it probably could survives in room temperature. Their results are shown in their paper. We can see that, though not varnishing to zero, the damping of the beat amplitudes by time is obvious.

Though large photosynthesis systems contain more bands and thus create a more complicated beating pattern than single complex, people began to
believe that coherent energy transfer exists widely among photosystems. Back in 1998, people already obtained the evidence of coherent hopping between B850 ring and B800 ring in LH2[12]. Although it does not appear large, the coherent times in both experiments in 2007 are relatively long comparing to the energy transfer time under $77 \mathrm{~K}(\sim 1 p s)$. This evidence is a challenge to existing theories. In next chapter we will review some important theoretical approaches on light harvesting complexes.

## Chapter 3

## Review of Existing Theories

For a long time, there were mainly two theories dominating this field. Förster theory is the first successful theory in history. The energy transfer between chromophores is assumed to be incoherent hoppings. It is pictured as random walks with a general downhill direction towards the reaction center. Redfield theory does include coherent hoppings. But it requires weak sitebath couplings, which is not applicable to photosystems. Both of them cannot explain the new experimental evidences well. In this chapter, we will go through these two theories and then introduce several latest attempts about how to explain this phenomenon.

In addition, these experiments suggested that in a strongly coupled, non-equilibrium systems, quantum behaviors can still survive long enough to finish "calculations" (i.e. transfer towards reaction centers). This coherent feature in a poorly controlled, decohering environment has already attracted attention from quantum information realms. At the end of this chapter, I will introduce some related explorations in this realm, including the entanglement dynamic and Feynman cursor computer.

### 3.1 Resonant Energy Transfer

A single chlorophyll is a typical resonant energy excitation system. A chlorophyll absorbs a photon and creates a hole-electron resonant pair between a conducting band and a valence band, which is so-called an "exicton". An exciton is a bound state of a electron-hole pair. It usually has a long lifetime. In biological molecules, the dielectric constant is usually very small compared with the Coulomb interaction between electrons and holes (about several electron volts). Thus the exciton tends to be much smaller, which is so-called the Frenkel exciton. [22] Electrons and holes are close in space, usually sit at same site and move together.

Through interactions between molecules, these resonant excitations spread throughout the whole system. The resonant energy transfer(RET) mechanism is first suggested by Oppenheimer[23]. The electron-hole pair in the donor merges together and the acceptor absorbs the energy to create a new


Figure 3.1: Model picture for resonant energy transfer showing fluorescence of the donor to the acceptor.
electron-hole pair. This mechanism is illustrated in Fig. 3.1. This coupling between chlorophylls, which is originally the Coulomb interaction, has a van der Waals like $R^{-6}$ distance dependence with a typical effective range for 2-5 nanometers[24]. In LH1 and LH2, typical distance between chlorophylls is about 1 nm , as described above. Henceforth the interaction range is about two times of the typical distance, which means we are only required to consider nearest-neighbor and second nearest-neighbor couplings. In most case nearest-neighbor couplings are enough to explain dynamics. But for FMO complexes, since it does not have a global symmetry and the chlorophylls in a same subunit are close in space, people usually include couplings between any two of them.

This mechanism itself is not complicated. At most it will be a Hamiltonian as a $N \times N$ matrix. Since N is not large (no more than 32), simple diagonalization will give us everything we want. However in biological systems, we cannot avoid influence from environment. There are not only chlorophylls responsible for energy transfers. Other factors such as amorphous cell tissues, auxiliary pigments, ionized solvent, and reaction catalysis also affect the transfer process. They change positions between chlorophylls, rotate their directions or polarize molecules. Figuring out their influence is the main problem of RET. Basically, how to treat surroundings separates theoretical approaches from each other.

### 3.2 Förster Theory

The phenomenon of RET was first observed at the beginning of last century. In the late 1940's, it was Förster who proposed a theory describing this interaction and derived a equation that relates the interchromophore distances to the spectroscopic properties between chromophores. [5] It then became the standard way of spectroscopic distance determination in biology $[8,25,24]$. Förster theory is a semi-classical theory which involves incoherent hoppings between different sites. Förster assumed weak inter-site couplings and assumed that one can use equilibrium Fermi Golden Rule to treat the electron coupling between site to site. This implies that 1) the timescales of the exciton transfer are much larger than that of the bath-exciton response, otherwise the bath cannot be treated as equilibrium; 2) the bath-exciton couplings are larger than the electron couplings, otherwise we should include the bath interactions into our calculation[5, 26]. In this theory, the effect of surrounding bath is to destroy all the quantum correlations between consecutive hoppings.

In Förster theory, the probability $P_{i}$ to find molecule i excited at time t can be determined by

$$
\begin{equation*}
\frac{d}{d t} P_{i}=\sum_{j}\left(W_{i j} P_{j}-W_{j i} P_{i}\right) \tag{3.1}
\end{equation*}
$$

$W_{i j}$ is the Förster transfer rate from molecule j to molecule i. Using Fermi Golden rule, we can get $P_{i}$ as a function of the electronic coupling $V_{i j}$ and the overlap spectral $J_{i j}(\omega)$

$$
\begin{equation*}
W_{i j}=\frac{\pi}{h} \int_{0}^{\infty} d \varepsilon\left|V_{i j}\right|^{2} J_{i j}(\varepsilon) \tag{3.2}
\end{equation*}
$$

If interactions are in dipole-dipole form, the $V^{2}$ term will be proportional to $R^{-6}$. This theory was successful in history. This sixth power dependence on distance was verified experimentally in 1978 [27]. Until now people are still working on this model and trying to improve its performance. Leegwater [28] shows that such model is even accurate to predict the decay time of excitation in LH2 when the ratio between the bath-exciton coupling $\Gamma$ and the inter-exciton coupling $J$ is not large enough. In his simulation, the dissipation effects due to RCs and surrounding baths are added as a nonHermitian term in Hamiltonian by hand. He claims that down to $\Gamma / J \sim 1$ region Förster theory still works well. However there is a fundamental flaw of Förster theory: the assumption of no coherence of hoppings and no time
correlation of bath fluctuations makes this theory impossible to study the new coherent transfer behavior in recent experiment.

### 3.3 Redfield Theory

The theory includes coherent hoppings was first introduced by Redfield[29]. Opposite to the Förster limit where $\Gamma \gg J$, Redfield assumes $\Gamma \ll J$ and thus treats the bath-excitation couplings as perturbation. Electron-phonon couplings are described by the fluctuation dynamics in the ground electronic stats. Diagonalizing the bare electronic Hamiltonian we find that eigenstates for excitons is a linear combination of the single site base, i.e.

$$
\begin{equation*}
|k\rangle=\sum_{i} a_{k i}|i\rangle \tag{3.3}
\end{equation*}
$$

The equation of motion for the diagonal density matrix elements are same with (3.1) except the site indices $i, j$ replaced by the exciton indices $k, k^{\prime}$

$$
\begin{equation*}
\frac{d}{d t} P_{k}=\sum_{k^{\prime}}\left(W_{k k^{\prime}} P_{k}-W_{k^{\prime} k} P_{k^{\prime}}\right) \tag{3.4}
\end{equation*}
$$

But $W_{k k^{\prime}}$ are calculated in a different way:

$$
\begin{equation*}
W_{k k^{\prime}}=2 R e \int_{0}^{\infty} d t e^{i\left(\omega_{k^{\prime}}-\omega_{l}\right) t}\left\langle e^{i H_{p h} t} H_{k^{\prime} k}^{e l-p h} e^{-i H_{p h} t} H_{k k^{\prime}}^{e l-p h}\right\rangle_{p h} \tag{3.5}
\end{equation*}
$$

$H_{p h}$ is the Hamiltonian of the phonon bath; $\langle\ldots\rangle$ indicates taking average over the phonon bath distribution. It is proportional to $e^{-\beta H_{p h}}$ when the bath is in thermal equilibrium. $H^{e l-p h}$ is the coupling between the bath and the excitons, i.e. $H_{k k^{\prime}}^{e l-p h}=\langle k| H^{e l-p h}\left|k^{\prime}\right\rangle$. The most important thing in Redfield's theory is to evaluate this correlation function. If the phonon modes in each monomer are independent, then

$$
\begin{equation*}
W_{k k^{\prime}}=\sum_{i}\langle k \mid i\rangle\left\langle i \mid k^{\prime}\right\rangle J_{n}\left(\omega_{k^{\prime}}-\omega_{k}\right) \tag{3.6}
\end{equation*}
$$

Here $J_{n}(\omega)$ is the phonon spectral function at site-n. [26]
Redfield theory provides a microscopic description of excitation dynamics via a master equation in a reduced space of excitons. However, in light harvesting molecules, the dipole transition is on order of $250 \mathrm{~cm}^{-1}$ and the spectrum linewidth induced by environmental coupling is about $120 \mathrm{~cm}^{-1}$. In this case the $\Gamma \ll J$ conditions is not satisfied; Föster theory fits better in this region.

Förster theory and Redfield theory are the two major theories in RET, and they have some features in common. One is that both theories are Markovian which means the system has no memory of past states. Second, since they are built to calculate the exciton life time, transfer efficiency and transfer time, neither of them include the off-diagonal terms in the reduced density matrix. [13]. In order to study the transfer dynamics between chlorophylls, the off-diagonal terms are essential to get correct coherent pattern. People began to explore other possibilities in this territory.

### 3.4 Recent Approaches

In 2008, Mohseni et al [30,31] proposed an environment-assisted quantum walk model. They rewrited the semi-classical Förster equation (3.1) into a quantum Lindblad master equation which involves a phonon bath linearly coupled to excitons. The resulting equation of motion under Born-Markov and secular approximations is

$$
\begin{equation*}
\frac{\partial \rho(t)}{\partial t}=-\frac{i}{h}\left[H_{C}+H_{L S}, \rho(t)\right]+L(\rho(t)) \tag{3.7}
\end{equation*}
$$

Here $\rho(t)$ is the density matrix of the central system and $H_{C}$ is its bare Hamiltonian. $H_{L S}$ is the lamb shift due to phonon bath coupling. L is the Lindbladian superoperator. Generally it can be written as

$$
\begin{equation*}
L(\rho)=\sum_{\omega} \sum_{m, n} \gamma_{m n}(\omega)\left[A_{m}(\omega) \rho A_{n}^{\dagger}(\omega)-\frac{1}{2} A_{m}(\omega) A_{n}^{\dagger}(\omega) \rho-\frac{1}{2} \rho A_{m}(\omega) A_{n}^{\dagger}(\omega)\right] \tag{3.8}
\end{equation*}
$$

Here $A_{m}(\omega)$ are Lindblad generators and $\gamma_{m n}(\omega)$ are the Fourier transformation of the bath correlation function. Based on such formalism, Mohseni et al found that in FMO complexes increasing temperature does raise the energy transfer efficiency by about $25 \%$. This approach partly explains the $99 \%$ efficiency in photosynthesis.

In the same year, another group from United Kingdom tried to prove that even at zero temperature, transport of excitations across dissipative quantum networks can be enhanced by local dephasing noise. [32] Their techniques are smiliar with Mohseni's: a Lindbladian master equation with dissipation and dephasing noise terms added by hand. But they argued that nature always choose the best way for energy transfer, so that they found a set of optimal parameters in their model and claimed that this is what happens in nature. They found that the maximum transfer rate happens at the point when the noise coupling strength term $\gamma_{k}$ is not zero. They
suggested that while dephasing noise destroys quantum correlations, it may at the same time enhance the transport of excitations.

Another approach is done by Joel Gilmore and Ross H Mckenzie[33], their model Hamiltonian is a central two level system (TLS) coupled to a boson bath.

$$
\begin{equation*}
H=\frac{1}{2} \varepsilon \sigma_{z}+\Delta \sigma_{x}+\sum_{k} \omega_{k} a_{k}^{\dagger} a_{k}+\sigma_{z} \sum_{k} M_{k}\left(a_{k}^{\dagger}+a_{k}\right) \tag{3.9}
\end{equation*}
$$

$\sigma$ s are pauli matrices; $a_{k}^{\dagger}, a_{k}$ are creation and annihilation operators of the phonon bath. The spectral function $J(\omega)=4 \pi \sum_{k} M_{k}^{2} / \omega \delta\left(\omega-\omega_{k}\right)$ determines the resistivity from the bath. $J(\omega)=\eta \omega$ is the Ohmic dissipation case. They followed the similar procedure of Feynmann and Calderia [34]. In spin boson model, there is a critical value $\omega_{c}$ which as if $\Delta \gg \omega_{c}$ then there is always coherent oscillations between two states; if $\Delta \ll \omega_{c}$ and with $\eta>\frac{1}{\pi}$ there is always incoherent relaxations; for $\eta<\frac{1}{\pi}$ coherent oscillations could occur, too. This minimal model illustrats how a bath can gradually turn a coherent quantum system into incoherent one. For more sites, in order to study the resonance energy transfer, more TLSs should be added into this Hamiltonian as a natural generalization of coupled biomolecules. They suggested that this generalized model could be employed to study the rings of chlorophyll molecules.

### 3.5 Quantum Information Considerations

Quantum decoherence itself is an important problem in physics. Practical realizations of quantum computers heavily depend on the conservation of quantum coherences in a relatively long time. Besides the last step from LH1 to RC, time for an energy signal to find a pathway towards the several LH1 among thousands surrounding molecules is about 3-5 picosecond in two-color pump-probe measurement. Compared with the coherent time determined in the experiment ( $>660$ femtosecond), this coherent time is not short. We might expect that in certain laboratory conditions the time will be even longer. Actually, biological molecules have already attracted attentions of quantum information theorists. [35, 36]

Biological environment are peculiar to physicists: the temperature is usually high (around room temperature), the bath is always far from equilibrium and we do not get complete knowledge about driven forces in a biological system. Before we could utilize light harvesting molecules, the first question will be whether entanglement exists. Generally, coherent behaviors
do not guarantee entanglement. Sarovar et al[37] studied the entanglement in FMO complex. Based on 2D femtosecond spectroscopy data, they did numeric simulations of the concurrency between any two sites of the FMO complexes. Their results are encouraging: non-zero entanglement exist sfor a time scale of 5 picosecond at 77 k and 2 picosecond at room temperature (300K). This result is illustrated in their paper.

We can see entanglement does not just exist between nearest sites. For example, the No. 1 and No. 3 chlorophylls are the second furthest pair in FMO complex (about $28 \AA$ ) and they are weakly coupled. But they do show large entanglement for more than 1 picosecond. Though the entanglement is probably a by-product of coherent behavior and does not impact the energy transfer properties much, it opens a door to build a naturally robust quantum devices. Global entanglement within a multichromophore subunit can be mapped into a reduced 3 -site model with entanglement between each other.[38] This model can be used to realize some quantum random walk computations.[39]

On probably practical way of quantum computer is Feynman cursor model[40]. The proposal is to couple the register with additional degrees of freedom, which is the cursor, together with a time independent Hamiltonian for desired evolution. The idea is simple. Consider a system composed by two subspaces: $\left|b_{i}\right\rangle$ as orthogonal set for register part and $\left|c_{i}\right\rangle$ for cursor part. Then due to the Schmidt decomposition of the state $|M(t)\rangle$, we can always find

$$
\begin{equation*}
|M(t)\rangle=\sum_{j} \sqrt{\lambda_{j}(t)}\left|b_{j}(t)\right\rangle \otimes\left|c_{j}(t)\right\rangle \tag{3.10}
\end{equation*}
$$

in which $\left\langle b_{j}(t) \mid b_{i}(t)\right\rangle=\left\langle c_{j}(t) \mid c_{i}(t)\right\rangle=\delta_{i j}, \forall i, j$. Then if at time t the cursor is found in state $\left|c_{j}(t)\right\rangle$, the register collapses into $\left|b_{j}(t)\right\rangle$. Feynman proved that this model is able to compute all the function computable by a deterministic Turing machine. In light harvesting molecules, if we imagine the hopping excitons as Feynman's pointer of cursor and the bath as registers in which results of computations are stored. When we control the excitons' movement, we also do transformation on bath register by coupling. Thus this photosynthetic system becomes a Feynman machine.

This is a new realm for quantum information technologies. How to utilize this biological complexes in quantum computation is still a open question. To study its application, in rest of this thesis we are trying to establish a proper theory to describe the coherent dynamics .

## Chapter 4

## Reduced Density Matrix and Influence Functional

Before introducing our model, I would like to introduce some fundamental concepts about decoherence and reduced density matrix formalism. Quantum mechanics was developed by understandings of microscopic worlds, for instance spins and atomic structures. If this theory is correct, then it should no contradict with the mesoscopic and macroscopic world. For a pure quantum state, the system is composed by the superposition of possible quantum states. The wave function describes the superposition of state in this systems. After you do measurement, the wave function collapses and the absolute value of certain superposition coefficient gives the probability you can find the system in this certain state. This property apparently does not exist in our daily life, which is dominated by probabilistically additive law. Then the issue about how the classical statistic behaviors appear within the framework of quantum mechanics arises. Though there is still no general agreement on the interpretation, mainly due to disputes around "measurement" and "observation", the understanding of decoherence is essentially connected to this problem.
"Decoherence" is the mechanism by which the classical limit emerges out of a quantum starting point. It can be viewed as the loss of information from a system in to environment. In this sense decoherence only happens in a open quantum system. We separate a quantum subsystem, which is usually called central system, from a global quantum system, which is usually called the environment or the bath. Due to couplings between them in some certain physical forms, the bath continually takes measurements on the central system, and leading to a destruction of quantum phase correlations. That may untangle the quantum state and produce our macroscopic realities. Thus, practically the rate of decoherence give us a boundary between quantum-classical theory. If the decoherence time is long enough for us to probing the quantum effects, then quantum theory should be employed, but otherwise classical theory is more applicable and for most of time, easier to handle. In addition, understanding the details of decoherence in many par-
ticular cases is of great technical importance. For example, in the quantum computing and communication field, one of the major problems that prevents a quantum computer becoming practical is decoherence, most qubits cannot survive decoherence before the operation finishes.

To study decoherence we need reduced density matrix formalism. Since now the isolated time evolution of the central system is not unitary any more because entanglements between the system and environment is introduced by coupling. Wave function itself is not enough to describe the system. In this chapter we begin with the concept of reduced density matrix in quantum mechanics. We introduce the influence functional theory, which is a rigorous method to obtain the dynamics of reduced density matrices. We show that the influence functional theory preserves the correlations between baths, which is omitted in popular master equation approaches. At the end we provide some examples of these subjects. The calculations will be useful in later chapters.

### 4.1 Reduced Density Matrix

For a pure state $|\phi\rangle$, we define the projection operator $\rho=|\phi\rangle\langle\phi|$ as its density operator. This is a equivalent form for wave function. However it is easy to be extended into a more generalized state which also includes classic probability additive law. For such generalized state it can be written as

$$
\begin{gather*}
\rho=\sum_{i} C_{i}\left|\phi_{i}\right\rangle\left\langle\phi_{i}\right|  \tag{4.1}\\
\sum_{i} C_{i}=1, \quad 0 \leq C_{i} \leq 1 \tag{4.2}
\end{gather*}
$$

This statistical mixture formation implies that at a particular time the state of a system is not perfectly known. Positive $C_{i}$ 's assure this sum is convex. An important example is the equilibrium density operator in which the $C_{i}$ are canonically distributed, and the $\left|\phi_{i}\right\rangle\left\langle\phi_{i}\right|$ are projectors on energy eigenstates.

$$
\begin{equation*}
\rho=\frac{1}{Z} \sum_{i} e^{-\beta E_{i}}\left|\phi_{i}\right\rangle\left\langle\phi_{i}\right|, \tag{4.3}
\end{equation*}
$$

where $Z=\sum_{i} e^{-\beta E_{i}}$ is the partition function. The expected value of a observable $G$ for a pure state $|\phi\rangle$ can be written as

$$
\begin{equation*}
\langle G\rangle=\langle\phi| G|\phi\rangle=\operatorname{tr}(G|\phi\rangle\langle\phi|) \tag{4.4}
\end{equation*}
$$

Then for a mixed state with density matrix $\rho$, the expectation value of $G$ is

$$
\begin{equation*}
\langle G\rangle=\operatorname{tr}(\rho G) \tag{4.5}
\end{equation*}
$$

Back to our "central system" plus "bath" model, we could consider it as a large system composed of two part A and B , each with a Hilbert space $H_{A}$ and $H_{B}$. For a pure state $|\phi\rangle_{A B} \in H_{A} \otimes H_{B}$, it can be written as a linear combination of orthogonal basis in each Hilbert space.

$$
\begin{equation*}
|\phi\rangle_{A B}=\sum_{i m} a_{i m}|i\rangle_{A}|m\rangle_{B}, \quad \sum_{i m}\left|a_{i m}\right|^{2}=1 \tag{4.6}
\end{equation*}
$$

We assume $F_{A}$ is an observable of subsystem A . In the view of the whole system $A+B$, this observable should be expressed as $F=F_{A} \otimes I_{B}$, with $I_{B}$ the identity operator of subsystem B . The expectation value of $F_{A}$ in state $\rho_{A B}$ is

$$
\begin{align*}
\left\langle F_{A}\right\rangle & =\operatorname{tr}_{A B}\left(\rho_{A B} F\right)=\operatorname{tr}_{A} B\left(\rho_{A B} F_{A} \bigotimes I_{B}\right) \\
& =\sum_{i m}\left\langle\left. i\right|_{A}\left\langle\left. m\right|_{B} \sum_{j n, k l} c_{j n, k l} \mid j\right\rangle_{A} \mid n\right\rangle_{B}\left\langle\left. k\right|_{A}\left\langle\left. l\right|_{B} F_{A} \bigotimes I_{B} \mid i\right\rangle_{A} \mid m\right\rangle_{B}  \tag{4.7}\\
& =\sum_{i}\left\langle\left. i\right|_{A} \sum_{j k}\left(\sum_{m} c_{j m, k m}\right) \mid j\right\rangle\langle k| F_{A}|i\rangle_{A} \\
& =\operatorname{tr}_{A}\left(\rho_{A} F_{A}\right)
\end{align*}
$$

We arrive with a expression for subsystem A which is apparently independent of subsystem B. But $\rho_{A}$ is actually dependent on $H_{B}$ since

$$
\begin{equation*}
\rho_{A} \equiv \sum_{j k}\left(\sum_{m} c_{j m, k m}\right)|j\rangle\langle k|=\operatorname{tr}_{B}(\rho) . \tag{4.8}
\end{equation*}
$$

We define $\rho_{A}$ as our reduced density matrix and define this operation $\operatorname{tr}_{B}$ as partial trace of B. Generally the reduced density matrix is not a pure state, which means if we only look at a specific small portion of a large quantum system, we cannot gain complete information of the system. If we consider A as our "central system" and B as the surrounding bath, $\rho_{A}$ determines the properties of the subsystem which we are interested in. The coupling between the bath and the system is the reason why decoherence exists. In the word of density matrix formalism, the effect of decoherence on density matrices is essentially the decay or rapid vanishing of the offdiagonal elements of the partial trace of the whole system's density matrix. Thus, in order to explore the time evolution of the reduced density matrix and study its decoherence, we need to find the equation of motion of reduced density matrix. However, this is not usually a straightforward calculation and in most cases there is no exact analytical answer.

### 4.2 Path Integral Formalism

We still start with the whole system $A+B . \mathbf{x}$ and $\mathbf{q}$ each labels the states in Hilbert space $H_{A}$ and $H_{B}$ respectively (as a generalized position). We assume the Hamiltonian ruled the global system is

$$
\begin{equation*}
H=H_{A}(\mathbf{x})+H_{B}(\mathbf{q})+H_{I}(\mathbf{x}, \mathbf{q}) \tag{4.9}
\end{equation*}
$$

To carry out the dynamics of reduced density matrix, we use the technique first introduced by Feynman and Vernon[41]. Based on path integral form, the time evolution of the whole system's density matrix $\rho_{A B}$ can be written as

$$
\begin{align*}
\rho_{A B}\left(\mathbf{x}_{f}, \mathbf{q}_{f} ; \mathbf{x}_{f}^{\prime}, \mathbf{q}_{f}^{\prime}\right)=\int & d \mathbf{q}_{i} d \mathbf{q}_{i}^{\prime} d \mathbf{x}_{i} d \mathbf{x}_{i}^{\prime} \rho_{A B}\left(\mathbf{x}_{i}, \mathbf{q}_{i} ; \mathbf{x}_{i}^{\prime}, \mathbf{q}_{i}^{\prime}\right)  \tag{4.10}\\
& \times J_{A B}\left(\mathbf{x}_{f}, \mathbf{q}_{f} ; \mathbf{x}_{f}^{\prime}, \mathbf{q}_{f}^{\prime} t ; \mathbf{x}_{i}, \mathbf{q}_{i} \mathbf{x}_{i}^{\prime}, \mathbf{q}_{i}^{\prime}, 0\right)
\end{align*}
$$

The subscripts $f, i$ indicate final and initial states respectively. And the integration kernel

$$
\begin{align*}
J_{A B} & \left(\mathbf{x}_{f}, \mathbf{q}_{f} ; \mathbf{x}_{f}^{\prime}, \mathbf{q}_{f}^{\prime} t ; \mathbf{x}_{i}, \mathbf{q}_{i} \mathbf{x}_{i}^{\prime}, \mathbf{q}_{i}^{\prime}, 0\right) \\
& =\int_{q(0)=q_{i}}^{q(t)=q_{f}} \mathcal{D} \mathbf{q} \int_{q^{\prime}(0)=q_{i}^{\prime}}^{q^{\prime}(t)=q_{f}^{\prime}} \mathcal{D} \mathbf{q}^{\prime} \int_{x(0)=x_{i}}^{x(t)=x_{f}} \mathcal{D} \mathbf{x} \int_{x^{\prime}(0)=x_{i}^{\prime}}^{x^{\prime}(t)=x_{f}^{\prime}} \mathcal{D} \mathbf{x}^{\prime} \exp \left\{\frac{i}{\hbar}\left(S_{A B}[\mathbf{x}, \mathbf{q}]-S_{A B}\left[\mathbf{x}^{\prime}, \mathbf{q}^{\prime}\right]\right)\right\} \tag{4.11}
\end{align*}
$$

$S_{A B}$ is the action of the Hamiltonian $H_{A B}$ and similarly we could write it as

$$
\begin{equation*}
S_{A B}[\mathbf{x}, \mathbf{q}]=S_{A}[\mathbf{x}]+S_{B}[\mathbf{q}]+S_{I}[\mathbf{x}, \mathbf{q}] \tag{4.12}
\end{equation*}
$$

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

$$
\begin{equation*}
\rho_{A B}(0)=\rho_{A}(0) \otimes \rho_{B}(0) \tag{4.13}
\end{equation*}
$$

Then we take partial trace over B in equation (4.10) and get

$$
\begin{align*}
\rho_{A}\left(\mathbf{x}_{f}, \mathbf{x}^{\prime}{ }_{f} ; t\right)=\int d \mathbf{x}_{i} d \mathbf{x}^{\prime}{ }_{i} & \int_{x(0)=x_{i}}^{x(t)=x_{f}} \mathcal{D} \mathbf{x} \int_{x^{\prime}(0)=x_{i}^{\prime}}^{x^{\prime}(t)=x_{f}^{\prime}} \mathcal{D} \mathbf{x}^{\prime} \\
& \exp \left\{\frac{i}{\hbar}\left(S_{A}[\mathbf{x}]-S_{A}\left[\mathbf{x}^{\prime}\right]\right)\right\} \mathcal{F}\left[\mathbf{x}(t), \mathbf{x}^{\prime}(t)\right] \rho_{A}\left(\mathbf{x}_{i}, \mathbf{x}_{i}^{\prime} ; 0\right) \tag{4.14}
\end{align*}
$$

With the kernel

$$
\begin{align*}
\mathcal{F}\left[\mathbf{x}_{f}, \mathbf{x}_{f}^{\prime}\right] \equiv & \int d \mathbf{q}_{f} d \mathbf{q}_{i} d \mathbf{q}^{\prime} \int_{q(0)=q_{i}}^{q(t)=q_{f}} \mathcal{D} \mathbf{q} \int_{q^{\prime}(0)=q_{i}^{\prime}}^{q^{\prime}(t)=q_{f}} \mathcal{D} \mathbf{q}^{\prime} \\
& \exp \left\{\frac{i}{\hbar}\left(S_{B}[\mathbf{q}]+S_{I}[\mathbf{q}, \mathbf{x}]-S_{B}\left[\mathbf{q}^{\prime}\right]-S_{I}\left[\mathbf{q}^{\prime}, \mathbf{x}^{\prime}\right]\right)\right\} \rho_{B}\left(\mathbf{q}, \mathbf{q}^{\prime} ; 0\right) \tag{4.15}
\end{align*}
$$

Here $\mathcal{D}$ indicate functional integration for all possible path from time 0 to $t$. Since we take trace over system B, the final state of B should be the same $q_{f}$ for both $q(t)$ and $q^{\prime}(t)$. This method is called the influence functional method and $\mathcal{F}\left[\mathbf{x}(t), \mathbf{x}^{\prime}(t)\right]$ is so called the "influence functional".

Generally, the influence functional $\mathcal{F}\left[\mathbf{x}(t), \mathbf{x}^{\prime}(t)\right]$ does not only depend on the initial and the end point of the path $\mathbf{x}(t)$ but also the positions at any time between them. In other words, the state of the central system in the moment is not solely depending on its state in previous instant. We need to include everything about its history after $t=0$ to predict its behavior thereafter. For superoperator $K\left(t, t^{\prime}\right)$ which is defined as $\rho(t)=K\left(t, t^{\prime}\right) \rho\left(t^{\prime}\right)$, this situation means

$$
\begin{equation*}
K(t, 0) \neq K\left(t, t^{\prime}\right) K\left(t^{\prime}, 0\right) ; \quad 0<t^{\prime}<t . \tag{4.16}
\end{equation*}
$$

This property implies that the effect of bath does not actually make the wave-function collapsed unless we do measurement on it. If we stop at a time $t^{\prime}$ and measure the properties of the system, then we actually do "environmental trace over" on our density matrix and make it from a pure state to a reduced mixture. After that if we let the system continue evolving to time $t$, it will be different from the one which evolves from 0 to $t$ without disturbation. How the system changes depends on our measurement base. For instance when we are studying the photoemission system, we could choose to study either the light from the atom, may it be emitted, absorbed or scattered; or the properties of the atom's variables before and after. Generally it will give different results. However, most master equations approaches,including quantum Langevin equation, Lindblad formalism and Zwinger equation, whose target is to find a equation of motion like $\frac{\partial}{\partial t} \rho(t)=\mathcal{L} \rho(t)$, omit this retarded effect. Markov approximation assumes that a given future state at any given moment depends only on its present state. Nowadays there are some modified non-Markovian models, such as [42, 43], introduce a time dependent kernel into the formation by hand.

Formally, equation (4.14) gives the time evolution of the reduced density matrix of the central system and it is a exact result. However, in most cases
it is not easy to calculate out this equation analytically. Next we provide two examples about path integral and influence functional. They both involve a particle hopping on a discrete ring and its influence functional kernel with environment.

### 4.2.1 Example I: Particle Moving On a Discrete Ring

Consider our N-site tight binding Hamiltonian as

$$
\begin{equation*}
H=\sum_{<i j>} \Delta_{o} e^{i \Phi / N} c_{i}^{\dagger} c_{j} \tag{4.17}
\end{equation*}
$$

with periodic boundary condition $c_{N+1}=c_{1} .\langle i j\rangle$ indicate nearest neighbor pairs. $\Phi$ is a flux term threading the ring. Then there is an accumulated phase depending on the winding number of each path. The standard way to calculate the Green function is through Fourier transformation

$$
\begin{align*}
c_{j}^{\dagger} & =\sqrt{\frac{1}{N}} \sum_{k_{n}} e^{i k_{n} j} c_{k_{n}}^{\dagger} \\
c_{k_{n}}^{\dagger} & =\sqrt{\frac{1}{N}} \sum_{\ell} e^{-i k_{n} \ell} c_{\ell}^{\dagger} \\
k_{n} & =\frac{2 \pi n}{N}, \quad n=0,1, \ldots, N-1 \tag{4.18}
\end{align*}
$$

the Hamiltonian is then diagonalized as

$$
\begin{equation*}
\mathcal{H}=\sum_{k_{n}} 2 \Delta_{o} \cos \left(k_{n}-\Phi / N\right) c_{k_{n}}^{\dagger} c_{k_{n}} \tag{4.19}
\end{equation*}
$$

Then the 1-particle Green function is

$$
\begin{align*}
G_{j j^{\prime}}^{o}(t) & \equiv\langle j| G^{o}(t)\left|j^{\prime}\right\rangle \equiv\langle j| e^{-i \mathcal{H}_{o} t}\left|j^{\prime}\right\rangle \\
& =\frac{1}{N} \sum_{n} e^{-i 2 \Delta_{0} t \cos \left(k_{n}-\Phi / N\right)} e^{i k_{n}\left(j^{\prime}-j\right)} . \tag{4.20}
\end{align*}
$$

We will then reproduce this result through path integral method, though since it is a dicrete model path integral reduces to countable path summation. The idea is to count possible paths start from site $j$ and end at site $j^{\prime}$. The contribution of each path is $\frac{1}{n!}\left(-i \Delta_{o} t\right)^{n} e^{i m \Phi+i\left(j-j^{\prime}\right) \Phi / N}$. Here $m$ is the winding number, $n$ is the number of total steps of this path. The factor $\frac{1}{n!}$ is due to permutation. Each path is composed by a clockwise
steps and $b$ counter-clockwise steps. For a given total step n and winding m , there are $\frac{n+m N-j^{\prime}+j}{2}$ clockwise steps and $\frac{n-m N+j^{\prime}-j}{2}$ counter-clockwise steps. Here $\frac{n \pm\left(m N-j^{\prime}+j\right)}{2} \in \mathbb{N}$ otherwise it is impossible. Therefore, there are $\frac{n!}{\left(\frac{n+m N-j^{\prime}+j}{2}\right)!\left(\frac{n-m N+j^{\prime}-j}{2}\right)!}$ possible path after permutation. We sum over all contributions by possible $m$ and $n$ to get the Green function in path integral form

$$
\begin{equation*}
G_{j j^{\prime}}^{o}(t)=\sum_{n=0}^{+\infty} \sum_{m \in \mathbb{Z}}^{\left[n \pm\left(m N-j^{\prime}+j\right)\right] / 2 \in \mathbb{N}} \frac{\left(-i \Delta_{0} t\right)^{n}}{\left(\frac{n+m N-j^{\prime}+j}{2}\right)!\left(\frac{n-m N+j^{\prime}-j}{2}\right)!} e^{i m \Phi+i\left(j-j^{\prime}\right) \Phi / N} \tag{4.21}
\end{equation*}
$$

Equation(4.21) looks quite different from (4.20), but they do agree with each other. Let me start with equation (4.20). Using the generation function of Bessel Function

$$
\begin{equation*}
e^{i z \cos \theta}=\sum_{m=-\infty}^{\infty} J_{m}(z) i^{m} e^{i m \theta} \tag{4.22}
\end{equation*}
$$

, we could rewrite (4.20) into

$$
\begin{equation*}
G_{j j^{\prime}}^{o}(t)=\frac{1}{N} \sum_{n=0}^{N-1} \sum_{m=-\infty}^{+\infty} J_{m}\left(2 \Delta_{0} t\right) i^{-m} e^{i m\left(k_{n}-\Phi / N\right)} e^{i k_{n}\left(j^{\prime}-j\right)} . \tag{4.23}
\end{equation*}
$$

Since $k_{n}=\frac{2 \pi n}{N}$, we do the summation over index $n$ at first:

$$
\begin{equation*}
\frac{1}{N} \sum_{n=0}^{N-1} e^{i k_{n}\left(j^{\prime}-j+m\right)}=\sum_{p} \delta_{j^{\prime}-j+m, p N} \tag{4.24}
\end{equation*}
$$

The delta function here is the Kronecker delta function. Then we can write this as a sum over winding numbers $p$, viz.,

$$
\begin{equation*}
G_{j j^{\prime}}^{o}(t)=\sum_{p} J_{p N+j-j^{\prime}}\left(2 \Delta_{0} t\right) e^{-i\left(p N+j-j^{\prime}\right)(\pi / 2+\Phi / N)} \tag{4.25}
\end{equation*}
$$

Then looking back at equation (4.21), using the Taylor expansion of Bessel function

$$
\begin{equation*}
J_{\alpha}(x)=\sum_{m=0}^{+\infty} \frac{(-1)^{m}}{m!\Gamma(m+\alpha+1)}\left(\frac{x}{2}\right)^{2 m+\alpha} \tag{4.26}
\end{equation*}
$$

we then transform (4.21) into (4.25) after we set $m \leftrightarrow p$. We can find that winding numbers enter the order of Bessel funcions.

### 4.2.2 Example II: Influence Functional

Let us start with the same Hamiltonian as (4.17) but this time the flux is depending on a environment coordinate $\Phi(x)$, and $x$ has its own Hamiltonian $h(x)$. Our new Hamiltonian is

$$
\begin{equation*}
H=\sum_{<i j>} \Delta_{o} e^{i \Phi(x) / N} c_{i}^{\dagger} c_{j}+h(x) \tag{4.27}
\end{equation*}
$$

For simplification, we assume that $\Phi(x)$ commutes with $h(x)$, i.e. $[\Phi(x), h(x)]=$ 0 and $h(x)$ does not contain time variables explicitly. Formally we can still write the Green function of the central system as

$$
\begin{equation*}
G_{j j^{\prime}}^{o}(t)=\sum_{p} J_{p N+j-j^{\prime}}\left(2 \Delta_{0} t\right) e^{-i\left(p N+j-j^{\prime}\right)(\pi / 2+\Phi(x) / N)} \tag{4.28}
\end{equation*}
$$

This expression contains a environment coordinate. If we partial trace over this environment coordinate, the phase factor becomes

$$
\begin{equation*}
F(t)=\left\langle e^{-i\left(p+\left(j-j^{\prime}\right) / N\right) \Phi(x)}\right\rangle=\operatorname{Tr}\left(e^{-i\left(p+\left(j-j^{\prime}\right) / N\right) \Phi(x)} e^{-i h(x) t} \rho_{0}\right) \tag{4.29}
\end{equation*}
$$

Here $\rho_{0}$ is the inital state of the bath. The Green function becomes

$$
\begin{equation*}
G_{j j^{\prime}}^{o}(t)=\sum_{p} J_{p N+j-j^{\prime}}\left(2 \Delta_{0} t\right) i^{-p N-j+j^{\prime}} F_{j, j^{\prime}}(p ; t) \tag{4.30}
\end{equation*}
$$

Then $F_{j, j^{\prime}}(p ; t)$ is the influence function defined in (4.15) [41]. It depends on properties of the bath (bath coupling ,bath Hamiltonian, initial bath state) as well as details of the path (start and end point, winding number, etc). These expressions are useful in later chapter.

## Chapter 5

## Coherent Hopping on a Ring with Spin Bath

For light harvesting molecules, there are mainly two bath models in the literature: white noise model and oscillator bath model. Both of them have non-physical part: white noise is under infinite temperature and completely random distributions; oscillator bath cannot avoid the energy loss to environment.

In this chapter, we begin with the reasons of using the spin bath. We argue that spin bath modes are also important in light harvesting molecules. It has some unique features which have not been understood well. We discuss dynamics of a general bath spin and assumptions we make. Then we show the general influence functional method which provides analytic results about the reduced density matrix, and parameterize its decoherence rate analytically. At the end, we put two initially separated wave-packets into this system to reproduce the coherent beating phenomenon in the molecules experiments. We see how sharp oscillating beat patterns are rapidly suppressed by surrounding environments.

### 5.1 Why Spin Bath

Spin bath models were developed in low temperature physics [44]. In low temperature, the physics is dominated by localized modes, such as defects, dislocations paramagnetic impurity spins. Due to their low characteristic energy scale, they often give decoherence with almost no dissipation. We have already known that there is almost no energy loss during the energy transfer in light harvesting molecules. When people are dealing with oscillator bath models, they need to find specific parameters(temperature, Ohmic constant, etc) to avoid energy loss. The reason is that in oscillator bath modes, dissipation is inevitable when dephasing is present due to fluctuation dissipation theorem. The central system are keeping exchanging energy with environment. However, spin bath models have a natural advantage which allows us
to study decoherence processes distinctively from dissipations.
The hopping energy in light harvesting complexes is usually 2 orders smaller than the on-site excitation energy. [17]. The energy level spacing of surrounding excitable molecules is large so that we are allowed to truncate them from multi energy levels to a simple two level system. The transfer seems impossible to cause multi excitations in these molecules. In addition, biological system is always far away from equilibrium and localized modes are generated constantly. These modes will not interact with delocalized ones quickly. Plus, people already proved that the light energy is absorbed one by one. We do not need to consider about multi-particle transfer.

At last, spin bath is not well-understood yet. Unlike oscillator models, which are analytically solvable with a classical analogy, spins are totally quantum. The general dynamic of a spin in a time-dependent field is not solvable. We see the general path integral formalism of spins later. In remains of this thesis we are all working in this model.

### 5.2 General Model for Spin Bath



Figure 5.1: An 8-site ring as a demonstration for B800 rings of LH2. At left it is shown in a site representation with nearest-neighbour hopping between the nodes. At right a potential $U(\mathbf{R})$ with 8 potential wells is shown as a contour map (with lower potential shown darker). When truncated to the 8 lowest eigenstates, this becomes equivalent to the site model shown at left.

In the ring-like structure of LH1 and LH2, this symmetric simplifies our
calculations. Consider the central system as a particle hopping on a close ring. Then the most general Hamiltonian for a system coupled to a spin bath is

$$
\begin{equation*}
H=H_{D}+H_{N D}+H_{S B} \tag{5.1}
\end{equation*}
$$

with diagonal (ie., on-site) terms

$$
\begin{equation*}
H_{D}=\sum_{j}\left(\varepsilon_{j}+\sum_{k} \omega_{k}^{j} \cdot \boldsymbol{\sigma}_{k}\right) c_{j}^{\dagger} c_{j} \tag{5.2}
\end{equation*}
$$

and non-diagonal terms, associated with inter-site hopping of form

$$
\begin{equation*}
H_{N D}=\sum_{<i j>}\left\{t_{i j} c_{i}^{\dagger} c_{j} \exp \left[i A_{i j}^{0}+i \sum_{k}\left(\phi_{k}^{i j}+\boldsymbol{\alpha}_{k}^{i j} \cdot \boldsymbol{\sigma}_{k}\right)\right]+H . c .\right\} \tag{5.3}
\end{equation*}
$$

The independent spin bath Hamiltonian is

$$
\begin{equation*}
H_{S B}=\sum_{k} \mathbf{h}_{k} \cdot \boldsymbol{\sigma}_{k}+\sum_{k, k^{\prime}} V_{k k^{\prime}}^{\alpha \beta} \sigma_{k}^{\alpha} \sigma_{k^{\prime}}^{\beta} \tag{5.4}
\end{equation*}
$$

The operator $c_{j}^{\dagger}$ creates a particle at site j. The $\left\{\boldsymbol{\sigma}_{k}\right\}$ are Pauli operators for the surrounding two level systems (TLSs), with $k=1,2, \ldots . N_{s}$. The phase factors $\left\{A_{i j}^{0}\right\}$ gives a topological feature between different path; there are different accumulated phases due to different winding number. The origin of such flux is not limited to magnetic field: it can be any general phase factor when particles travel around the ring, for example the spin orbit coupling or the interaction between reaction center. Since our ring is symmetric, so that the hopping matrix elements $t_{i j} \rightarrow \Delta_{0}$, and we assume $A_{i j}^{0}=2 \pi \Phi / N \Phi_{0}$, where $\Phi_{0}$ is the flux quantum. For nonsymmetric case ,such as FMO complex, on-site energy is different for site to site and the problem is more complicated which we need to consider the localization problem around certain site. In this thesis we only consider a completely symmetric ring like LH1, the site energy $\varepsilon_{j} \rightarrow \varepsilon_{0}, \forall j$, and we henceforth ignore it; this leaves only the on-site interaction $\omega_{k}^{j}$ with the bath.

The origin of non-diagonal terms is a little more subtle. Suppose there were no spin bath in the problem, so that our "bare" ring had a Hamiltonian

$$
\begin{equation*}
H_{o}=\sum_{\langle i j>}\left[t_{i j} c_{i}^{\dagger} c_{j} e^{i A_{i j}^{0}}+H . c .\right]+\sum_{j} \varepsilon_{j} c_{j}^{\dagger} c_{j} \tag{5.5}
\end{equation*}
$$

This "1-band" Hamiltonian is the result of truncating of a Hamiltonian of form:

$$
\begin{equation*}
H_{V}=\frac{P^{2}}{2 M}+U(\boldsymbol{R}) \tag{5.6}
\end{equation*}
$$

where a particle of mass M moves in a potential $U(\boldsymbol{R})$ characterized by N potential wells in a ring array (see again Figure.5.1). Then $\varepsilon_{j}$ is the energy of the lowest state in the j -th well, and $t_{i j}$ is the tunneling amplitude between the i-th and j-th wells. In path integral language, this tunneling is over a semiclassical "instanton" trajectory $\mathbf{R}_{\text {ins }}(\tau)$, and this occurs over a timescale $\tau_{B}$ in $1 / \Omega_{0}$ (the "bounce time" [45]), where $\Omega_{0}$ is roughly the small oscillation frequency of the particle in the potential wells.

Consider now what happens when we couple to the spin bath. The bath spins couple to the position of the particle via an interaction [46]

$$
\begin{equation*}
H_{\text {int }}(\mathbf{R})=\sum_{k} \boldsymbol{F}\left(\boldsymbol{R}-\boldsymbol{r}_{k}\right) \cdot \boldsymbol{\sigma}_{k}=\sum_{k} H_{i n t}^{k}(\mathbf{R}) \tag{5.7}
\end{equation*}
$$

where $\boldsymbol{F}(\boldsymbol{r})$ is some vector function, and $\boldsymbol{r}_{k}$ is the position at the k -th bath spin. The diagonal coupling $\boldsymbol{\omega}_{k}^{j} \cdot \boldsymbol{\sigma}_{k}$ is easily obtained from (5.7) when we truncate to the single band form. But the term (5.7) must also generate a non-diagonal term. We can see this by defining the operator

$$
\begin{equation*}
\hat{T}_{i j}^{k}=\exp \left[-i / \hbar \int_{\tau_{i n}\left(R_{i}\right)}^{\tau_{f}\left(R_{j}\right)} d \tau H_{i n t}^{k}\left(R, \sigma_{k}\right)\right] \tag{5.8}
\end{equation*}
$$

where the particle is assumed to start in the i-th potential well centered at position $\mathbf{R}_{i}$, at the initial time $\tau_{i n}$, 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 $\boldsymbol{\sigma}_{k}$ with $\hat{T}_{i j}^{k}$, to get

$$
\begin{equation*}
\left|\boldsymbol{\sigma}_{k}^{f}\right\rangle=\hat{T}_{i j}^{k}\left|\boldsymbol{\sigma}_{k}^{i n}\right\rangle=e^{i\left(\phi_{k}^{i j}+\boldsymbol{\alpha}_{k}^{i j} \cdot \boldsymbol{\sigma}_{k}\right)}\left|\boldsymbol{\sigma}_{k}^{i n}\right\rangle \tag{5.9}
\end{equation*}
$$

where we note that both the phase $\phi_{k}^{i j}$ multiplying the unit Pauli matrices, and the vector $\boldsymbol{\alpha}_{k}^{i j}$ multiplying the other 3 Pauli matrices, 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[44, 47].

Note that there will also in general be a coupling of the bath spins to the momentum of the particle, of form

$$
\begin{equation*}
H_{i n t}(\mathbf{P})=\sum_{k} \boldsymbol{G}\left(\boldsymbol{P}-\boldsymbol{r}_{k}\right) \cdot \boldsymbol{\sigma}_{k}=\sum_{k} H_{i n t}^{k}(\mathbf{P}) \tag{5.10}
\end{equation*}
$$

which will also generate a non-diagonal interaction between the particle and the spins, of the same form as in (5.3). Now, if we know $U(\mathbf{R}), \boldsymbol{F}(\boldsymbol{R}-$


Figure 5.2: A typical path(solid line) for a particle moving in a discrete ring coupled to environmental modes(wavy lines) as a function of time.
$\left.\boldsymbol{r}_{k}\right)$, and $\boldsymbol{G}\left(\boldsymbol{P}-\boldsymbol{r}_{k}\right)$, we can then calculate the parameters $\phi_{k}^{i j}$ and $\boldsymbol{\alpha}_{k}^{i j}$ by various methods [44, 48]. However we are interested here in the generic case, and our object is to study the dynamics of decoherence as one varies the $\boldsymbol{\alpha}_{k}^{i j}$; thus we simply assume these parameters to be given. Actually, the biological solvent is quite dirty, it contains many different effects such as ionized charges, molecule amorphous and . It is almost impossible to determine these parameters specifically in these systems.

In this thesis we mainly focus on a special case of the general Hamiltonian in equations (5.1)-(5.4), given by

$$
\begin{equation*}
H_{\phi}=-\Delta_{0} \sum_{<i j>}\left[c_{i}^{\dagger} c_{j} e^{i\left(A_{i j}^{0}+\sum_{k} \boldsymbol{\alpha}_{k}^{i j} \cdot \boldsymbol{\sigma}_{k}\right)}+H . c .\right]+\sum_{k} \mathbf{h}_{k} \cdot \boldsymbol{\sigma}_{k} \tag{5.11}
\end{equation*}
$$

This Hamiltonian is chosen because it isolates the processes contributing to pure phase decoherence without energy dissipation, as we discussed above. We drop the the diagonal interaction $\boldsymbol{\omega}_{k}^{j}$ to avoid complications of the energy relaxation. For other terms, we drop the interaction $V_{k k^{\prime}}^{\alpha \beta}$, between bath spins. Since we have already mentioned that in light harvesting molecules, couplings between environment molecules are 2 orders smaller than its own on-site energy. It is often a good approximation. Since it is a symmetric ring, we put $\varepsilon_{j}=0$, and absorb the phases $\phi_{k}^{i j}$ into a renormalization of $\Delta_{0}$ $\left(\right.$ from $\left.\sum_{k} \operatorname{Im} \phi_{k}^{i j}\right)$, and of $A_{i j}^{0}\left(\right.$ from $\left.\sum_{k} \operatorname{Re} \phi_{k}^{i j}\right)$.

### 5.3 Path Integral Formalism for Spin Bath

To calculate the influence functional, we need to at first written the spin Hamiltonian in to path integral form. Consider the Hamiltonian of a spin,

$$
\begin{equation*}
H=\mathbf{B} \cdot \mathbf{S} \tag{5.12}
\end{equation*}
$$

Here $\mathbf{B}$ is a function of t and $\mathbf{S}=\frac{1}{2} \sigma$ for spin $1 / 2$ system. Since $e^{i a(\mathbf{n} \cdot \sigma)}=$ $\cos a+i(\mathbf{n} \cdot \sigma) \sin a$, we can always transform our equation (5.11) in to this form. To get a path integral form, we consider the coherent state $|\mathbf{n}\rangle$, which satisfy

$$
\begin{equation*}
\mathbf{n} \cdot \sigma|\mathbf{n}\rangle=|\mathbf{n}\rangle \tag{5.13}
\end{equation*}
$$

Here $\mathbf{n}$ is a $3-\mathrm{D}$ unit vector. In $\sigma_{z}$ representation, this state can be written as

$$
\begin{equation*}
|\mathbf{n}\rangle=|z\rangle=\binom{e^{-i \phi} \cos \frac{\theta}{2}}{\sin \frac{\theta}{2}} \tag{5.14}
\end{equation*}
$$

$(\theta, \phi)$ are the spherical angles of vector $\mathbf{n}$. The phase space is a sphere. This coherent state set is complete. The normalization is

$$
\begin{equation*}
\int \frac{d^{2} \mathbf{n}}{2 \pi}|\mathbf{n}\rangle\langle\mathbf{n}|=1 \tag{5.15}
\end{equation*}
$$

But they are not orthogonal. The inner product between any two states $\left|\mathbf{n}_{a}\right\rangle$ and $\left|\mathbf{n}_{b}\right\rangle$ is

$$
\begin{equation*}
\left\langle\mathbf{n}_{a} \mid \mathbf{n}_{b}\right\rangle=z_{a}^{\dagger} z_{b} \tag{5.16}
\end{equation*}
$$

Then for the propagator $G\left(\mathbf{n}_{\mathbf{a}}, \mathbf{n}_{\mathbf{b}}, t\right)=-i\left\langle\mathbf{n}_{a}\right| e^{-i \int d t^{\prime} \mathbf{B} \cdot \mathbf{S}}\left|\mathbf{n}_{b}\right\rangle$, we slice the time interval $[0, t]$ into N parts and plug (5.15) in, we have
$G\left(\mathbf{n}_{\mathbf{a}}, \mathbf{n}_{\mathbf{b}}, t\right)=-i \int\left\langle\mathbf{n}_{a}\right| e^{-i \delta t \mathbf{B} \cdot \mathbf{S}}\left|\mathbf{n}_{1}\right\rangle\left\langle\mathbf{n}_{1}\right| e^{-i \delta t \mathbf{B} \cdot \mathbf{S}}\left|\mathbf{n}_{2}\right\rangle\left\langle\mathbf{n}_{2}\right| \ldots\left|\mathbf{n}_{N}\right\rangle\left\langle\mathbf{n}_{N}\right| e^{-i \delta t \mathbf{B} \cdot \mathbf{S}}\left|\mathbf{n}_{b}\right\rangle$
Here $\delta t=t / N$ and $\int$ indicate all the integrals from all plug-ins. If $N \rightarrow \infty$, we only keep the first order of $\delta t$. Noticing that $z_{j+1} \approx z_{j}+\dot{z}(j) \delta t$, the quantity

$$
\begin{align*}
\left\langle\mathbf{n}_{j+1}\right| e^{-i \delta t \mathbf{B} \cdot \mathbf{S}}\left|\mathbf{n}_{j}\right\rangle & \approx\left\langle\mathbf{n}_{j+1} \mid \mathbf{n}_{j}\right\rangle+\left\langle\mathbf{n}_{j+1}\right| i \delta t \mathbf{B} \cdot \mathbf{S}\left|\mathbf{n}_{j}\right\rangle \approx z_{j+1}^{\dagger} z_{j}-i \frac{1}{2} \mathbf{B} \cdot \mathbf{n}_{j} \\
& \approx 1+\dot{z}_{j}^{\dagger} z_{j}-i \frac{1}{2} \mathbf{B} \cdot \mathbf{n}_{j} \approx e^{i \delta t\left(-i \dot{z}_{j}^{\dagger} z_{j}-\frac{1}{2} \mathbf{B} \cdot \mathbf{n}_{j}\right)} \tag{5.18}
\end{align*}
$$

Therefore, we get the path integral form for spin as

$$
\begin{array}{r}
G\left(\mathbf{n}_{\mathbf{a}}, \mathbf{n}_{\mathbf{b}}, t\right)=-i \int \frac{\mathcal{D}^{2} \mathbf{n}(\mathbf{t})}{2 \pi} e^{i S[n(t)]} \\
\quad S[n(t)]=\int_{0}^{t} d t^{\prime}\left(-i \dot{z}^{\dagger} z-\frac{1}{2} \mathbf{B} \cdot \mathbf{n}\right) \tag{5.20}
\end{array}
$$

Unless in some special cases (e.g. $\mathbf{B}(t)=$ constant, or $\left.\mathbf{B}(t)=\left(B_{1} \cos \omega t, B_{1} \sin \omega t, B_{0}\right)\right)$, this integral cannot be evaluated analytically. In spin bath case, $\mathbf{B}(t)$ usually depends on the path chosen by the central system, which means principally we cannot make any assumption in $\mathbf{B}(t)$. There is no general method about how to make approximations here. In the later sections, we deal with two special case: $h_{k}=0$ (no intrinsic dynamics of bath spin); and $h_{k} \rightarrow \infty$ (high field limit).

### 5.4 Bare Ring Dynamics

At first we consider the dynamics of a particle(exciton) moving on the N -site ring described by $H_{o}$ in (5.5), with no bath. This is basically depending on the excitation energy and overlap integral between chlorophylls. We have already solved the Green function in previous sections, see (4.25). We are using this result to get some useful expression in this section.

Before we start, 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. One has, for the 'bare' density matrix of the system at time $t$,

$$
\begin{equation*}
\rho^{o}(t)=e^{-i \mathcal{H}_{o} t} \rho_{o}(0) e^{i \mathcal{H}_{o} t} . \tag{5.21}
\end{equation*}
$$

Thus, suppose we have an initial density matrix $\rho_{l, l^{\prime}}^{o}=\langle l| \rho(t=0)\left|l^{\prime}\right\rangle$ at time $t=0$ (where $l$ and $l^{\prime}$ are site indices), then at a later time $t$ we have

$$
\begin{align*}
\rho_{j j^{\prime}}^{o}(t) \equiv\langle j| \rho^{o}(t)\left|j^{\prime}\right\rangle & =\langle j| e^{-i \mathcal{H}_{o} t}|l\rangle \rho_{l, l^{\prime}}\left\langle l^{\prime}\right| e^{i \mathcal{H}_{o} t}\left|j^{\prime}\right\rangle \\
& =\rho_{l, l^{\prime}} G_{j l}^{o}(t) G_{j^{\prime} l^{\prime}}^{o}(t)^{\dagger} . \tag{5.22}
\end{align*}
$$

where we use the Einstein summation convention (summing over $l, l^{\prime}$ ). In what follows we will often choose the special case where the particle begins at $t=0$ on site 0 , so that $\rho_{l, l^{\prime}}=\delta_{0 l} \delta_{l^{\prime} 0}$, and then we have

$$
\begin{equation*}
\langle j| \rho_{o}(t)\left|j^{\prime}\right\rangle=G_{j 0}^{o}(t) G_{j^{\prime} 0}^{o}(t)^{\dagger} . \tag{5.23}
\end{equation*}
$$

### 5.4. Bare Ring Dynamics

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:

$$
\begin{align*}
\rho_{j j^{\prime}}^{o}(t) & =\sum_{l, l^{\prime}} \rho_{l, l^{\prime}} \sum_{p p^{\prime}} e^{i\left(p-p^{\prime}\right) \Phi} e^{i \Phi\left(j-j^{\prime}+l-l^{\prime}\right) / N} i^{N\left(p^{\prime}-p\right)+j^{\prime}-j+l-l^{\prime}} J_{N p+j-l}\left(2 \Delta_{o} t\right) J_{N p^{\prime}+j^{\prime}-l^{\prime}}\left(2 \Delta_{o} t\right) \\
& =\sum_{l, l^{\prime}} \rho_{l, l^{\prime}} \sum_{p p^{\prime}} e^{i(\Phi / N+\pi / 2)\left[N\left(p^{\prime}-p\right)+j^{\prime}-j+l-l^{\prime}\right]} J_{N p+j-l}\left(2 \Delta_{o} t\right) J_{N p^{\prime}+j^{\prime}-l^{\prime}}\left(2 \Delta_{o} t\right) \tag{5.24}
\end{align*}
$$

This expression contains two path interferences which is clear by physical understanding. However it is somewhat unwieldily, 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. To do this we use Graf's summation theorem for Bessel functions[49]

$$
\begin{equation*}
J_{\nu}\left(2 x \sin \frac{\theta}{2}\right)\left(-e^{-i \theta}\right)^{\frac{\nu}{2}}=\sum_{\mu=-\infty}^{+\infty} J_{\nu+\mu}(x) J_{\mu}(x) e^{i \mu \theta} \tag{5.25}
\end{equation*}
$$

We set $\theta=0, \frac{2 \pi}{N}, \ldots \frac{2 \pi m}{N}, \ldots \frac{2 \pi(N-1)}{N}$, which is the $k_{m}$ in (4.18) and multiply $e^{-i(j-l) \theta}$ on each side. We then have

$$
\begin{equation*}
J_{\nu}\left(2 x \sin \frac{k_{m}}{2}\right) e^{-i\left(k_{m}+\pi\right) \frac{\nu}{2}} e^{-i(j-l) k_{m}}=\sum_{\mu=-\infty}^{+\infty} J_{\nu+\mu}(x) J_{\mu}(x) e^{i(\mu-j+l) k_{m}} \tag{5.26}
\end{equation*}
$$

Noticing then that

$$
\begin{equation*}
\sum_{m=0}^{N-1} e^{i k_{m} n}=\sum_{p} \delta_{N p, n} \tag{5.27}
\end{equation*}
$$

we do the sum over $m$; only $\mu-j+l=N p$ survives, and thus

$$
\begin{equation*}
\frac{1}{N} \sum_{m=0}^{N-1} J_{\nu}\left(2 x \sin \frac{k_{m}}{2}\right) e^{-i\left(k_{m}+\pi\right) \frac{\nu}{2}} e^{-i(j-l) k_{m}}=\frac{1}{N} \sum_{p} J_{N p+j-l+\nu}(x) J_{N p+j-l}(x) \tag{5.28}
\end{equation*}
$$

Setting $\nu=N p^{\prime}+j^{\prime}-l^{\prime}-N p-j+l, x=2 \Delta_{o} t$, we then substitute (5.28)back
into (5.22), to get

$$
\begin{align*}
\rho_{j j^{\prime}}^{o}(t)= & \sum_{l l^{\prime}} \rho_{l l^{\prime}} \sum_{p p^{\prime}} e^{i(\Phi / N+\pi / 2)\left(N p^{\prime}-N p+j^{\prime}-j+l-l^{\prime}\right)} J_{N p+j-l}\left(2 \Delta_{o} t\right) J_{N p^{\prime}+j^{\prime}-l^{\prime}}\left(2 \Delta_{o} t\right) \\
= & \frac{1}{N} \sum_{l l^{\prime}} \rho_{l l^{\prime}} \sum_{p} e^{i\left(N p+j^{\prime}-j+l-l^{\prime}\right)\left(\frac{\Phi}{N}+\frac{\pi}{2}\right)} \sum_{m=0}^{N-1} J_{N p+j^{\prime}-j+l-l^{\prime}}\left(4 \Delta_{o} t \sin \frac{k_{m}}{2}\right) \\
& \times e^{-i\left(k_{m}+\pi\right) \frac{N p+j^{\prime}-j+l-l^{\prime}}{2}} e^{-i(j-l) k_{m}} \\
= & \frac{1}{N} \sum_{l l^{\prime}} \rho_{l l^{\prime}} \sum_{p} \sum_{m=0}^{N-1} J_{N p+j^{\prime}-j+l-l^{\prime}}\left(4 \Delta_{o} t \sin \frac{k_{m}}{2}\right) \\
& \times e^{i\left(N p+j^{\prime}-j+l^{\prime}-l\right) \frac{\Phi}{N}-i k_{m}\left(j+j^{\prime}+N p-l-l^{\prime}\right) / 2} \tag{5.29}
\end{align*}
$$

If we start with $\rho(0)=|0\rangle\langle 0|$, the expression is shortened to
$\rho_{j j^{\prime}}=\frac{1}{N} \sum_{m=0}^{N-1} \sum_{p=-\infty}^{\infty} J_{N p+j^{\prime}-j}\left[4 \Delta_{o} t \sin \left(k_{m} / 2\right)\right] \times e^{i \Phi\left(p+\left(j^{\prime}-j\right) / N\right)-i k_{m}\left(j+j^{\prime}+N p\right) / 2}$
In this expression we use the fact that density matrix $\rho$ is Hermitian, i.e., $\rho_{j j^{\prime}}=\rho_{j^{\prime} j}^{*}$. By setting $p \rightarrow-p, k_{m} \rightarrow-k_{m}$, we have

$$
\begin{align*}
\rho_{j j^{\prime}}^{o}(t) & =\frac{1}{N} \sum_{p} \sum_{m=0}^{N-1} J_{-N p+j-j^{\prime}}\left(4 \Delta_{o} t \sin \frac{k_{m}}{2}\right) e^{-i\left(-N p+j-j^{\prime}\right) \frac{\Phi}{N}+i k_{m}\left(j+j^{\prime}-N p\right) / 2} \\
& =\frac{1}{N} \sum_{m=0}^{N-1} \sum_{p=-\infty}^{\infty} J_{N p+j^{\prime}-j}\left[4 \Delta_{o} t \sin \left(k_{m} / 2\right)\right] e^{i \Phi\left[p+\left(j^{\prime}-j\right) / N\right]-i k_{m}\left(j+j^{\prime}-N p\right) / 2} \tag{5.31}
\end{align*}
$$

From either $G_{j j^{\prime}}^{o}(t)$ or $\rho_{j j^{\prime}}^{o}(t)$ we may immediately compute two useful physical quantities. First, the probability to find the particle at time $t$ at site $j$, assuming it starts at the origin, is

$$
\begin{equation*}
P_{j 0}^{(o)}(t)=\langle j| \rho_{o}(t)|j\rangle=\left|G_{j 0}^{o}(t)\right|^{2} \tag{5.32}
\end{equation*}
$$

which from above can be written as

$$
\begin{equation*}
P_{j 0}^{(o)}(t)=\sum_{p p^{\prime}} J_{N p+j}\left(2 \Delta_{o} t\right) J_{N p^{\prime}+j}\left(2 \Delta_{o} t\right) e^{-i N\left(p^{\prime}-p\right)\left(\Phi / N+\frac{\pi}{2}\right)} \tag{5.33}
\end{equation*}
$$

or in single sum form as

$$
\begin{equation*}
P_{j 0}^{o}(t)=\frac{1}{N} \sum_{m=0}^{N-1} \sum_{p=-\infty}^{\infty} e^{i p\left(\Phi+N k_{m} / 2\right)} J_{N p}\left[4 \Delta_{o} t \sin \left(k_{m} / 2\right)\right] . \tag{5.34}
\end{equation*}
$$



Figure 5.3: 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 (eg., the 2nd moment $j^{2} P_{j 0}^{o}(t)$ tells us the rate at which a density matrix spreads in time).

The bare density matrix is of course strictly periodic in time, as seen most obviously in (5.34). To give some idea of how the free particle behaves, it is useful to look at plots of these results for a small 3 -site ring, where the oscillation periods are quite short. One then has, for the case where the
particle starts at the origin, that

$$
\begin{align*}
P_{j 0}^{o}(t)= & \frac{1}{3}\left(1+\left(3 \delta_{j, 0}-1\right)\left[J_{0}\left(2 \Delta_{o} \sqrt{3} t\right)+2 \sum_{p=1}^{\infty} J_{6 p}\left(2 \Delta_{o} \sqrt{3} t\right) \cos (2 p \Phi)\right]\right. \\
& \left.+\left(\delta_{j, 1}-\delta_{j, 2}\right) 2 \sqrt{3} \sum_{p=1}^{\infty} J_{6 p-3}\left(2 \Delta_{o} \sqrt{3} t\right) \sin ((2 p-1) \Phi)\right) . \tag{5.35}
\end{align*}
$$

In Fig. 5.3 the return probability $P_{00}^{(o)}(t)$ is plotted for $N=3$; we see that the periodic behavior depends strongly on the flux $\Phi$.

The second useful quantity is the current between site $j$ and site $j+1$; since the equation of motion of $\rho_{n n}$ reads

$$
\begin{equation*}
i \frac{d}{d t} \rho_{n n}=\sum_{n^{\prime}}\left[\langle n| H\left|n^{\prime}\right\rangle\left\langle n^{\prime}\right| \rho|n\rangle-\langle n| \rho\left|n^{\prime}\right\rangle\left\langle n^{\prime}\right| H|n\rangle\right] \tag{5.36}
\end{equation*}
$$

Thus we define the current $I_{n n^{\prime}}$, which is the current from $n^{\prime}$ to n , as

$$
\begin{equation*}
I_{n n^{\prime}}=-i\left(\Delta_{n n^{\prime}} \rho_{n^{\prime} n}-\rho_{n n^{\prime}} \Delta_{n^{\prime} n}\right) . \tag{5.37}
\end{equation*}
$$

In our bare ring model here, it reads

$$
\begin{equation*}
I_{j, j+1}^{o}(t)=2 \operatorname{Im}\left[\Delta_{0} e^{-i \Phi / N} \rho_{j+1, j}^{o}(t)\right] \tag{5.38}
\end{equation*}
$$

Again, one can write the current as either a double sum over pairs of winding numbers, or as a single sum. The derivation is same as the reduce density matrix. For the case where the particle starts from the origin, these expressions reduce to

$$
\begin{align*}
I_{j+1, j} & =2 \Delta_{o} \sum_{p p^{\prime}} J_{N p+j}\left(2 \Delta_{o} t\right) J_{N p^{\prime}+j+1}\left(2 \Delta_{o} t\right) \cos \left[\left(\frac{\pi}{2} N+\Phi\right)\left(p^{\prime}-p\right)\right] \\
& =\frac{2 \Delta_{o}}{N} \sum_{m=0}^{N-1} \sum_{p} J_{N p+1}\left(4 \Delta_{o} t \sin \frac{k_{m}}{2}\right) e^{-i k_{m}\left(\frac{N p+1}{2}+j\right)} i^{N p+1} \cos \left[\left(\frac{\pi}{2} N+\Phi\right) p\right] \tag{5.39}
\end{align*}
$$

for the double and single sums respectively. An interesting special case is the current between the site of origin and the adjacent site $I_{01}$. One can simplify this to

$$
\begin{equation*}
I_{01}^{o}(t)=\frac{1}{2} \frac{\partial\left|G_{00}\right|^{2}}{\partial t}+\frac{N}{t}\left|G_{00}\right|^{2} \frac{\partial \arg G_{00}}{\partial \Phi} . \tag{5.40}
\end{equation*}
$$

To derive (5.40), we notice that

$$
\begin{equation*}
\sum_{p} J_{p N+1}(x)=J_{1}(x)+\sum_{l=1}^{+\infty}\left(J_{l N+1}(x)+(-1)^{l N-1} J_{l N-1}(x)\right) \tag{5.41}
\end{equation*}
$$

And

$$
\begin{align*}
& J_{l N-1}(x)-J_{N l+1}(x)=2 J_{l N}^{\prime}(x)  \tag{5.42}\\
& J_{l N-1}(x)+J_{N l+1}(x)=\frac{2 l N}{x} J_{N l}(x) \tag{5.43}
\end{align*}
$$

Substituting back into (5.68) to make orders of all Bessel functions as $N l$, , we could use (4.23) to absorb the sum. It yields

$$
\begin{align*}
I_{01}^{o}(t) & =\Delta_{0}\left[\frac{1}{2 \Delta_{0}}\left(\frac{\partial G_{00}}{\partial t}+\frac{N i}{t} \frac{\partial G_{00}}{\partial \Phi}\right) G_{00}^{*}+\frac{1}{2 \Delta_{0}}\left(\frac{\partial G_{00}^{*}}{\partial t}-\frac{N i}{t} \frac{\partial G_{00}^{*}}{\partial \Phi}\right) G_{00}\right] \\
& =\frac{1}{2} \frac{\partial\left|G_{00}\right|^{2}}{\partial t}+\frac{N i}{2 t}\left(G_{00} \frac{\partial G_{00}^{*}}{\partial \Phi}-G_{00}^{*} \frac{\partial G_{00}}{\partial \Phi}\right) \\
& =\frac{1}{2} \frac{\partial\left|G_{00}\right|^{2}}{\partial t}+\frac{N}{t}\left|G_{00}\right|^{2} \frac{\partial \arg G_{00}}{\partial \Phi} \tag{5.44}
\end{align*}
$$

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

$$
\begin{equation*}
I_{0,1}=\frac{2 \Delta_{o}}{3} \sum_{m=1}^{2} \sum_{p} J_{3 p+1}\left(4 \Delta_{o} t \sin \frac{m \pi}{3}\right) e^{-i m \pi(3 p+1) / 3} i^{3 p+1} \cos \left[\left(\frac{3 \pi}{2}+\Phi\right) p\right] \tag{5.45}
\end{equation*}
$$

which we can also write in the form

$$
\begin{equation*}
I_{0,1}=\frac{2 \Delta_{o}}{3} \sum_{p} J_{3 p+1}\left(2 \sqrt{3} \Delta_{o} t i^{3 p+1} \cos \left[\left(\frac{3 \pi}{2}+\Phi\right) p\right] \sum_{m=1}^{2}\left(e^{-i \pi(3 p+1) / 3}+e^{-i 2 \pi(3 p+1) / 3}\right)\right. \tag{5.46}
\end{equation*}
$$

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

$$
\begin{align*}
& I_{0,1}=\frac{2}{3} \Delta_{o} \sum_{p=-\infty}^{\infty} J_{3 p+1}\left(2 \Delta_{o} \sqrt{3} t\right) K(p, \Phi) \\
& K(p, \Phi)=\sin (p \Phi) \quad \text { if } p=\text { odd } \\
& K(p, \Phi)=\sqrt{3} \cos (p \Phi) \quad \text { if } p=\text { even } . \tag{5.47}
\end{align*}
$$

These results are shown in Fig. 5.3. Notice that in this special case the result is periodic in $\Phi$; this is not however true for a general initial density matrix $\rho_{l, l^{\prime}}$, when the periodicity is in $\Phi / N$. This is due to our symmetric flux distribution assumption on each bond.

### 5.5 Ring Plus Bath

From now on we are going 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 (5.11). We have already discussed it in previous sections. A typical paths for a particle is shown in Fig. 5.4.


Figure 5.4: A particular path in a path integral for the particle, shown here for an $N=4$ ring. This path, from site 0 to site 1 , has winding number $p=1$.

Let us rewrite (4.30) into a influence functional form for density matrices. If we can parameterize a path for the angular coordinate $\Theta(t)$ which includes $m$ transitions between sites in the form

$$
\begin{equation*}
\Theta_{(m)}(t)=\Theta(t=0)+\sum_{i=1}^{m} \sum_{q_{i}= \pm} q_{i} \theta\left(t-t_{i}\right) \tag{5.48}
\end{equation*}
$$

where $\theta(x)$ is the step-function. The propagator $K(1,2)$ for the particle reduced density matrix between times $\tau_{1}$ and $\tau_{2}$ is then

$$
\begin{equation*}
K\left(\Theta_{2}, \Theta_{2}^{\prime} ; \Theta_{1}, \Theta_{1}^{\prime}\right)=\int_{\Theta\left(\tau_{1}\right)=\Theta_{1}}^{\Theta\left(\tau_{2}\right)=\Theta_{2}} d \Theta \int_{\Theta^{\prime}\left(\tau_{1}\right)=\Theta_{1}^{\prime}}^{\Theta^{\prime}\left(\tau_{2}\right)=\Theta_{2}^{\prime}} d \Theta^{\prime} e^{-\frac{i}{\hbar}\left(S_{o}[\Theta]-S_{o}\left[\Theta^{\prime}\right]\right)} \mathcal{F}\left[\Theta, \Theta^{\prime}\right] \tag{5.49}
\end{equation*}
$$

where $S_{o}[\Theta]$ is the free particle action, and $\mathcal{F}\left[\Theta, \Theta^{\prime}\right]$ is the influence functional, defined by

$$
\begin{equation*}
\mathcal{F}\left[\Theta, \Theta^{\prime}\right]=\prod_{k}\left\langle\hat{U}_{k}(\Theta, t) \hat{U}_{k}^{\dagger}\left(\Theta^{\prime}, t\right)\right\rangle, \tag{5.50}
\end{equation*}
$$

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 $\Theta^{\prime}(t)$ on its "return" voyage. Thus $\mathcal{F}\left[\Theta, \Theta^{\prime}\right]$ acts as a weighting function, over different possible paths $\left(\Theta(t), \Theta^{\prime}(t)\right)$. The difference between (4.30) and (5.50) is that this one contains the interference between two path $\Theta$ and $\Theta^{\prime}$.

To see the explicit form, let us write the "bare" free particle density matrix in the form of a double sum over winding numbers

$$
\begin{equation*}
\rho_{j j^{\prime}}^{o}(t)=\sum_{p p^{\prime}} \rho_{j j^{\prime}}^{o}\left(p, p^{\prime} ; t\right) \tag{5.51}
\end{equation*}
$$

Then the key result is that in the presence of phase coupling to the spin bath, the reduced density matrix takes the form

$$
\begin{equation*}
\rho_{j j^{\prime}}(t)=\sum_{p p^{\prime}} \sum_{l l^{\prime}} \rho_{j-l, j^{\prime}-l^{\prime}}^{o}\left(p, p^{\prime} ; t\right) F_{j, j^{\prime}}^{l, l^{\prime}}\left(p, p^{\prime}\right) \rho_{l l^{\prime}} \tag{5.52}
\end{equation*}
$$

where the influence functional, initially over the entire pair of paths for the reduced density matrix, has now reduced to the much simpler function

$$
\begin{equation*}
\mathcal{F}_{j, j^{\prime}}^{l, l^{\prime}}\left(p, p^{\prime}\right)=\rho_{j-l, j^{\prime}-l^{\prime}}^{o}\left(p, p^{\prime} ; t\right) F_{j, j^{\prime}}^{l, l^{\prime}}\left(p, p^{\prime}\right) \tag{5.53}
\end{equation*}
$$

involving only the initial and final states, as well as the 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

$$
\begin{equation*}
\exp \left\{-i p \sum_{k}\left(\sum_{\langle m n\rangle=\langle 01\rangle}^{\langle N 0\rangle}-i \sum_{\langle m n\rangle=\langle l, l+1\rangle}^{\langle j-1, j\rangle}\right)\left(\boldsymbol{\alpha}_{k}^{m n} \cdot \boldsymbol{\sigma}_{k}\right)\right\} \tag{5.54}
\end{equation*}
$$

and for fixed initial and final sites, this additional phase only depends on the winding number. One thing to notice is that in this factor we make the assumption that

$$
\begin{equation*}
\left[e^{i \alpha \cdot \sigma}, e^{i \alpha^{\prime} \cdot \sigma}\right] \approx 0 \tag{5.55}
\end{equation*}
$$

Actually this commutator is proportional to $\left(\sin \alpha \sin \alpha^{\prime}\right)\left(n_{\alpha} \times n_{\alpha^{\prime}}\right)$, we drop it since the coupling $\alpha$ is usually very small and along similar directions. Performing the sums over the two paths as before, but now including the phase factors (5.54), we get:

$$
\begin{align*}
& F_{j, j^{\prime}}^{l, l^{\prime}}\left(p, p^{\prime}\right)=\left\langle e^{-i\left(p-p^{\prime}\right) \sum_{k} \sum_{\langle m n\rangle\langle\langle 0,1\rangle}^{\langle N-1, N\rangle} \boldsymbol{\alpha}_{k}^{m n} . \boldsymbol{\sigma}_{k}} e^{-i\left(p-p^{\prime}\right) \sum_{k} \sum_{\langle m n\rangle\left\langle\left\langle\left\langle l^{\prime}, l^{\prime}+1\right\rangle\right.\right.}^{\langle l-1, l} \boldsymbol{\alpha}_{k}^{m n} \cdot \boldsymbol{\sigma}_{k}}\right. \\
& \times e^{\left.-i \sum_{k} \sum_{\langle m n\rangle=\left\langle j^{\prime}, j^{\prime}+1\right\rangle}^{\langle j+1\rangle} \boldsymbol{\alpha}_{k}^{m n} \cdot \boldsymbol{\sigma}_{k}\right\rangle} \tag{5.56}
\end{align*}
$$

In the purely symmetric case where $\boldsymbol{\alpha}_{k}^{i j} \rightarrow \boldsymbol{\alpha}_{k}$ for every link, the influence function reduces to the much simpler result

$$
\begin{equation*}
F_{j, j^{\prime}}^{l, l^{\prime}}\left(p, p^{\prime}\right)=\left\langle e^{\left.-i\left[N\left(p-p^{\prime}\right)+\left(j-j^{\prime}+l-l^{\prime}\right)\right] \sum_{k} \boldsymbol{\alpha}_{k} \cdot \boldsymbol{\sigma}_{k}\right\rangle}\right. \tag{5.57}
\end{equation*}
$$

which for a particle being launched from the origin gives the result (5.60) quoted in the main text.

If we start with initial density matrix $\rho(t=0)=|0\rangle\langle 0|$, then the reduced density matrix at time $t$ is

$$
\begin{align*}
\rho_{j j^{\prime}}(t)= & \sum_{p p^{\prime}} \rho_{j j^{\prime}}^{o}\left(p, p^{\prime} ; t\right)\left\langle e^{-i\left(p-p^{\prime}\right) \sum_{k} \sum_{\langle m n\rangle=\langle 01\rangle}^{\langle N 0\rangle} \boldsymbol{\alpha}_{k}^{m n n} \cdot \boldsymbol{\sigma}_{k}} e^{-i \sum_{k} \sum_{\langle m n\rangle=\left\langle j^{\prime}, j^{\prime}+1\right\rangle}^{\langle j-1, j\rangle} \boldsymbol{\alpha}_{k}^{m n} \cdot \boldsymbol{\sigma}_{k}}\right\rangle \\
\equiv & \sum_{p p^{\prime}} e^{i\left(p-p^{\prime}\right) \Phi} e^{i \Phi\left(j-j^{\prime}\right) / N}(-i)^{N p+j}(i)^{N p^{\prime}+j^{\prime}} J_{N p+j}\left(2 \Delta_{o} t\right) J_{N p^{\prime}+j^{\prime}}\left(2 \Delta_{o} t\right) \\
& \times\left\langle e^{-i\left(p-p^{\prime}\right) \sum_{k} \sum_{\langle m n\rangle=\langle 01\rangle}^{\langle N 0\rangle} \boldsymbol{\alpha}_{k}^{m n \cdot} \cdot \boldsymbol{\sigma}_{k}} e^{\left.-i \sum_{k} \sum_{\langle m n\rangle=\left\langle j^{\prime}, j^{\prime}+1\right\rangle}^{\langle j-1\rangle, j} \boldsymbol{\alpha}_{k}^{m n} \cdot \boldsymbol{\sigma}_{k}\right\rangle}\right. \tag{5.58}
\end{align*}
$$

However, as noted above, we are interested in the purely symmetric case where $\boldsymbol{\alpha}_{k}^{i j} \rightarrow \boldsymbol{\alpha}_{k}$ for every link. In this case the expression (5.58) reduces to a much simpler result:

$$
\begin{equation*}
\rho_{j j^{\prime}}(t)=\sum_{p p^{\prime}} e^{i\left(p-p^{\prime}\right) \Phi} e^{i \Phi\left(j-j^{\prime}\right) / N} i^{\left[N\left(p-p^{\prime}\right)+\left(j-j^{\prime}\right)\right]} J_{N p+j}\left(2 \Delta_{o} t\right) J_{N p^{\prime}+j^{\prime}}\left(2 \Delta_{o} t\right) F_{j-j^{\prime}}\left(p, p^{\prime}\right) \tag{5.59}
\end{equation*}
$$

in which the influence functional reduces for the symmetric ring is defined by

$$
\begin{equation*}
F_{j-j^{\prime}}\left(p, p^{\prime}\right)=\left\langle e^{-i N\left(p-p^{\prime}\right) \sum_{k} \boldsymbol{\alpha}_{k} \cdot \boldsymbol{\sigma}_{k}} e^{-i\left(j-j^{\prime}\right) \sum_{k} \boldsymbol{\alpha}_{k} \cdot \boldsymbol{\sigma}_{k}}\right\rangle \tag{5.60}
\end{equation*}
$$

Now consider the current $I_{j, j+1}(t)$, which is given in general by:

$$
\begin{equation*}
I_{j, j+1}=-i\left\langle\tilde{\Delta}_{j, j+1} \rho_{j+1, j}-\tilde{\Delta}_{j+1, j} \rho_{j, j+1}\right\rangle \tag{5.61}
\end{equation*}
$$

where we define

$$
\begin{equation*}
\tilde{\Delta}_{j, j+1}=\Delta_{o} e^{i \Phi / N} e^{i \sum_{k} \boldsymbol{\alpha}_{k}^{j, j+1} \cdot \boldsymbol{\sigma}_{k}} \tag{5.62}
\end{equation*}
$$

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

$$
\begin{align*}
& I_{j, j+1}=-2 \Delta_{o} \sum_{p p^{\prime}} J_{N p+j-l}\left(2 \Delta_{o} t\right) J_{N p^{\prime}+j+1-l^{\prime}}\left(2 \Delta_{o} t\right) \\
& \times \operatorname{Re}\left\langle\rho_{l, l^{\prime}} i^{N\left(p-p^{\prime}\right)} e^{i\left[\left(p-p^{\prime}\right)+\frac{1}{N}\right] \Phi} e^{-i\left(p-p^{\prime}\right) \sum_{k} \sum_{\langle m n\rangle=\langle 01\rangle}^{\langle N 0\rangle} \boldsymbol{\alpha}_{k}^{m n} \cdot \boldsymbol{\sigma}_{k}}\right.  \tag{5.63}\\
& \quad \cdot e^{\left.2 i \sum_{k} \sum_{\langle m n\rangle=\left\{j^{\prime}, j^{\prime}+1\right\rangle}^{\langle j-1, j} \boldsymbol{\alpha}_{k}^{j, j+1} \cdot \boldsymbol{\sigma}_{k}\right\rangle} \tag{5.64}
\end{align*}
$$

Again, we make the assumption of a completely ring-symmetric bath, so that $\boldsymbol{\alpha}_{k}^{i j} \rightarrow \boldsymbol{\alpha}_{k}$. Then we get

$$
\begin{align*}
I_{j+1, j}=2 \Delta_{o} \sum_{p p^{\prime}} \sum_{l, l^{\prime}} & J_{N p+j-l}\left(2 \Delta_{o} t\right) J_{N p^{\prime}+j+1-l^{\prime}}\left(2 \Delta_{o} t\right) F_{l, l^{\prime}}\left(p^{\prime}, p\right)  \tag{5.65}\\
& \times \operatorname{Re}\left[\rho_{l l^{\prime}} e^{\left.i \Phi\left[p^{\prime}-p+\left(l-l^{\prime}\right) / N\right)\right]}\right]
\end{align*}
$$

From this we can derive the single Bessel Function summation form as follows. Using the equation

$$
\begin{equation*}
\sum_{p} J_{N p+n-l}(x) J_{N p+n-l+\nu}(x)=\frac{1}{N} \sum_{m=0}^{N-1} J_{k}\left(2 x \sin \frac{k_{m}}{2}\right) e^{-i(n-l) k_{m}-i\left(k_{m}-\pi\right) \nu / 2} \tag{5.66}
\end{equation*}
$$

which is another form of Graf's identity[49], we set $\nu=N\left(p^{\prime}-p\right)+1+l-l^{\prime}$, $x=2 \Delta_{o} t$; then

$$
\begin{align*}
I_{j+1, j}=\frac{2 \Delta_{o}}{N} \sum_{m=0}^{N-1} \sum_{p} \sum_{l, l^{\prime}} & J_{N p+1+l-l^{\prime}}\left(4 \Delta_{o} t \sin \frac{k_{m}}{2}\right) e^{-i k_{m}\left[\frac{N p+1}{2}+n-\left(l+l^{\prime}\right) / 2\right]} \\
& \times i^{N p+1+l-l^{\prime}} F_{l l^{\prime}}(p) \operatorname{Re}\left[\rho_{l, l^{\prime}} e^{\left.i \Phi\left[\left(p^{\prime}-p+l-l^{\prime}\right) / N\right)\right]}\right] \tag{5.67}
\end{align*}
$$

where we define $F_{l l^{\prime}}(p, 0) \equiv F_{l l^{\prime}}(p)$.

If we make the assumption that the particle starts at the origin, these results simplify considerably; one gets

$$
\begin{align*}
& I_{j+1, j}= 2 \Delta_{o} \sum_{p p^{\prime}} J_{N p+j}\left(2 \Delta_{o} t\right) J_{N p^{\prime}+j+1}\left(2 \Delta_{o} t\right) F_{j, j}\left(p^{\prime}, p\right) \cos \left[\left(\frac{\pi}{2} N+\Phi\right)\left(p^{\prime}-p\right)\right] \\
&=\frac{2 \Delta_{o}}{N} \sum_{m=0}^{N-1} \sum_{p} J_{N p+1}\left(4 \Delta_{o} t \sin \frac{k_{m}}{2}\right) e^{-i k_{m}\left(\frac{N p+1}{2}+j\right)} i^{N p+1}  \tag{5.68}\\
& \times F_{j, j}(p) \cos \left[\left(\frac{\pi}{2} N+\Phi\right) p\right] \tag{5.69}
\end{align*}
$$

for the double and single sums over winding numbers, respectively; In later expression we might use $F_{0}(p)$ instead of $F_{j, j}(p, 0)$ for practical analysis. In the later sections we evaluate this influence function in different limit. Before we continue, it is useful to note what are the important parameters in this problem. In symmetric case, assuming that $\left|\boldsymbol{\alpha}_{k}\right| \ll 1$ for all $k$, as discussed above, then it has been usual to define a parameter[44, 47]

$$
\begin{equation*}
\lambda=\frac{1}{2} \sum_{k}\left|\boldsymbol{\alpha}_{k}\right|^{2} \tag{5.70}
\end{equation*}
$$

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[44]).

### 5.5.1 Phase Averaging

In this and next subsections, we assume that there is no external field acting on bath spin, i.e. $\mathbf{h}_{k}=0, \forall k$. This means the bath does not have intrinsic dynamics. In light harvesting molecules, such modes are caused by localized phonons, distortions of bacteria tissues as well as surrounding ions in the biological solvent. They can freely change from one state to another. We consider the problem in tow conditions: general strong decoherence limit and particular intermediate decoherence region.
(i)If the number N of bath spin is large, though $\alpha_{k}$ is small, we still can have a large $\lambda \gg 1$. This is the limit of strong decoherence limit. The additional phase is accumulated by each successive hoppings of the spin environment. In fact, the universal behavior comes from complete phase phase randomisation, so that all possible phases contribute equally to the answer.[47, 48] In this case, the 'influence function' $F_{j-j^{\prime}}\left(p . p^{\prime}\right)=\delta_{j, j^{\prime}} \delta_{p, p^{\prime}}$, ie., only on-site terms are allowed. This is what has been assumed in Förster
and Redfield theories. The resulting density matrix is always diagonal, with matrix elements

$$
\begin{equation*}
\rho_{j, j^{\prime}}(t)=\delta_{j, j^{\prime}} \sum_{p=-\infty}^{+\infty} J_{N p+j}^{2}\left(2 \Delta_{o} t\right) \tag{5.71}
\end{equation*}
$$

We notice that in this strong decoherence limit, since the flux $\Phi$ enters the final result via the term $e^{i\left(p-p^{\prime}\right) \Phi}$ and only $p=p^{\prime}$ terms are allowed, there is no dependence on the flux at all. To see how these results works out in practise, consider again the 3 -stie ring; we evaluate the 'return' probability $P_{00}(t)$. In strong coherence limit the behavior simplifies to

$$
\begin{equation*}
P_{00}(t)=\delta_{j, j^{\prime}} \sum_{p=-\infty}^{+\infty} J_{3 p}^{2}\left(2 \Delta_{o} t\right)=\frac{1}{3}\left(1+2 J_{0}\left(2 \Delta_{o} \sqrt{3} t\right)\right) \tag{5.72}
\end{equation*}
$$

It is shown in Fig. 5.5 And for the current, we could do the same thing. In


Figure 5.5: Plot of $P_{j 1}(t)$ 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. 5.3). The results do not depend on $\Phi$.
strong decoherence limit, one has

$$
\begin{equation*}
I(0,1)=\frac{2 \sqrt{3}}{3} \Delta_{o}\left(\rho_{0,0}-\rho_{1,1}\right) J_{1}\left(2 \Delta_{o} \sqrt{3} t\right) . \tag{5.73}
\end{equation*}
$$

Again we see that the result is completely independent of the flux.
(ii) If the decoherence is not large, i.e. for the intermediate decoherence limit, the form of $F_{j-j^{\prime}}\left(p, p^{\prime}\right)$ is not just a delta function. In room temperature(or 77 K which is still high enough) we can assume that such
modes is equally distributed. Therefore the initial distribution is an equally populated states, we then get

$$
\begin{align*}
F_{j, j^{\prime}}\left(p, p^{\prime}\right) & =\prod_{k} \cos \left(\left(N\left[p-p^{\prime}\right]+j-j^{\prime}\right)\left|\boldsymbol{\alpha}_{k}\right|\right)  \tag{5.74}\\
& \approx e^{-\lambda\left(N\left[p-p^{\prime}\right]+j-j^{\prime}\right)^{2}}
\end{align*}
$$

$\lambda$ is the same definition in (5.70). The last line is valid when any single $\left|\alpha_{k}\right| \ll 1$. The limit $\lambda \rightarrow \infty$ is the "strong decoherence" limit for this distribution. Other initial distributions for spin bath are easily evaluated from (5.60).

From expressions like (5.74) one can then write down expectation values of physical quantities as a function of time by using (5.59) and (5.68). This derivation is pretty the same so we just list results. The possibilities to find a particle at site j is

$$
\begin{equation*}
P_{j 0}(t)=\sum_{p p^{\prime}} J_{N p+j}\left(2 \Delta_{o} t\right) J_{N p^{\prime}+j}\left(2 \Delta_{o} t\right) e^{-i N\left(p^{\prime}-p\right)\left(\Phi / N+\frac{\pi}{2}\right)} F_{0}\left(p, p^{\prime}\right) \tag{5.75}
\end{equation*}
$$

The current $n+1 \rightarrow n$ is
$I_{n, n+1}=-2 \Delta_{o} \sum_{p p^{\prime}} J_{N p+n}\left(2 \Delta_{o} t\right) J_{N p^{\prime}+n+1}\left(2 \Delta_{o} t\right) F_{0}\left(p^{\prime}, p\right) \cos \left[\left(\frac{\pi}{2} N+\Phi\right)\left(p^{\prime}-p\right)\right]$

One can compare it with the strong decoherence limit result. In this intermediate decoherence regime, where the effects of the flux $\Phi$ are still visible, the effect of $\lambda$ here acts as an perturbation to the flux. To see this we expand $F_{0}\left(p, p^{\prime}\right)$ around $\alpha_{k}=0$ point:

$$
\begin{equation*}
F_{0}\left(p, p^{\prime}\right)=1-N^{2}\left(p-p^{\prime}\right)^{2} \lambda+O\left(\lambda^{2}\right) \tag{5.77}
\end{equation*}
$$

Then $P_{j 0}$ can be written as

$$
\begin{align*}
P_{j 0}(t, \Phi) & \approx P_{j 0}^{0}(t, \Phi)-\sum_{p p^{\prime}} J_{N p+j}\left(2 \Delta_{o} t\right) J_{N p^{\prime}+j}\left(2 \Delta_{o} t\right) e^{-i N\left(p^{\prime}-p\right)\left(\Phi / N+\frac{\pi}{2}\right)}\left(p-p^{\prime}\right)^{2} N^{2} \lambda \\
& =P_{j 0}^{0}(t, \Phi)+N^{2} \lambda \frac{\partial^{2} P_{j 0}^{0}(t, \Phi)}{\partial \Phi^{2}}+O\left(\lambda^{2}\right) \tag{5.78}
\end{align*}
$$

Here $P_{j 0}^{0}(t, \Phi)$ is the probability when there is no bath present. Again, we consider the 3 -site ring, we could get the probabilities and currents as

$$
\begin{equation*}
P_{1}(t)=\frac{1}{3}\left(1+2\left[J_{0}\left(2 \Delta_{o} \sqrt{3} t\right)+4 \sum_{p=1}^{\infty} J_{6 p} \cos (2 p \Phi) F_{0}(6 p)\right]\right) . \tag{5.79}
\end{equation*}
$$

$$
\begin{align*}
I(0 \rightarrow 1)= & \frac{2}{3} \Delta_{o} \sum_{p=-\infty}^{\infty} J_{3 p+1}\left(2 \Delta_{o} \sqrt{3} t\right) K(p, \phi) \\
& K(p, \phi)=\sin (3 p \phi) \quad \text { if } p=\text { odd } \\
& K(p, \phi)=\sqrt{3} \cos (3 p \phi) \quad \text { if } p=\text { even } . \tag{5.80}
\end{align*}
$$

These results are shown in Fig. 5.7 and Fig. 5.6

## Wave-packet Interference

Using the formalism of previous chapters, we could try to reproduce the quantum beating phenomenon in our model ring. In experiments, people put 2 pairs of coherent signals into the system: one to create the coherent interference; another one to detect it. In theory, since we can directly calculate the transfer amplitude, only pair of coherent signals is required. We use signals in form of wave-packet instead of a single site state because single site states collapse pretty quickly in time due to uncertainty principle. We can that if a proper center speed of a wave-packet is chosen, it will survive a long time with little dispersion.

We 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

$$
\begin{equation*}
\Psi(t)=\frac{1}{\sqrt{2}}\left(\psi_{1}(t)+\psi_{2}(t)\right) \tag{5.81}
\end{equation*}
$$

The free-particle wave function in real space is then

$$
\begin{align*}
\left|\Psi_{j}(t)\right\rangle= & \sum_{n=0}^{N-1} e^{-\left(k_{n}-\pi / 2\right)^{2}}\left(e^{i\left(j-j_{0}\right) k_{n}} e^{-2 i \Delta_{o} t \cos \left(k_{n}+\Phi / N\right)}\right.  \tag{5.82}\\
& \left.+e^{-i j k_{n}} e^{-2 i \Delta_{o} t \cos \left(k_{n}-\Phi / N\right)}\right)|j\rangle
\end{align*}
$$

so that the probability to find a particle at time $t$ on site $j$ is $P_{j}(t)=\left|\Psi_{j}(t)\right|^{2}$.

The two wave-packets are assumed to have Gaussian form:

$$
\begin{align*}
\left|\psi_{1}(t)\right\rangle & =\sum_{n=0}^{N-1} e^{-\left(k_{n}-\pi / 2\right)^{2} D / 2} \\
& \times e^{-i x_{0} k_{n}-i 2 \Delta_{0} t \cos \left(k_{n}-\Phi / N\right)}\left|k_{n}\right\rangle  \tag{5.83}\\
\left|\psi_{2}(t)\right\rangle & =\sum_{n=0}^{N-1} e^{-\left(k_{n}-\pi / 2\right)^{2} D / 2}\left|2 \pi-k_{n}\right\rangle \tag{5.84}
\end{align*}
$$

At $t=0$, one of the packets is centered at the origin, and the other at site $j_{o}$, and they both have width $D$. Note that the velocity of each wavepacket is conserved, and at times such that $\Delta_{o} t=2 n$, they cross each other. From (5.83) 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 wavepackets disperse in real space - this dispersion rate is at a minimum when $\phi=\frac{\pi}{2}$. The interference pattern is shown in Fig. 5.8

In this graph we can see that there are very sharp interference peaks when they meet each other. Since there is completely no decoherence in this system, this is what we expected. If we put flux in this system, it will not change this pattern much. To see this point, let us look back to (5.82) when $N \rightarrow \infty$. In this limit, we can always find a $k_{m}$ which satisfies $k_{n}-\phi=k_{m}$ hence we can replace $k_{n} \mathrm{~s}$ with $k_{m} \mathrm{~s}$ and do not need to change boundaries of the sum due to periodicity. The resulting wave function is

$$
\begin{equation*}
\left|\psi_{1}\right\rangle=e^{-i \phi x_{0}} \sum_{n=0}^{N-1} e^{-\left(k_{m}+\phi-\pi / 2\right)^{2} D / 2} e^{-i x_{0} k_{m}-i 2 \Delta_{0} t \cos \left(k_{m}\right)}\left|k_{m}\right\rangle \tag{5.85}
\end{equation*}
$$

It is a wave-packet with central speed $\pi / 2-\phi$. This means that the effect of flux is to shift the central speed of a wave-packet. In finite $N$ cases, Fig. 5.9 still shows that the flux shifts the central speed. In this figure the wave-packets have initial central momentum 0 . They are totally driven by external flux.

Let us now consider the effect of phase decoherence from the spin bath. Using the results for $P_{j j^{\prime}}(t)$ from the last section, with an initial reduced density matrix given by

$$
\begin{equation*}
\rho\left(j, j^{\prime} ; t=0\right)=\left|\Psi_{j}(t=0)\right\rangle\left\langle\Psi_{j^{\prime}}(t=0)\right| \tag{5.86}
\end{equation*}
$$

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

$$
\begin{align*}
P_{j}(t)= & \sum_{n, n^{\prime}=0}^{N-1} \sum_{m=-\infty}^{+\infty} e^{-\left(\left(k_{n}-\pi / 2\right)^{2}+\left(k_{n^{\prime}}-\pi / 2\right)^{2}\right) D / 2} F_{0}(m) \\
\times & \left\{e^{i\left(j-j_{0}\right)\left(k_{n}-k_{n^{\prime}}\right)} J_{m}\left(4 \Delta_{o} t \sin \left(\left(k_{n}-k_{n^{\prime}}\right) / 2\right)\right) e^{i m\left(\left(k_{n}+k_{n^{\prime}}\right) / 2+\Phi / N\right)}+\right. \\
& +e^{-i\left(k_{n}-k_{n^{\prime}}\right) j} J_{m}\left(4 \Delta_{o} t \sin \left(\left(k_{n}-k_{n^{\prime}}\right) / 2\right)\right) e^{i m\left(\left(k_{n}+k_{n^{\prime}}\right) / 2-\Phi / N\right)}+ \\
& \left.+\left[e^{i\left(\left(j-j_{0}\right) k_{n}+j k_{n^{\prime}}\right)} J_{m}\left(4 \Delta_{o} t \sin \left(\left(k_{n}+k_{n^{\prime}}\right) / 2\right)\right) e^{i m\left(\left(k_{n}-k_{n^{\prime}}\right)-\Phi / N\right)}+\text { h.c. }\right]\right\} \tag{5.87}
\end{align*}
$$

Here we again use (4.22).
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 (5.87) are too unwieldy for simple analysis. However in the strong decoherence limit (5.87) simplifies to:

$$
\begin{align*}
P_{j}(t)=\sum_{n, n^{\prime}=0}^{N-1} & e^{-\left(\left(k_{n}-\pi / 2\right)^{2}+\left(k_{n^{\prime}}-\pi / 2\right)^{2}\right) D / 2}\left\{e^{i\left(j-j_{0}\right)\left(k_{n}-k_{n^{\prime}}\right)} J_{0}\left(4 \Delta t \sin \left(\left(k_{n}-k_{n^{\prime}}\right) / 2\right)\right)\right. \\
& +e^{-i j\left(k_{n}-k_{n^{\prime}}\right)} J_{0}\left(4 \Delta t \sin \left(\left(k_{n}-k_{n^{\prime}}\right) / 2\right)\right) \\
& \left.+\left[e^{i\left(\left(j-j_{0}\right) k_{n}+j k_{n^{\prime}}\right)} J_{0}\left(4 \Delta t \sin \left(\left(k_{n}+k_{n^{\prime}}\right) / 2\right)\right)+h . c .\right]\right\} \tag{5.88}
\end{align*}
$$

and again we see that the flux has disappeared from this equation. This result is shown in Fig 5.10.

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).

We can try another decoherence methods which there is a coefficient controlled the decoherence rate. We put decoherence term (5.74) into (5.87) by using the similar method stated in previous sections. Now the influence functional has the form $F_{0}(m)=\prod_{k} \cos m \alpha_{k}$. If $\alpha_{i}$ is very small, then basically decoherence rate is determined by $\lambda=\sum_{i=1}^{N}\left(\alpha_{i}\right)^{2}$ as discussed above. It is shown in Figure 5.11. We can see that the wave-packet coherence is pretty fragile, it is completely suppressed when $\lambda>3 \times 10^{-3}$.

### 5.5.2 High Field Limit

Until now, we ignore the 'transverse field' term $\sum_{k} \mathbf{h}_{k} \cdot \sigma_{k}$ in the Hamiltonian (5.4). We are going to study this term in this section. In light harvesting complexes, it is the high excitation energy on surrounding molecules responsible for this high external field. The excitation energy of biological molecules is about $10^{0} \mathrm{eV}$, which is equivalently $10^{5} \mathrm{~K}$. This large field divides surrounding bath spins into certain polarization groups and makes the hoppings between different polarization groups forbidden. These effects greatly change the effect of our central system as many strong coupling models do. We are still studying in this limit and that is the reason I put his part at the end of this chapter.

The Hamiltonian we are considering now is becoming

$$
\begin{equation*}
H=\Delta e^{i \sum_{i j}\left(\phi_{i j}+\sum_{k} \alpha_{k}^{i j} \cdot \sigma_{k}\right)} c_{i}^{\dagger} c_{j}+\sum_{k} h_{k} \sigma_{k}^{z} \tag{5.89}
\end{equation*}
$$

The fields $\mathbf{h}_{k}$ act on each spin in bath may not always point in z-direction. This effective "magnetic field" has many origins. But we can rotate every $\sigma_{k}$ to let $\mathbf{h}_{k}$ acting along its "z-direction". Now the dynamics of spin baths are entangled with the central system. We have a roughly argument on this issue. When $\alpha_{k}$ is small then $e^{i \alpha_{k}^{i j} \cdot \sigma_{\mathbf{k}}} \approx 1+i \alpha_{k}^{i j} \cdot \sigma_{\mathbf{k}}$. The dynamic terms of the surrounding spin k in this system is

$$
\begin{equation*}
\left(\mathbf{h}_{k}+i \Delta \sum_{i j} \alpha_{k}^{i j} c_{i}^{\dagger} c_{j}\right) \cdot \sigma_{\mathbf{k}} \tag{5.90}
\end{equation*}
$$

The external field a bath spin feels is affected by the path chosen by the central particle. By each hopping in the ring, spins take precession along different axes. If $\alpha_{k}$ is large, the precession can be completely random. This kind of entangled precession is a unique source of decoherence in spin bath. To make things simple we assume all $\mathbf{h}_{k}$ for surrounding spins are equal and we have totally $K$ spins in the bath. The spin bath space is split into 2 K energy degenerate subspaces, which are distinguished by their polarization $M=\sum_{k} \sigma_{k}^{z}$. Each "polarization group" M is $C_{K}^{(K+M) / 2}$ fold degenerated.

We can solve this model in a particular limit when $h_{k} \gg|\alpha|$, which is so-called the "high field limit". The intrinsic dynamics of spin bath in this limit is strictly restrained. There is a selection rule which only allows transitions within same polarization subspaces. In other words, transitions in bath spins always conserve the quantity $M$. Considering the rotation symmetry of the ring, we assume that by rotating along z-direction most of
$\left\{\alpha_{k}^{i j}\right\}$ can point along x-axis. This simplified Hamiltonian reads

$$
\begin{equation*}
H=\Delta e^{i \sum_{i j}\left(\phi_{i j}+\sum_{k} \alpha_{k}^{i j} \sigma_{k}^{x}\right)} c_{i}^{\dagger} c_{j}+\sum_{k} h_{k} \sigma_{k}^{z} \tag{5.91}
\end{equation*}
$$

In order to enforce the restriction to a polarization group $M$, we use the projection operator

$$
\begin{equation*}
P_{M} \equiv \delta\left(\sum_{k} \sigma_{k}-M\right)=\int_{0}^{2 \pi} \frac{d \xi}{2 \pi} e^{i \xi\left(\sum_{k} \sigma_{k}^{z}-M\right)} \tag{5.92}
\end{equation*}
$$

Consider a path composed by $L$ steps $\left\{i_{0}, i_{1}, \ldots . i_{L}\right\}$, with $i_{0 \ldots \ldots L} \in\{1,2, \ldots ., N\}$ indicate the past site sequence. The contribution of this path in the probability amplitude is
$W_{i_{0} \ldots i_{L}}=e^{i m \phi} \frac{(i \Delta t)^{L}}{L!}\left\langle\delta\left(\sum_{k} \sigma_{k}^{z}-M\right) e^{i \sum_{k} \alpha_{k}^{i_{L} i_{L-1}} \sigma_{k}^{x}} \ldots \ldots \delta\left(\sum_{k} \sigma_{k}^{z}-M\right) e^{i \sum_{k} \alpha_{k}^{i_{1} i_{0}} \sigma_{k}^{x}}\right\rangle$
m is the winding number. $\phi=\sum \phi_{i j}$ is the total flux. Then the total probability amplitude from site $i_{0}$ to $i_{L}$ is

$$
\begin{equation*}
G\left(i_{L}, i_{0} ; t\right)=\sum_{\text {all possible path }} W_{i_{0} \ldots i_{L}} \tag{5.94}
\end{equation*}
$$

And the density matrix is given by

$$
\begin{equation*}
\rho i j(t)=\sum_{k, l} G(i, k ; t) G^{\dagger}(j, l ; t) \rho_{l k}(t=0) . \tag{5.95}
\end{equation*}
$$

To solve this quantity, we define the operator

$$
\begin{equation*}
T_{L} \equiv \delta\left(\sum_{k} \sigma_{k}^{z}-M\right) e^{i \sum_{k} \alpha_{k}^{i_{L} i_{L-1}} \sigma_{k}^{x} \ldots \ldots . \delta\left(\sum_{k} \sigma_{k}^{z}-M\right) e^{i \sum_{k} \alpha_{k}^{i_{1} i_{0}} \sigma_{k}^{x}} . . . . . .} \tag{5.96}
\end{equation*}
$$

Substitute (5.96) into (5.92). We do Taylor expansion to second order of $\alpha_{k}$ :

$$
\begin{align*}
T_{L}|\uparrow\rangle= & e^{i\left(\sum_{n=1}^{L} \xi_{n}-M \sum_{n=1}^{L} \xi_{n}\right)}\left\{|\uparrow\rangle+i \sum_{n=1}^{L} \alpha_{k}^{i_{n}} e^{-2 i \sum_{m=n}^{L} \xi_{m}}|\downarrow\rangle\right. \\
& \left.-\left(\sum_{n=1}^{L}\left(\alpha_{k}^{i_{n}}\right)^{2}+\sum_{m<n} \alpha_{k}^{i_{n}} \alpha_{k}^{i_{m}}\right) e^{-2 i \sum_{j=m}^{n-1} \xi_{j}}|\uparrow\rangle\right\} \\
T_{L}|\downarrow\rangle= & e^{-i\left(\sum_{n=1}^{L} \xi_{n}-M \sum_{n=1}^{L} \xi_{n}\right)}\left\{|\downarrow\rangle+i \sum_{n=1}^{L} \alpha_{k}^{i_{n}} e^{2 i \sum_{m=n}^{L} \xi_{m}}|\uparrow\rangle\right.  \tag{5.97}\\
& \left.-\left(\sum_{n=1}^{L}\left(\alpha_{k}^{i_{n}}\right)^{2}+\sum_{m<n} \alpha_{k}^{i_{n}} \alpha_{k}^{i_{m}}\right) e^{2 i \sum_{j=m}^{n-1} \xi_{j}}|\downarrow\rangle\right\}
\end{align*}
$$

Here we still assume the equally distributed initial state. Then the total contribution of all configurations with $\frac{K+M}{2}$ spin-ups and $\frac{K-M}{2}$ spin-downs, which compose the $\sum_{k} \sigma_{k}^{z}=M$ subspace, is

$$
\begin{gather*}
\prod_{k} A_{k}^{ \pm}\left(L, L^{\prime}\right) \equiv\langle\uparrow(\downarrow)| T_{L^{\prime}}^{\dagger} T_{L}|\uparrow(\downarrow)\rangle  \tag{5.98}\\
A_{k}^{ \pm}\left(L, L^{\prime}\right)=1-\sum_{n=1}^{L} \sum_{n=1}^{L}\left(\alpha_{k}^{i_{n}}\right)^{2}-\sum_{n=1}^{L^{\prime}}\left(\alpha_{k}^{i_{n}^{\prime}}\right)^{2}-\sum_{m<n}^{L} \alpha_{k}^{i_{n}} \alpha_{k}^{i_{m}} e^{ \pm 2 i \sum_{j=m}^{n-1} \xi_{j}} \\
-\sum_{m<n}^{L^{\prime}} \alpha_{k}^{i_{n}^{\prime}} \alpha_{k}^{i_{m}^{\prime}} e^{\mp 2 i \sum_{j=m}^{n-1} \xi_{j}^{\prime}}-\sum_{n=1}^{L} \sum_{n^{\prime}=1}^{L^{\prime}} \alpha_{k}^{i_{n}} \alpha_{k}^{i_{n^{\prime}}^{\prime}} e^{ \pm 2 i\left(\sum_{m=n}^{L} \xi_{m}-\sum_{m^{\prime}=n^{\prime}}^{L^{\prime}} \xi_{m^{\prime}}\right)} \tag{5.99}
\end{gather*}
$$

Here the plus sign + is for spin-up $\uparrow$; the minus sign - is for spin-down $\downarrow$. This production is for a particular arrangement of spins. The next step is to average this value over all possible spin configurations. Notice that small $M$ configurations has a way larger phase space, i.e. more possible permutations. Most of them comes out from $\frac{M}{K} \approx 0$ region where we can almost find a complex conjugate of every $A_{k}$. Therefore,

$$
\begin{align*}
\bar{A}_{k}\left(L, L^{\prime}\right)=\exp \{ & -\sum_{n=1}^{L} \sum_{k}\left[\left(\alpha_{k}^{i_{n}}\right)^{2}+\sum_{m<n}^{L} \alpha_{k}^{i_{n}} \alpha_{k}^{i_{m}} \cos \left(2 \sum_{j=m}^{n-1} \xi_{j}\right)\right] \\
& -\sum_{n=1}^{L^{\prime}} \sum_{k}\left[\left(\alpha_{k}^{i_{n}^{\prime}}\right)^{2}+\sum_{m<n}^{L^{\prime}} \alpha_{k}^{i_{n}^{\prime}} \alpha_{k}^{i_{m}^{\prime}} \cos \left(2 \sum_{j=m}^{n-1} \xi_{j}^{\prime}\right)\right]  \tag{5.100}\\
& \left.-\sum_{n=1}^{L} \sum_{n^{\prime}=1}^{L^{\prime}} \alpha_{k}^{i_{n}} \alpha_{k}^{i_{n^{\prime}}^{\prime}} \cos \left[ \pm 2 i\left(\sum_{m=n}^{L} \xi_{m}-\sum_{m^{\prime}=n^{\prime}}^{L^{\prime}} \xi_{m^{\prime}}\right)\right]\right\}
\end{align*}
$$

To deal with this equation, we make variables:

$$
\begin{align*}
\chi_{n} & =2 \sum_{p=n}^{L} \xi_{p} \\
\chi_{n}^{\prime} & =2 \sum_{p=n}^{L^{\prime}} \xi_{p}^{\prime}  \tag{5.101}\\
\vec{s}_{k}^{n} & =\alpha_{k}^{i_{n}}\left(\cos \chi_{n}, \sin \chi_{n}\right) \\
{\overrightarrow{s^{\prime}}}_{k}^{n} & =\alpha_{k}^{i_{n}^{\prime}}\left(\cos \chi_{n}^{\prime}, \sin \chi_{n}^{\prime}\right)
\end{align*}
$$

One thing we should notice here is that this transformation is only valid when $\alpha_{k}^{i_{n}} \neq 0$. If $\alpha_{k}=0$ for some k , then $A_{k}$ is simply equals to 1 . All following calculations are based on $\alpha_{k}^{i_{n}} \neq 0, \forall k, i_{n}$. Define $\vec{S}=\sum_{n, k} \vec{s}_{k}^{n}+\sum_{n, k} \overrightarrow{s^{\prime}}{ }_{k}^{n}$, the total average contribution of such paths is

$$
\begin{equation*}
\bar{A}_{k}\left(L, L^{\prime}\right)=e^{-\frac{1}{2}\left(\sum_{n, k}\left|\vec{s}_{k}^{n}\right|^{2}-\sum_{n, k}\left|{\overrightarrow{s^{\prime}}}_{k}^{n}\right|^{2}\right)-\frac{1}{2}|\vec{S}|^{2}} \delta\left(\vec{S}-\sum_{n, k} \vec{s}_{k}^{n}-\sum_{n, k}{\overrightarrow{s^{\prime}}}_{k}^{n}\right) \tag{5.102}
\end{equation*}
$$

Here we include the constraint

$$
\begin{equation*}
\delta\left(\vec{S}-\sum_{n, k} \vec{s}_{k}^{n}-\sum_{n, k}{\overrightarrow{s^{\prime}}}_{k}^{n}\right)=\int d \vec{z} e^{i \vec{z} \cdot\left(\vec{S}-\sum_{n, k} \vec{s}_{k}^{n}-\sum_{n, k}{\overrightarrow{s_{k}^{\prime}}}_{k}^{n}\right)} \tag{5.103}
\end{equation*}
$$

Remember that from (5.92) we introduce an integral over $\xi$, which is now transformed into $\chi$. By putting them together, we have the expression for the density matrix,

$$
\begin{align*}
& \rho\left(i_{L}, i_{L^{\prime}}^{\prime}, t\right)= \sum_{L, L^{\prime}} \sum_{i_{0}, i_{0}^{\prime}} \sum_{m, m^{\prime}} \frac{(\Delta t)^{L+L^{\prime}} i^{L-L^{\prime}}}{\left(\frac{L+m N}{2}\right)!\left(\frac{L-m N}{2}\right)!\left(\frac{L^{\prime}+m^{\prime} N}{2}\right)!\left(\frac{L^{\prime}-m^{\prime} N}{2}\right)!} e^{i\left(m-m^{\prime}\right) \phi} \\
& \cdot \prod_{k} B_{k}\left(L, L^{\prime}\right) \rho\left(i_{0}, i_{0}^{\prime}\right)  \tag{5.104}\\
& B_{k}\left(L, L^{\prime}\right)= \int_{0}^{\infty} z d z \prod_{n}\left(\int_{0}^{2 \pi} d \frac{\chi_{n}}{2 \pi}\right) \prod_{n^{\prime}}\left(\int_{0}^{2 \pi} d \frac{\chi_{n}^{\prime}}{2 \pi}\right) e^{i z\left(\vec{S}-\sum_{n, k} \overrightarrow{s_{k}}{ }_{k}^{n}-\sum_{n, k} \overrightarrow{s^{\prime} n_{k}^{n}}\right)} \\
& \times e^{-\frac{1}{2}\left(\sum_{n, k}\left|\vec{s}_{k}^{n}\right|^{2}-\sum_{n, k}\left|\overrightarrow{s^{\prime}}{ }_{k}^{n}\right|^{2}\right)-\frac{1}{2}|\vec{S}|^{2}} \\
&= \int_{0}^{\infty} d z \quad z \prod_{n=1}^{L} J_{0}\left(\alpha_{k}^{i_{n}} z\right) \prod_{n^{\prime}=1}^{L^{\prime}} J_{0}\left(\alpha_{k}^{i_{n}^{\prime}} z\right) e^{\left.-\frac{z^{2}}{2}-\frac{1}{2}\left(\sum_{n}\left(\alpha_{k}^{i_{n}}\right)^{2}+\sum_{n^{\prime}}\left(\alpha_{k}^{i_{n}^{\prime}}\right)^{\prime}\right)^{2}\right)} \tag{5.105}
\end{align*}
$$

$m$ and $m^{\prime}$ as winding numbers. Here we use the integral presentation of Bessel functions

$$
\begin{equation*}
J_{n}(x)=\frac{1}{2 \pi} \int_{-\pi}^{\pi} e^{-i(n \tau-x \sin \tau)} d \tau \tag{5.106}
\end{equation*}
$$

If $\alpha_{k}^{i_{n} i_{n+1}}=\alpha_{k}$ for every site, which is the perfect symmetric case, then it becomes

$$
\begin{equation*}
B_{k}\left(L, L^{\prime}\right)=\int_{0}^{\infty} d z \quad\left(J_{0}(z) e^{-\frac{1}{2} \alpha_{k}^{2}}\right)^{L+L^{\prime}} e^{-\frac{1}{2} z^{2}} z \tag{5.107}
\end{equation*}
$$

From (5.104), we find the term $J_{0}(z) e^{-\frac{1}{2} \alpha_{k}^{2}}$ can be absorbed into $\Delta_{o} t . e^{-\frac{1}{2} z^{2}}$ is independent of path length and winding number. Therefore, if the bare system density matrix is $\rho_{i j}^{0}\left(\Delta_{o} t\right)$ (without bath), then we have the density matrix $\rho_{i j}(t)$ in the high field limit is

$$
\begin{equation*}
\rho_{i j}(t)=\prod_{k}\left(\int_{0}^{\infty} d z_{k} \quad e^{-\frac{z_{k}^{2}}{2}} z_{k}\right) \rho_{i j}^{0}\left(\Delta_{o} t \prod_{k} J_{0}\left(z_{k}\right) e^{-\lambda}\right) \tag{5.108}
\end{equation*}
$$

The definition of $\lambda$ is the same as (5.70). This is our main result for high field limit. Due to our discussion of (5.101), this equation is puzzling at first glance: if we substitute $\lambda=0$, which is the no coupling case, into (5.108), we cannot go back to the bare ring expression which means that even very small $\lambda$ can make a fundamental change to the result. This is because the selection rule for bath transitions gives a strong restriction to hoppings in the central system. We also neglect the fact that the transition between different polarization groups. To include this effect we should use a more decent path integral method, which remains unavailable. At last we can see a example of our result. Again for a bare 3-site ring with flux $\phi$ threading it, we know that the probability $P_{0}^{o}(t)$ to stay at the initial site after time t is

$$
\begin{equation*}
P_{0}^{o}(t)=\frac{1}{3}\left[1+2 J_{0}(2 \sqrt{3} \Delta t)+4 \sum_{p=1}^{\infty} J_{6 p}(2 \sqrt{3} \Delta t) \cos (6 p \phi)\right] \tag{5.109}
\end{equation*}
$$

Then in this high field limit, we can see that

$$
\begin{align*}
P_{0}(t)=\frac{1}{3} \prod_{k} & \left(\int_{0}^{\infty} d z_{k} \quad e^{-\frac{z_{k}^{2}}{2}} z_{k}\right)\left[1+2 J_{0}\left(2 \sqrt{3} \Delta t e^{-\lambda} J_{0}\left(z_{k}\right)\right)\right. \\
& \left.+4 \sum_{p=1}^{\infty} J_{6 p}\left(2 \sqrt{3} \Delta t e^{-\lambda} J_{0}\left(z_{k}\right)\right) \cos (6 p \phi)\right] \tag{5.110}
\end{align*}
$$



Figure 5.6: The current $I_{01}^{o}(t)$ from site 0 to site 1 , for $N=3$ and for $\Phi=0$ (top) and $\Phi=\pi / 4$ (bottom) in the intermediate decoherence region. Different color indicate different $\lambda$. Blue: $\lambda=0$; Red: $\lambda=0.01$; Cyan: $\lambda=0.05$; Black: $\lambda=0.20$


Figure 5.7: The probability $P_{00}(t)$ for the particle to return to the origin from site 0 to site 1 , for $N=3$, in intermediate decoherence region. The flux threading is $0.4 \pi$. Different color indicate different $\lambda$. Yellow: $\lambda=0$; Green: $\lambda=0.01$; Cyan: $\lambda=0.05$; Blue: $\lambda=0.20$; Black: $\lambda=0.50$


Figure 5.8: Two wave packets interference without bath. The size of the ring is 100 . The three axis are site number ( n ), time $(t)$ and probability at this site (P). Two wave packets start at 0th site and 50th site and then move towards each other with central speed $\frac{\pi}{2}$


Figure 5.9: The evolution of wave packets with different external flux. The size of the ring is 100 . The wave packet starts rest at the 50 th site. In the first graph, $\phi=0$. In the second graph, $\phi=\frac{\pi}{5}$. In the third graph, $\phi=\frac{\pi}{2}$


Figure 5.10: Interference between 2 wave-packets in the strong decoherence limit. The packets start at site 0 and site $j_{o}=50$ respectively at $t=0$, and their relative velocity is $\frac{\pi}{2}$, in phase units.


Figure 5.11: Two wave-packets interference in a topological bath. They start at 0 th site and 50 th site respectively, and then move towards each other with central speed $\frac{\pi}{2}$. In the first graph, the strength of the coupling $\lambda=0$. In the second graph, $\lambda=10^{-3}$. In the third graph, $\lambda=1.5 \times 10^{-3}$. In the fourth graph, $\lambda=2 \times 10^{-3}$. In the fifth graph, $C=2.5 \times 10^{-3}$. In the sixth graph, $\lambda=3 \times 10^{-3}$.

## Chapter 6

## Conclusions

We studied the phase decoherence in a particular light harvesting complex which bears a symmetric ring-like multichromophore structure. We modeled a light harvesting complex as a particle hopping on an N -site ring, coupled to a spin bath. This is a simplified model since we are only interested in the decoherence phenomenon in recent experiments. Analytic results were found for the dynamics of the influence functional and of the reduced density matrix of the central exciton. The dynamic of particles in the spin bath acted differently from ones in oscillator baths, and we found that coherent beating phenomenon is quite sensitive to coupling constants.

We reviewed the structures of light harvesting complexes determined by recent x-ray diffraction measurement. Some of them bear C8 or C16 global spatial symmetries. We reviewed resonant energy transfer both between chlorophylls within the same complex and between different complexes. We then, reviewed the recent experimental evidences which showed the quantum beating between two coherent signals in the chlorophyll networks. We witnessed the beating surviving longer than most previous theoretical predictions. Photosynthesis has been studied for many years, but a full quantum mechanical description of the mechanism leading to this remarkable phenomenon is yet not available. We pointed out that this is also important to quantum information considerations due to the transfer's long coherent time and swiftness in the completion of calculations(i.e. finding a pathway towards the signal's destination, which is, the reaction centers).

We reviewed some significant theories in history about RET in light harvesting molecules, including Förster theory, Redfield theory and some recent development. The assumption previously was that there is no coherent hopping between different chlorophylls. This has been challenged by new experimental evidences. Recent development include environment-assisted quantum walks and multi-spin-boson model. People continue to try to explain photosynthetic energy transfer through coherent hopping descriptions. We reviewed some quantum information applications in this field such as entanglement between neighboring chlorophylls, as well as the Feynman cursor computer.

The essential problem here is to understand how surrounding proteins and biological solvent affect the energy transfer. We suggested modeling this system as a spin bath model instead of an oscillator bath model. We argued that the localized modes are also important in biological systems and that their high excitation energies make the truncation valid. In spin bath, the energy dissipation and phase decoherence can be separated and thus we were able to focus on the decoherence phenomenon. We employed the influence functional method to study dynamics of a particle moving on a ring coupled to a spin bath. To avoid complications, we made several assumptions on couplings and spin dynamics to keep our result analytical.

We first studied the bare ring without bath. We introduced some important properties to depict the system: the reduced density matrices and the bond current from one site to another. The flux in the system gives a topological feature to distinguish different elements in its 1st homotopy group. We then, added a pure phase coupling to explore its influence on central particle. The dynamics were described in Feynman-Vernon influence functional forms. In our problems, we obtained a series expansion over Bessel functions with winding numbers in their orders. The forward and backward paths are coupled and the influence functional kernel between these paths are determined by different coupling forms. We calculated them in both a strong decoherence limit and the intermediate decoherence regime. We then put two initially separated wave-packets into this model to reproduce the coherent beating phenomenon in light harvesting molecule experiments. We found that the sharp oscillating beat patterns are rapidly suppressed by small coupling parameters.

### 6.1 Open Questions

This work is still far from gaining a full understanding of photosynthetic energy transfers. Its features are not determined solely by spin bath model. To try to provide a realistic model which is able to explain its features, we should include couplings of the excitons to both delocalized and localized modes. To achieve the latter, we will need a great deal of information about the effective coupling parameters in the molecules, but we may be able to make predictions about the effects of temperature and size of rings on the exciton dynamics. Further works should also investigate other light harvesting molecules which do not have ring structures such as FMO complexes.

We also have many open questions concerning the spin bath model. Our assumptions of commutation and $h_{k}=0$ do not include the time correla-

### 6.1. Open Questions

tions of bath fluctuations. The calculations in high field limit conserve such correlations. We plan to further explore this limit. Also the correlations in time will affect the error correction scheme in fault-tolerant quantum computation. It has been proven that spatially correlated quantum noise will generate a minimal error which cannot be corrected[50]. Applying the spin bath model to discuss the decoherence effects on quantum computation, is a largely unexplored field.

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