Understanding and manipulating electronic quantum coherence in photosynthetic light-harvesting

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Abstract

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Ultrafast spectroscopy experiments show that photosynthetic systems can preserve quantum beats in the process of electronic energy transfer between pigments, even at room temperature. But what does this discovery imply for biology – and for quantum mechanics? This dissertation examines photosynthesis through the tools of quantum information science. We evaluate to what extent photosynthesis can be thought of as a type of quantum technology, and consider how we can apply experimental tools widely used for quantum technologies (state tomography and coherent control) to photosynthesis. Throughout, we use the Fenna-Matthews-Olson (FMO) complex of greens sulfur bacteria as a model photosynthetic pigment-protein complex.

In Part I, we evaluate two mechanisms for the possible biological relevance of quantum coherent motion. First, we consider the extent to which dynamics in light-harvesting systems exhibit the quantum speedups characteristic of quantum algorithms and quantum walks. Second, we demonstrate a ratchet effect in electronic energy transfer enabled by partially coherent dynamics. To do so, we build a new model of energy transfer between weakly coupled light-harvesting complexes to understand how electronic coherence arises under natural conditions.

In Part II we present proposals for experimental probes of light harvesting dynamics with ultrafast spectroscopy. We show how the signal from pump-probe spectroscopy can be formally inverted to determine the excited state electronic density matrix. Finally, we examine the feasibility of coherent control experiments on light-harvesting systems, and provide two realistic targets feasible with present-day technology.
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Chapters 2-5 in this dissertation are adaptations of the following published papers:


Sections 4.7.6 and 5.7.2 present proposals that were not part of these published works.
Chapter 1

Introduction to excitonic energy transfer and non-linear spectroscopy

1.1 Model Hamiltonian

To model light-harvesting in photosynthetic systems, we use the Heitler-London model Hamiltonian \[ 3 \] 93, written as a sum of terms including an electronic system (S), a vibrational reservoir (R) and light (L):

\[
H = H_S + H_{S-R} + H_R + H_{S-L}. 
\]  

(1.1)

We use a Frenkel exciton model for the system,

\[
H_S = \sum_n \mathcal{E}_n a_n^\dagger a_n + \sum_{n \neq m} J_{nm} a_n^\dagger a_m
\]  

(1.2)

where \( a_n \) is the annihilation operator for an electronic excitation on pigment \( n \), \( \mathcal{E}_n \) the excitation energy on pigment \( n \) and \( J_{nm} = J_{mn} \) the dipole-dipole coupling between pigments \( n \) and \( m \). We treat these excitations as hard-core bosons (that is, not allowing double excitations of a single pigment), and restrict our consideration to only one possible excitation per pigment molecule. The excitation energies \( \mathcal{E}_n \) are nominally identical for all pigments of the same type, but in practice are shifted significantly between different pigments because of differences in their local electrostatic environments.

For consideration of transport properties, it is sometimes convenient to restrict our consideration to exactly one excitation in the entire system. In such a case, we define the states \( |n\rangle = a_n^\dagger |g\rangle \), where \( g \) denotes the electronic ground state of the entire system, and use them to write the system Hamiltonian restricted to the single excitation manifold,

\[
H_S^{1\text{-excitation}} = \sum_n \mathcal{E}_n |n\rangle \langle n| + \sum_{n \neq m} J_{nm} |n\rangle \langle m|.
\]  

(1.3)
We refer to these individual pigment states \( |n\rangle \) as site states and the eigenstates of Eq. (1.3) as exciton states. The site basis refers to the basis of individual pigments in which these equations are written; the exciton basis refers to the basis constructed from the exciton states in which \( H_S \) is diagonal.

The reservoir (bath) is modeled as a collection of harmonic oscillators initially at thermal equilibrium,

\[
H_R = \sum_{\xi} \hbar \omega_{\xi} b_{\xi}^\dagger b_{\xi}
\]  

(1.4)

where \( b_{\xi} \) denotes a reservoir annihilation operator and \( \hbar \omega_{\xi} \) the energy of an excitation in reservoir mode \( \xi \). From a physical perspective, the reservoir represents a normal mode expansion of all external degrees of freedom beyond the electronic state of each pigment, including internal intra-pigment vibrations, as well as motion of the surrounding protein and solvent. The system-reservoir coupling is taken to be a sum of linear couplings between the transition energy of pigments and the displacement of a bath mode,

\[
H_{S-R} = \sum_{n,\xi} \hbar \omega_{\xi} g_{n\xi} a_n^\dagger a_n q_{\xi},
\]  

(1.5)

where \( g_{n\xi} \) denotes the unit-less strength of the coupling between electronic excitation \( n \) and bath mode \( \xi \), and \( q_{\xi} = b_{\xi} + b_{\xi}^\dagger \) is the unit-less displacement operator for mode \( \xi \). All information regarding the reservoir is contained in the spectral density function \( J_n(\omega) = \sum_{\xi} g_{n\xi}^2 \delta(\omega - \omega_{\xi}) \). Lastly, for far-field interactions between the system and applied fields, the system-light interaction is given by

\[
H_{S-L} = \mu \cdot E(t)
\]  

(1.6)

where \( E(t) \) is the semi-classical electric field of the incident light and \( \mu = \sum_n d_n (a_n + a_n^\dagger) \) is the transition dipole operator, where \( d_n \) is the transition dipole vector of pigment \( n \).

The equations above describe the standard effective theory used for modeling energy transfer in light harvesting systems [93]. In the later chapters of this dissertation, we choose particular parameter values as determined by model fitting in prior experimental and theoretical studies [2, 62, 94]. These values can, at least in principle, also be determined by ab-initio quantum chemical calculations [97, 142]. However, my focus is on the features of dynamics resulting from this model, not its experimental or microscopic derivation.

### 1.2 Energy transfer dynamics

Both transport and optical properties can be described in terms of operators defined in the electronic system. Hence, the main quantity of interest is usually the reduced density operator \( \sigma \) describing the electronic system. According to the usual terminology for density operators, we refer to the diagonal elements of density operators as populations and the
off-diagonal elements as coherences. The exact evolution of $\sigma$ is given by a partial trace over the reservoir states [12],

$$\sigma(t) = \text{Tr}_R[e^{-iHt/\hbar}\rho(0)e^{iHt/\hbar}],$$  

(1.7)

where $\rho(0)$ denotes the initial state, usually taken to be the equilibrium density matrix $e^{-\beta H}/\text{Tr}[e^{-\beta H}]$, where $\beta = 1/k_B T$ is the inverse temperature. However, because the full Hamiltonian describes a many body quantum system, it is typically not feasible to use Eq. (1.7) directly. When strictly the electronic Hamiltonian is considered, we see that the off-diagonal elements $\langle \alpha | \sigma | \beta \rangle$ in the energy eigenbasis oscillate like $e^{-i\omega_{\alpha\beta}t}$, where $\omega_{\alpha\beta} = (E_\alpha - E_\beta)/\hbar$. Such electronic quantum coherences, especially between one-excitation states, are a central focus of this work, because their presence indicates the possibility that quantum wave-like motion is relevant to transport in light-harvest harvesting systems.

The original approach to modeling excitonic energy transfer, known as Förster theory, is a perturbation theory expansion of all inter-pigment couplings $J_{nm}$ to yield energy transfer rates between pigment molecules of the form

$$k_{n \to m} = \frac{J_{nm}^2}{2\pi\hbar^2} \int_{-\infty}^{\infty} d\omega E_D(\omega)I_A(\omega),$$  

(1.8)

where $E_D(\omega)$ is the donor lineshape (for pigment $n$) and $I_A(\omega)$ is the acceptor lineshape (for pigment $m$) [78, 93]. The integral over the donor and acceptor lineshapes provides the density of states for the transition between the deexcitement of pigment $n$ and excitement of pigment $m$ according to Fermi’s golden rule. Although these lineshapes can be difficult to calculate from first principles, they are proportional to the donor emission and acceptor absorption spectra [93], respectively, quantities that can be easily measured in the lab. The resulting dynamics, which in most cases constitutes a qualitatively accurate model of energy transfer between pigments, are a classical random walk in continuous time with transition rates given by Eq. (1.8). However, since Förster theory ignores coherences, it is not suitable for calculations that require a full density matrix. Moreover, in cases where electronic quantum beats or excitons delocalized between multiple pigments have been observed, Förster theory is clearly outside of its realm of validity.

Under the approximation that the interactions between the system and the bath are Markovian (memory less), we can prescribe the most general possible dynamics of a reduced density matrix such that it remains a valid. The result is that all such dynamics can be written in the form of the Lindblad master equation [12],

$$\frac{d\sigma}{dt} = -\frac{i}{\hbar}[H_S, \sigma] + \sum_{k=1}^{N^2-1} \gamma_k \left(A_k \sigma A_k^\dagger - \frac{1}{2} A_k^\dagger A_k \sigma - \frac{1}{2} \sigma A_k^\dagger A_k \right),$$  

(1.9)

in terms of non-negative real valued constants $\gamma_k$ and a set of operators $A_k$. Although this Markovian approximation is not necessarily valid for energy transfer in light-harvesting
systems, models that take the form of Eq. (1.9) are highly useful because of their simple and computationally tractable form.

The simplest quantum model we use for energy transfer is the Haken-Strobl model [55], which takes the form of Eq. (1.9) with operators $A_k = a_k^\dagger a_k$ for each site $k$. In the literature of open quantum systems, this model is known as a pure dephasing model. The Haken-Strobl model can be derived under the assumption that each bath mode is actually a classical Gaussian random variable $q_\xi(t)$ with a delta-function time-correlation $\langle q_\xi(t) q_\xi(0) \rangle \propto \delta(t)$, and that each mode is only coupled to one pigment. It can also be derived from a fully quantum model of the reservoir in a high temperature limit [12, 118], in order to estimate the dephasing rates $\gamma_k$ for each site in terms of the spectral density $J_k(\omega)$. The main advantage of the Haken-Strobl model is its ability to provide a simple transition from quantum to classical motion. The interpretation of the model is simple as well: the non-unitary contribution to dynamics is simply an exponential decay of coherences between site states. In the long time limit, one can show that the resulting density matrix for any finite system is diagonal and that all site states $n$ and $m$ with $J_{nm} \neq 0$ have equal populations.

The Redfield model is a master equation model with a fully quantum microscopic derivation. It requires the assumptions that the system-reservoir coupling $H_{S,R}$ is weak and that the bath is Markovian. In such a case, the equilibrium density matrix can be factorized between the system and bath, and a standard treatment using 2nd-order perturbation theory [93, 104] arrives at the Bloch-Redfield master equation,

$$
\frac{d\sigma_{ab}}{dt} = \left( -\frac{i}{\hbar} [H_S, \sigma] \right)_{ab} + \sum_{cd} R_{ab,cd} \sigma_{cd}.
$$

We sometimes call this equation the “full” Redfield theory, in contrast to the “secular” Redfield theory discussed below. The Redfield tensor $R_{ab,cd}$, which is written in terms of the spectral density and terms in the system Hamiltonian, contains all dissipative dynamics. When written in the exciton basis, its terms are many be classified into three types:

1. $a = b, c = d$: Population transfer $(a \neq c)$ and decay $(a = c)$.

2. $a = c, b = d, a \neq b$: Coherence decay.

3. All others: Coherence to coherence, coherence to population and population to coherence transfer terms.

The Redfield master equation cannot necessarily be written in the form of a Lindblad master equation, since the third type of these terms can lead to dynamics that do not preserve the positivity of the system density matrix. An additional approximation, the secular approximation, neglects these terms, since unlike the population transfer/decay and coherence decay terms, they oscillate with a non-zero frequency $\omega_{ab} - \omega_{cd}$ when the system density matrix is written in the interaction picture with respect to $H_S$, and thus their contribution should average out to zero. Because only the population transfer and coherence decay terms
remain, secular Redfield theory can be interpreted intuitively in the exciton basis, as a classical random walk in continuous time with exponentially decaying coherences. A particularly convenient feature of secular Redfield theory is that, in contrast to the Haken-Strobl model, in the long time limit the state arrives at the correct equilibrium, \( \sigma_{eq} \propto e^{-\beta H_S} \).

Although Lindblad master equations are convenient, for most light-harvesting systems, models with a high temperature (classical) bath or weak system-bath coupling are not accurate. Indeed, natural light harvesting systems typically exhibit a convergence of energy scales, \(|E_n - E_m| \sim J_{nm} \sim |H_{S,R}| \sim k_B T \sim \hbar/\tau_R \) (\( \tau_R \) denotes the time-scale of reservoir motion). To meet the challenge of solving exact energy transfer dynamics, a variety of computationally expensive exact numerical methods have been developed [76, 122, 72, 146, 33]. In some later chapters, we use a technique known as the 2nd-order cumulant time-nonlocal (2CTNL) quantum master equation or the hierarchical equations of motion (HEOM) approach [76], which results in computationally tractable equations of motion for particular forms of the spectral density. This model is quantitatively accurate in the regimes of validity of both the Förster and Redfield approaches [76].

### 1.3 Non-linear optical spectroscopy

We can experimentally observe how energy moves through light harvesting systems with time-resolved spectroscopy, that is, measurements of how they absorb and emit light. Because energy transfer dynamics in natural light harvesting systems take place over femto- to picosecond timescales, ultrafast laser pulses are required for the necessary time resolution.

Experiments on natural light harvesting systems use weak laser fields, because strong fields, which can be defined as fields strong enough to excite more than a small fraction of the pigment molecules, quickly destroy most molecular light harvesting systems. Naturally then, the theoretical formalism for these experiments is a perturbation theory in terms of the system-field interaction \( H_{S-L} \). The experimental signal field \( E_S(t) \) is proportional to the \( n \)th order polarization, which is given by

\[
\mathbf{P}^{(n)}(t) = \text{Tr} \ \mathbf{\mu} \rho^{(n)}(t),
\]

where \( \rho^{(n)}(t) \) is the density matrix to \( n \)th order in \( H_{S-L} \). An additional important factor is that each applied fields \( E_i(t) \) has an associated wave-vectors \( \mathbf{k}_i \), so the final signal field must have a wave-vector of the form \( \mathbf{k}_S = \sum_i \pm \mathbf{k}_i \), in terms of the positive or negative contributions from each pulse. The particular choice of \( \mathbf{k}_S \), as determined by the experimental geometry, thus allows for selecting particular experimental signals with this phase-matching condition. The ability to neglect components of \( \rho^{(n)}(t) \) that oscillate in non-observed directions turns out to considerably simplify the interpretation of experimental signals.

There are a wide range of possible non-linear spectroscopic measurements [98], determined by the choice of signal orientation and polarization, in addition to the polarizations, orientations and time-profiles of all applied fields. In the last part of this dissertation, we focus on third-order spectroscopy, the lowest order spectroscopy at which energy transfer
dynamics are directly observable. As has been shown elsewhere [1], the phase-matched contribution to the third-order polarization can be written in the response function formalism as

\[ P^{(3)}_{k_s}(t) = \int_0^\infty dt_3 dt_2 dt_1 R^{(3)}_{k_s}(t_3, t_2, t_1) E^{u_3}(t - t_3) E^{u_2}(t - t_3 - t_2) E^{u_1}(t - t_3 - t_2 - t_1) \]  

(1.12)

assuming that the electric fields \( E^{u_i}(t) \) interact with the system in the numbered order (as guaranteed by a lack of temporal pulse overlap) and invoking the rotating wave approximation, which is generally valid for resonant excitation (the case considered in this dissertation). The rotating wave approximation is important for efficient calculations because it removes extremely fast oscillations due to applied fields, which are \( \sim 100 \) times faster than energy transfer dynamics. The quantity \( k_S = u_1 k_1 + u_2 k_2 + u_3 k_3 \) is the signal wave-vector, where \( (u_1, u_2, u_3) \in \{(-, +, +), (+, -, +), (+, +, -)\} \) correspond to the three experimental geometries with non-zero signal (rephasing, non-rephasing and double-quantum-coherence, respectively) and \( E^{\pm}_i(t) \) denotes the complex profile of the \( i \)th pulse (we use the convention \( E^- = (E^+)^* \)). The system dynamics are contained in the phase-matched components of the third order response function \( R^{(3)}_{k_s}(t_3, t_2, t_1) \), which is given by

\[ R^{(3)}_{k_s}(t_3, t_2, t_1) = \left( \frac{i}{\hbar} \right)^3 \text{Tr} \left[ \mu^{(-)} G(t_3) V^{u_3} G(t_2) V^{u_2} G(t_1) V^{u_1} \rho_0 \right], \]  

(1.13)

where we defined the annihilation portion of the dipole operator \( \mu^{(-)} = \sum_n d_n a_n \) and the creation portion \( \mu^{(+)} = (\mu^{(-)})^\dagger \), the Liouville space operator \( G(t) \) is the retarded material Green function for evolution for time \( t \) and \( V^{(\pm)} \cdot \equiv [\mu^{(\pm)}, \cdot] \).

Figure 1.1 illustrates the experimental geometries for a generic third-order spectroscopy setup (such the photon-echo) and for a pump-probe setup. Pump-probe is a special case of third-order spectroscopy that we focus on in later chapters, in which the first two interactions are with the same pulse \( (k_1 = k_2) \), called the pump, and the third interaction is with the probe field. The signal is observed in the direction \( k_S = k_3 \), so \( u_1 = -u_2 \). Accordingly, the signal is given by adding together the rephasing and non-rephasing interactions, and both pulse orderings 1-2-3 and 2-1-3. Since light absorbed directly from the probe pulse (a first-order signal) also appears in the signal direction, the third-order signal in the probe direction is calculated as the differential absorption in the probe direction with and without the pump pulse.

This response function formalism neatly separates the system and field related quantities, and provides a benchmark method for calculating non-linear spectroscopy signals (directly using these equations). For the state tomography and control studies of pump-probe spectroscopy discussed in Chapters 4 and 5, we use a more computationally efficient technique that we introduce in Chapter 4 and which we extend to simulating general third-order signals in Section 5.7.2. These alternate simulation approaches use equations of motion explicitly.
including the system-light coupling $H_{S,L}$ in place of calculating the complete third-order response function. Since the third-order response function provides information sufficient to calculate any conceivable third-order experiment, these alternate approaches can sometimes result in significant computational savings.

1.4 Flexible simulation of dynamics and spectroscopy

The diversity of methods for simulating both the dynamics and spectroscopy of light-harvesting systems, as outlined in the preceding sections, presents an interesting software engineering challenge, since it is impractical to individually code each possible combination of different dynamics and spectroscopy methods. Accordingly, we have designed an application programming interface (API) that provides a sufficient interface to couple any method for efficient simulating of energy transfer dynamics with any method for calculating a spectroscopic signal. The API is described here and also implemented in a software package currently under development.

The core this API is the dynamical model interface, which specifies a sufficient set of operations for manipulating the arbitrary state vectors $\mathbf{x}$ which describe the complete electronic and vibrational system under any model. For example, for a treatment with a Markovian bath, $\mathbf{x}$ could be a Liouville space representation of the system density operator. The interface consists of three parts. First, the initial condition $\mathbf{x}_0$ provides the overall state for the system in the ground electronic state. Second, an equation of motion $f(t, \mathbf{x})$ specifies the free evolution of the system in the absence of a probe field,

$$\frac{\partial \mathbf{x}}{\partial t} = f(t, \mathbf{x}).$$  \hfill (1.14)

Finally, creation and annihilation dipole operators, are defined by objects obeying a system-operator interface defined by the action (in term of the state vector) of left-multiplication

![Figure 1.1: (a) The setup for a generic third-order spectroscopy experiment. (b) The setup for a pump-probe experiment.](image-url)
Vρ, right-multiplication ρV and expectation values Tr[V ρ] of arbitrary electronic operators V on states x equivalent to the density operator ρ.

To enable efficient calculations, the dynamical model interface also allows for following only particular Liouville space pathways [98]. These Liouville space pathways are important because the only part of the Hamiltonian which changes the total number of electronic excitations is the system-field coupling. In the absence of a system-field interaction, the right and left sides of the density matrix remain in fixed subspaces in terms of the number of electronic excitations. Because the dipole-operator is applied a fixed number of times in non-linear spectroscopy, we can explicitly map the possible pathways between states in different subspaces. Ignoring redundant or irrelevant subspaces allows for significant improvements in computational efficiency, particularly because the number of distinct states with a fixed number of excitations grows rapidly with the total number of sites. For example, if the ground, 1-excitation and 2-excitation subspaces are denoted by the letters g, e and f, the only states relevant to the calculation of a pump-probe signal are of the form |g⟩⟨g|, |g⟩⟨e|, |e⟩⟨g|, |e⟩⟨e| and |f⟩⟨e|. Accordingly, the interface allows for specifying the initial condition and equation of motion restricted to any desired subspace, and we should be able to restrict the action of the dipole operators to a fixed transition between subspaces.
Part I

Biological relevance of quantum coherence
Chapter 2

Limits of quantum speedup in photosynthetic light harvesting

Summary

It has been suggested that excitation transport in photosynthetic light-harvesting complexes features speedups analogous to those found in quantum algorithms. Here we compare the dynamics in these light-harvesting systems to the dynamics of quantum walks, in order to elucidate the limits of such quantum speedups. For the Fenna–Matthews–Olson complex of green sulfur bacteria, we show that while there is indeed speedup at short times, this is short lived (70 fs) despite longer-lived (ps) quantum coherence. Remarkably, this timescale is independent of the details of the decoherence model. More generally, we show that the distinguishing features of light-harvesting complexes not only limit the extent of quantum speedup but also reduce the rates of diffusive transport. These results suggest that quantum coherent effects in biological systems are optimized for efficiency or robustness rather than the more elusive goal of quantum speedup.

2.1 Introduction

In the initial stages of photosynthesis, energy collected from light is transferred across a network of chlorophyll molecules to reaction centers [9, 30]. Recent experimental evidence showing long lived quantum coherences in this energy transport in several photosynthetic light-harvesting complexes suggests that coherence may play an important role in the function of these systems [44, 86, 75, 21, 37, 108]. In particular, it has been hypothesized that excitation transport in such systems to feature speedups analogous to those found in quantum algorithms [44, 96]. These comments have attracted much interest from quantum information theorists [96, 118, 117, 111, 26, 25, 34, 125, 152, 11], although clearly photosynthesis is not implementing unitary quantum search [96]. The most direct analogy to such transport is found in quantum walks, which form the basis of a powerful class of quantum algorithms
CHAPTER 2. LIMITS OF QUANTUM SPEEDUP

including quantum search \cite{5, 32, 141, 4, 6, 31}. Unlike idealized quantum walks, however, real light harvesting complexes are characterized by disorder, energy funnels and decoherence. Whether any quantum speedup can be found in this situation has remained unclear.

Quantum walks are an important tool for quantum algorithms \cite{5, 32, 141, 4, 6, 31}. On the line, quantum walks feature ballistic spreading, $\langle x^2 \rangle \propto t^2$, compared to the diffusive spreading of a classical random walk, $\langle x^2 \rangle \propto t$, where $\langle x^2 \rangle$ denotes the mean squared displacement. Moreover, because they use superpositions instead of classical mixtures of states, on any graph with enough symmetry to be mapped to a line, quantum walks spread along that line in linear time – even when classical spreading is exponentially slow \cite{32}. We shall refer to this enhanced rate of spreading as a generic indicator of “quantum speedup.” Such quantum speedup is important in quantum information processing, where it can lead to improved scaling of quantum algorithms relative to their classical alternatives. Examples of such algorithmic speedup include spatially structured search \cite{141}, element distinctness \cite{1} and evaluating AND-OR formulas \cite{6}. Quantum walks even provide a universal implementation for quantum computing \cite{31}.

Quantum walks also constitute one of the simplest models for quantum transport on arbitrary graphs. As such they provide a theoretical framework for several physical processes, including the transfer of electronic excitations in photosynthetic light harvesting complexes \cite{44, 96}. The closed system dynamics in a light-harvesting complex are generally well described by a tight-binding Hamiltonian that is restricted to the single excitation subspace \cite{30},

$$H = \sum_n E_n |n\rangle \langle n| + \sum_{n \neq m} J_{nm} |n\rangle \langle m|.$$  \hspace{1cm} (2.1)

Here $|n\rangle$ represents the state where the $n$th chromophore (site) is in its electronic excited state and all other chromophores are in their ground state. $E_n$ is the electronic transition energy of chromophore $n$ and $J_{nm}$ is the dipole-dipole coupling between chromophores $n$ and $m$. This is a more general variant of the Hamiltonian for standard continuous-time quantum walks, where $E_n = 0$ and $J_{nm} \in \{0, 1\}$. The salient differences of the general model, variable site energies and couplings, arise naturally from the structure and role of light-harvesting complexes. Non-constant site energies can serve as energy funnels and can enable the complex to absorb at a broader range of frequencies, while variable couplings between sites reflect their physical origin as dipole-dipole interactions. These differences yield excitation dynamics that can deviate significantly from quantum walks.

Here we study the key question of whether excitation transport on light-harvesting complexes shows quantum speedup. Such quantum speedup would be necessary for any quantum algorithm that offers algorithmic speedup relative to a classical search of physical space. (Achieving true algorithmic speedup, i.e., improvement over the best classical algorithms, would also require suitable scaling of the space requirements \cite{10}.) We address this with a study of the Fenna-Matthews-Olson (FMO) complex of green sulfur bacteria, a small and very well-characterized photosynthetic complex \cite{9, 30, 17, 2}, the same complex for which long lived quantum coherences were recently observed and suggested to reflect execution of a
Figure 2.1: (a) Crystal structure of FMO complex of \textit{C. tepidum} (Protein Data Bank accession 3ENI), with lines between the chromophores representing dipolar couplings. The thickness of the lines indicates the coupling strengths. Only couplings above 15 cm$^{-1}$ are shown; the largest coupling is 96 cm$^{-1}$. The full Hamiltonian is given in 2.8.1. (b) Site energies, shown relative to 12 210 cm$^{-1}$, in the reduced dimensionality model derived from mapping the strongest couplings onto a one-dimensional graph. The red sites (1, 6) are source sites at which the excitation enters the complex and the black site (3) is the trap site from which the excitation is transferred to the reaction center [2, 151].

natural quantum search [44]. We also consider the dynamics of transport along a theoretical model of an extended chain of chromophores to elucidate the systematic influence of variable site energies and dephasing on transport.

2.2 Fenna-Matthews-Olson complex

The FMO complex acts as a quantum wire, transporting excitations from a large, disordered antennae complex to a reaction center. In addition to the possibility of quantum speedup [44, 96], recent studies have speculated that coherence may assist unidirectional transport along this wire [75] or suggested that it may contribute to overall efficiency [117]. The crystal structure of FMO shows three identical subunits that are believed to function independently, each with seven bacteriochlorophyll-a molecules embedded in a dynamic protein cage [47]. A refined model Hamiltonian for the single excitation subspace is available from detailed quantum chemical calculations [2], and the orientation of the complex was recently verified experimentally [151]. By neglecting the weakest couplings in this model Hamiltonian, we see that transport in an individual monomer of FMO can be mapped to a one-dimensional path between chromophores, as shown in Figure 2.1. This mapping of the excitation transport in FMO to a single dimension allows us to make contact with known results for quantum transport in one dimension and to quantitatively assess the extent of quantum speedup.
2.3 Coherent dynamics

Under Hamiltonian dynamics, quantum walks on highly symmetric graphs can spread ballistically, but any significant lack of symmetry can lead to localization. Consider transport along the infinite line. Here, a random variation of any magnitude in the site energies leads to Anderson localization [110]. Similarly, random variations in the coupling strengths contribute to localization [48]. Systematic variations in site energies or coupling strengths can also cause localization [138], with the well-known instance of Bloch oscillations and Stark localization deriving from a linear bias in site energies [61]. Unitary transport without disorder, and under Anderson and Stark localization is illustrated in Fig. 2.2. Figure 2.3 highlights the particular case of Stark localization with ascending site energies $E_k = kF$ by plotting
the eigenvectors of the Hamiltonian, which are given by

$$|k\rangle = \sum_n J_{n-k}(2J/F)|n\rangle,$$  \hspace{1cm} (2.2)

where $J_\alpha(x)$ denotes the Bessel function of the first-kind of order $\alpha$, and $J$ is the constant coupling between all adjacent sites. Both systematic and random variations in site energies remove the symmetry necessary for Bloch’s theorem, so it is not surprising that their combination leads to localization as well [90, 81], as illustrated in Fig. 2.4. Adding disorder into the graph structure also usually causes localization [100] (although such disorder can also reduce localization if it makes an already disordered graph more connected [52]). The varied couplings, energy funnel and disordered energies evident in the FMO Hamiltonian depicted in Figure 2.1 suggest that localization due to several of these effects will be significant for light-harvesting complexes. The standard measure of localization under coherent dynamics, the inverse participation ratio \[110\] $\xi = \sum_i |\psi_i|^2/\sum_i |\psi_i|^4$, for the amplitudes $\psi_i$ in the site basis of an eigenstate $\psi$ of our model Hamiltonian confirms this intuition, since the typical eigenstate for FMO occupies only $\xi \sim 2$ sites (see also Ref. [14]).

We can estimate the timescale for localization $t_{\text{loc}}$ based upon the experimentally accessible parameters of geometry, localization length $\xi$ and an average coupling strength $J$. Consider the speed of the quantum walk as an upper bound on excitation transport speed prior to localization. For the continuous-time quantum walk on the infinite line, it is well known that $\langle x^2 \rangle \sim 2J^2t^2/\hbar^2$ [83]. Similarly, starting at one end of an infinite line, $\langle x^2 \rangle \sim 3J^2t^2/\hbar^2$. This gives an average speed $gJ/\hbar$, where $g = \sqrt{2}$ and $g = \sqrt{3}$ respectively, yielding the bound $t_{\text{loc}} \gtrsim \hbar\xi/gJ$. Our simulations of strict Hamiltonian dynamics (no decoherence) with

Figure 2.3: (a) The energy eigenfunctions under Stark localization as given by Eq. (2.2) for $J/F = 5$. (b) A position-energy plot of these energy eigenfunctions for a finite chain of 100 sites. An excitation initially at the position shown by the dashed line only has finite overlap with the states highlighted in green, and thus is localized to this region.
Figure 2.4: Panels (a) and (b) show the spread of an initially localized state over time under the two Hamiltonians with varying site-energies shown in (c) and (d). In panels (c) and (d), the energy-eigenfunctions are plotted in black, blue lines show the central energies $E_n$, and red lines shows the boundaries of the “forbidden zone” hypothesized by Ref. [138] as $E_n \pm 2J$.

FMO as described below find the onset of localization at $t_{\text{loc}} \sim 70$ fs, which is close to the bound $\hbar \xi/gJ \sim 100$ fs from the mean inverse participation ratio $\xi_{\text{avg}} \approx 2$, the mean coupling strength $J_{\text{avg}} \approx 60$ cm$^{-1}$ and $g = \sqrt{3}$ (this value for $g$ is suggested by the dominant pathways in Figure 2.1 for transport starting at sites 1 or 6, which are the chromophores closest to the antenna complex [2][151]).

### 2.4 Decoherence

Decoherence, i.e. non-unitary quantum evolution, is also an essential feature of excitation dynamics in real systems. In light harvesting complexes decoherence arises from interactions with the protein cage, the reaction center and the surrounding environment. Recently it has
been shown that some degree of fluctuation of electronic transition energies (i.e. dephasing in the site basis) increases the efficiency of transport in FMO and other simple models otherwise limited by Anderson localization. The intuition is that at low levels dephasing allows escape from localization by removing destructive interference, but at high levels it inhibits transport by inducing the quantum Zeno effect \[96, 118, 111, 26\].

We consider here two essential types of decoherence: dephasing in the site basis and loss of excitations. Under the Born–Markov approximation, time evolution with this decoherence model is determined by the system Hamiltonian $H$ and a sum of Lindblad operators $L$ according to \[12\]

$$\frac{\partial \rho}{\partial t} = -\frac{i}{\hbar}[H, \rho] + L_{\text{loss}}(\rho) + L_{\text{deph}}(\rho).$$

$L_{\text{loss}}$ describes loss of excitations with site dependent rates $\gamma_n$, including trapping to a reaction center, and is specified by the operator

$$\langle n | L_{\text{loss}}(\rho) | m \rangle = -\gamma_n + \gamma_m \frac{1}{2} \langle n | \rho | m \rangle,$$

which results in exponential decay of the diagonal elements of the density matrix $\rho$ (and corresponding decay of off-diagonal elements, which ensures positivity). $L_{\text{deph}}$ describes dephasing, which is specified by the operator

$$\langle n | L_{\text{deph}}(\rho) | m \rangle = -\frac{\Gamma_n + \Gamma_m}{2} (1 - \delta_{nm}) \langle n | \rho | m \rangle$$

with site dependent dephasing rates $\Gamma_n$, and yields exponential decay of the off-diagonal elements of $\rho$.

A remarkable feature of our results for FMO is that, as we shall demonstrate, they are independent of the finer details of the bath dynamics and system-bath coupling. Thus for simplicity, we specialize here to the Haken-Strobl model \[56\] and restrict losses to trapping by the reaction center. The ease of calculations with the Haken-Strobl model has made it popular for simulating the dynamics of light harvesting complexes \[118, 111, 26, 88, 49\]. Following Rebentrost et al. \[118\], we use the spatially uniform, temperature dependent dephasing rate $\Gamma = 2\pi k_B T E_R/\hbar^2 \omega_c$, for an ohmic spectral density with bath reorganization energy $E_R = 35 \text{ cm}^{-1}$ and cut-off frequency $\omega_c = 150 \text{ cm}^{-1}$. This dephasing rate holds when chromophores are treated as qubits coupled to independent reservoirs in the spin-boson model, in the thermal (or Markovian) regime $t \gg \hbar/k_B T$ \[12\], which corresponds to $t \gg 25 \text{ fs}$ at 300 K. Although the exact parameters of the protein environment surrounding FMO are unclear \[75\], these are reasonable estimates. This model gives dephasing rates $(69 \text{ fs})^{-1}$ at $77 \text{ K}$ and $(18 \text{ fs})^{-1}$ at $300 \text{ K}$. Also, as in Ref. \[118\] we restrict trapping to site 3 at a rate of $\gamma_3 = 1 \text{ ps}^{-1}$. Finally, we neglect exciton recombination since it occurs on much slower timescales ($\sim 1 \text{ ns}^{-1}$) and in any case it does not alter the mean-squared displacement. Therefore, we set $\gamma_i = 0$ for $i \neq 3$. While more realistic decoherence models would incorporate thermal relaxation, spatial and temporal correlations in the bath and strong system-bath coupling \[76\], this treatment is sufficient for analyzing the quantum speedup,
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as justified in detail by comparison with the corresponding analysis using more realistic simulations of FMO \[76\] in \[2.8.2\]

2.5 Limits of quantum speedup

To access the extent of quantum speedup for a system that can be mapped to a line, a natural measure is the exponent $b$ of the power law for the mean squared displacement $\langle x^2 \rangle \propto t^b$. In particular, we use the best-fit exponent $b$ from the slope of the log-log plot of the mean squared displacement $\langle x^2 \rangle = \text{Tr}[\rho x^2] / \text{Tr} \rho$ versus $t$. The value $b = 1$ corresponds to the limit of diffusive transport, whereas $b = 2$ corresponds to ideal quantum speedup as in a quantum walk (ballistic transport).

The timescale for quantum speedup is generally bounded above by both the timescale for dephasing, $t_{\text{deph}} = 1/\Gamma$, and the timescale for static disorder to cause localization, $t_{\text{loc}}$. To see this, it is illustrative to consider transport along a linear chain with constant nearest neighbor couplings $J$. For dephasing but no static disorder or energy gradient ($E_n = 0$), the mean squared displacement shows a smooth transition from ballistic to diffusive transport \[135, 53\]

\[
\langle x^2 \rangle = \frac{4J^2}{\hbar^2 \Gamma} \left[ t + \frac{1}{\Gamma} (1 - e^{-\Gamma t}) \right].
\] (2.6)

The corresponding power law transition is shown in Figure 2.5a. Technically, transport remains super-diffusive even after $t_{\text{deph}}$, since the power never drops below $b = 1$. In contrast, for static disorder but no dephasing, there is a sudden transition from ballistic transport to essentially no transport at all (localization). The power law starts at $b = 2$, then drops and begins to oscillate wildly after $t_{\text{loc}}$ as the wave function continues to evolve in a confined region. Several examples are shown in Figure 2.5b for variable strengths of disorder. Figure 2.5c shows the behavior with both strong static disorder and dephasing, as in light harvesting complexes. In this case, the transport can even exhibit a sub-diffusive power law. The reason for this sub-diffusive behavior may be easiest to understand by analogy to the Anderson model (random site energies) in an infinite chain. Consider transport in such a system under weak dephasing and with an ensemble average over different realizations of strong static disorder. In this case, one expects transport must transition from ballistic ($b = 2$) at short times, to localized ($b = 0$) at intermediate times, to diffusive at long times ($b = 1$). (The situation at long times is analyzed more explicitly in Section 2.6 and 2.8.3.) For stronger dephasing as in Figure 2.5c (and as we shall see with FMO), the fully localized regime with no transport may never be realized, but transport will still be sub-diffusive for intermediate times.

Figure 2.6 shows the results of a simulation of FMO dynamics made with our simple decoherence model. The displacement $x_i$ of a site $i$ is given by its position in the one-dimensional mapping that is presented in Figure 2.1b. Note that our simulations use the

\[1\] This result, obtained in the context of excitation transport in molecular crystals, also applies to decoherent continuous-time quantum walks since they use the same tight-binding Hamiltonian.
Figure 2.5: The best fit power law exponent $b$ for the mean-squared displacement with $J/\hbar = 1$, for transport along a linear chain with either (a) increasing dephasing ($\Gamma = 1, 3, 9$) and no static disorder ($E_n = 0$), (b) no dephasing ($\Gamma = 0$) and increasing static disorder (independent site energies $E_n$ from a single Gaussian distribution normalized to standard deviation $\sigma = 1, 3, 9$) or (c) same disorder as (b), but with finite dephasing rate $\Gamma = 1$. Panels (b) and (c) show results for single instances of disorder. When an ensemble average over different realizations of static disorder is taken, the power law varies smoothly instead of oscillating as in (b) and (c).
Figure 2.6: Results of simulations on FMO with the decoherence model described in the text. (a) Log-log plot of mean-squared displacement $\langle x^2 \rangle$ as a function of time, for an initial excitation at site 6. (b) Power law exponent for the mean-squared displacement, given by the slope of the plot in panel a. The dashed line $b = 1$ separates super- and sub-diffusive transport (see text). (c) Total site coherence, given by the sum of the absolute value of all off-diagonal elements of the density matrix in the site basis, indicates persistent coherence for $\sim 500$ fs. (d) Oscillating site populations (shown for $77$ K only) also indicate persistent coherence for hundreds of femtoseconds.

Our results show that even though coherence in this simple model lasts for $\sim 500$ fs (see Figure 2.6c), a transition from initially ballistic to sub-diffusive transport occurs after only $\sim 70$ fs, independent of the dephasing rate. While increased dephasing causes a faster initial decrease of the power law, dephasing alone cannot lead to sub-diffusive transport, as is clear
from Equation (2.6). We note that the transition to sub-diffusive transport at 70 fs occurs at the same time-scale as the onset of localization (Section 2.3), implying that even though there is persistent coherence beyond this time, it no longer yields quantum speedup because of static disorder. The sub-diffusive power law at intermediate times ($\sim 100 \text{ fs} - 2 \text{ ps}$) arises from the interplay of this disorder-induced localization and dephasing that is discussed above for the linear chain model. At longer times the power law exponent $b$ goes to zero because of the finite size of the system. Since complete energy transfer through FMO takes picoseconds, this analysis shows that most of the excitation transport is formally sub-diffusive.

While FMO is a relatively small system, so that terms such as “ballistic” and “diffusive” cannot literally describe transport across its seven chromophores, this time dependence of the power law of spreading would also characterize larger artificial or natural systems. Our results here are robust to variations in the strength of the trap, and to whether the initial excitation is at site 1 or 6, the sites believed to be the primary source for excitations in FMO \cite{2}. They are also independent to variations of the map to a one-dimensional system in Figure 2.1 such as counting the number of chromophores away from the trap site instead of along the entire line, or using the real space distance between adjacent chromophores instead of assuming that each pair is merely separated by a unit lattice distance.

Our timescale for short-lived quantum speedup in FMO should be largely independent of the details of the decoherence model, since the non-uniform energy landscape will always limit ballistic transport to times prior to $t_{\text{loc}} \sim 70 \text{ fs}$. This is confirmed by applying our analysis to the results of recent calculations for FMO made with a considerably more sophisticated decoherence model that incorporates thermal relaxation, temporal correlations in the bath and strong system-bath coupling \cite{76}. As demonstrated in 2.8.2, these more realistic calculations also predict a loss of quantum speedup after 70 fs.

### 2.6 Diffusive transport

To gain general insight into the interplay between disorder and dephasing for light harvesting complexes, we now consider the dynamics of an infinite linear chain at long times with variable site energies, couplings and dephasing rates. By extending an analysis for damped Bloch oscillations \cite{82}, we find that any set of non-zero dephasing rates $\Gamma_n$ asymptotically leads to diffusive transport $\langle x^2 \rangle \sim 2 Dt$. Haken and Reineker also performed a reduction of the Haken-Strobl model without disorder to a diffusion equation along similar lines \cite{54}. Note that since the Haken-Strobl model does not include energy relaxation, no classical drift velocity will be obtained from these dynamics. The time evolution of an arbitrary density matrix element for an infinite linear chain under site dependent dephasing rates is given by

$$
\dot{\rho}_{nm} = -\frac{i}{\hbar} \left( J_{n-1} \rho_{n-1,m} + J_n \rho_{n+1,m} - J_m \rho_{n,m+1} - J_{m-1} \rho_{n,m-1} \right) \\
- \left[ \frac{i}{\hbar} (E_n - E_m) + \frac{\Gamma_n + \Gamma_m}{2} (1 - \delta_{nm}) \right] \rho_{n,m},
$$

(2.7)
where $J_n \equiv J_{n,n+1}$. If we neglect terms in the second off-diagonal relative to the diagonal terms (see justification in 2.8.3) we obtain

$$\dot{\rho}_{n+1,n} = -\frac{i}{\hbar} J_n (\rho_{n,n} - \rho_{n+1,n+1}) - \left( \frac{i}{\hbar} \Delta_n + \Gamma'_n \right) \rho_{n+1,n}, \tag{2.8}$$

where $\Delta_n \equiv E_{n+1} - E_n$ and $\Gamma'_n \equiv (\Gamma_n + \Gamma_{n+1})/2$. This equation has the solution

$$\rho_{n+1,n} = \frac{i}{\hbar} e^{-\left( \frac{i}{\hbar} \Delta_n + \Gamma'_n \right) t} \int_0^t J_n (\rho_{n+1,n+1} - \rho_{n,n}) e^{\left( \frac{i}{\hbar} \Delta_n + \Gamma'_n \right) t'} dt' \approx \frac{J_n (\rho_{n+1,n+1} - \rho_{n,n})}{\Delta_n - i\hbar \Gamma'_n}, \tag{2.9}$$

in the nearly stationary regime where site populations vary slowly compared to $1/\Gamma'_n$ and $\hbar/\Delta_n$. Inserting (2.9) and the corresponding result for $\rho_{n-1,n}$ into (2.7) we obtain

$$\dot{\rho}_{nn} = \frac{2J^2_n \Gamma'_n}{\Delta^2_n + \hbar^2 \Gamma^2_n} (\rho_{n+1,n+1} - \rho_{n,n}) + \frac{2J^2_{n-1} \Gamma'_{n-1}}{\Delta^2_{n-1} + \hbar^2 \Gamma^2_{n-1}} (\rho_{n-1,n-1} - \rho_{n,n}). \tag{2.10}$$

This is now a classical random walk with variable bond strengths between sites. For asymptotically large times it has been proven to approximate the diffusion equation with coefficient given by

$$D = \left( \frac{\Delta^2_n + \hbar^2 \Gamma^2_n}{2J^2_n \Gamma'_n} \right)^{-1}, \tag{2.11}$$

as long as the average over sites in the diffusion coefficient is well-defined [71]. With $\Delta_n$, $J_n$ and $\Gamma_n$ constant, this matches the known diffusion coefficient [72, 41]. For constant coupling $J_n = J$ and constant dephasing $\Gamma'_n = \Gamma$, we note that (2.11) reduces to

$$D = \frac{2J^2 \Gamma}{\langle \Delta^2_n \rangle + \hbar^2 \Gamma^2}, \tag{2.12}$$

which is plotted as a function of $\langle \Delta^2_n \rangle^{1/2}$ and $\Gamma$ in Figure 2.7. Note that with $\langle \Delta^2_n \rangle = 0$, this is the long time limit of (2.6). In the case of Equation (2.12), for a given degree of static disorder, we find an optimal dephasing rate $\hbar \Gamma = \langle \Delta^2_n \rangle^{1/2}$. However, Figure 2.7 shows that for a given dephasing rate, excitation transport would be improved by reducing the static disorder to further delocalize the system.

### 2.7 Conclusions

These principles show that quantum speedup across a photosynthetic or engineered system requires not only long-lived quantum coherences but also excitons delocalized over the entire

---

2 We note that the parameter $\langle \Delta^2_n \rangle^{1/2}$ does not completely specify the degree of localization, although it does show that Stark and Anderson localization equivalently influence diffusive transport. For example, the inverse participation ratio in these two cases differs, even with the same value of $\langle \Delta^2_n \rangle^{1/2}$. 
complex. Such completely delocalized excitons do not exist in FMO and are also unlikely in other light harvesting complexes because of the presence of energy gradients and disorder. Moreover, Equation (2.12) makes it clear that the conditions needed for longer lived quantum speedup (reduced dephasing and static disorder) are those necessary for faster diffusive transport as well.

The short-lived nature of quantum speedup in light harvesting complexes that we have established here implies that the natural process of energy transfer across these complexes does not correspond to a quantum search. Indeed, neither a formal quantum nor classical search may be necessary, since pre-determined (evolved) energy gradients can guide relaxation to reaction centers, even though such gradients suppress coherent and dephasing-assisted transport. This is particularly relevant for systems such as FMO which either receive excitations one at a time or have isolated reaction centers. Instead of yielding dynamical speedup like that in quantum walk algorithms, quantum coherence in photosynthetic light harvesting appears more likely to contribute to other aspects of transport, such as overall efficiency or robustness. We emphasize that a restricted extent of quantum speedup does not imply that there is no significant quantum advantage due to long-lived coherence in electronic excitation energy transfer. Identifying the specific nature of any “quantum advantage” for FMO will clearly require more detailed analysis of the dynamics, particularly in the sub-diffusive regime. Related examples of such “quantum advantage” are found in the LH2 complex of purple bacteria, where coherence has been specifically shown to improve both the speed and robustness of transport from the B800 to B850 ring.
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Note added

While revising this manuscript, a reduction of the Haken-Strobl model to a classical random walk similar to the one we perform in Section 2.6 was published by Cao and Silbey [23].

2.8 Appendices

2.8.1 FMO Hamiltonian

In all of our calculations, we use the Hamiltonian calculated for \textit{C. tepidum} by Adolphs and Renger [2]. In the site basis, this is given by

\[
H_{\text{FMO}} = \begin{pmatrix}
200 & -96 & 5 & -4.4 & 4.7 & -12.6 & -6.2 \\
-96 & 320 & 33.1 & 6.8 & 4.5 & 7.4 & -0.3 \\
5 & 33.1 & 0 & -51.1 & 0.8 & -8.4 & 7.6 \\
4.7 & 4.5 & 0.8 & -76.6 & 270 & 78.3 & -0.1 \\
-12.6 & 7.4 & -8.4 & -14.2 & 78.3 & 420 & 38.3 \\
-6.2 & -0.3 & 7.6 & -67 & -0.1 & 38.3 & 230 \\
\end{pmatrix},
\]

with units of cm$^{-1}$ and a total offset of 12210 cm$^{-1}$. Bold entries indicate those shown in Figure 2.1. In units with $\hbar = 1$, we note that the rate $1 \text{ps}^{-1} \equiv 5.3 \text{cm}^{-1}$.

2.8.2 Reduced hierarchy equations model for FMO

Energy transfer dynamics in photosynthetic complexes can be difficult to model because perturbations from the surrounding protein environment can be large, and the timescale of the protein dynamics is similar to the timescales of excitation transport. This makes common approximations involving perturbative treatments of system-bath coupling and Markovian assumptions on the bath invalid. Recently a non-perturbative, non-Markovian treatment of energy transfer has been formulated by Ishizaki and Fleming [76]. This model assumes: (i) a bilinear exciton-phonon coupling, (ii) protein fluctuations that are described by Gaussian processes, (iii) a factorizable initial state of chromophores and protein environment, (iv) protein fluctuations that are exponentially correlated in time, and (v) no spatial correlations of fluctuations.

To verify our results in Figure 2.6 of the main paper with this more realistic model for excitation dynamics, we apply the power law analysis of mean squared displacement to the results of the simulations that were used to calculate entanglement dynamics in Ref. [125] using the non-perturbative non-Markovian method of Ref. [75]. These simulations used a reorganization energy of the protein environment of 35 cm$^{-1}$, phonon relaxation time of 100 fs, and a reaction center trapping rate of $(4 \text{ps})^{-1}$, all of which are consistent with literature on FMO [2, 35]. Figure 2.8 shows the power law analysis for 2 different temperatures, 77 K.
and 300 K. Our analysis of these realistic simulations show that longer lasting coherences (as discussed in Refs. [75, 76]) are evident in the power law oscillations, but that transport is still nevertheless sub-diffusive after $\sim 70$ fs, for both temperatures.

It is particularly noteworthy that our results for FMO hold even under a model incorporating finite temperature relaxation. In principle, thermal relaxation could bias the dynamics on a linear chain with a classical drift velocity [113] to give the power law $\langle x^2 \rangle \propto t^2$ even without quantum speedup. However, the above analysis of FMO simulations made with the most realistic treatment of relaxation available today (Figure 2.8) shows that this is not the case in this system.

### 2.8.3 Decay of coherences in linear transport

For a constant dephasing rate $\Gamma \gg J/\hbar$, there is a simple analytical argument that the off-diagonal elements of the density matrix in the site basis can be neglected relative to the main diagonal [45]. In the case of transport along a line, application of the analysis of Ref. [45] to Equation (2.7) shows that the first off-diagonal elements decay at rate $\Gamma$, unless more coherence is generated from the main diagonal. If the main diagonal elements have order 1, then the first off-diagonal elements cannot have magnitude greater than order $J/\hbar \Gamma$. A similar argument bounds the second diagonal elements as less than $(J/\hbar \Gamma)^2$ and so forth. For large $\Gamma$, this justifies neglecting this second off-diagonal relative to the main diagonal. The higher order terms in this expansion can also be calculated explicitly [23].

From extensive numerical experiments with infinite chains, we have found uniformly that
Figure 2.9: Decay of coherences. Log-log plot of the sum of the absolute values $k$th off-diagonal elements of the density matrix over time for constant dephasing and coupling strengths $\Gamma = J/h = 1$. Panels show the quantum walk with dephasing (a), and Stark (b) and Anderson (c) localization with dephasing and $\langle \Delta_n^2 \rangle^{1/2} = \pi/2$. Note that the main diagonal always sums to 1.

the off-diagonal elements of the density matrix decay nearly monotonically after time $1/\Gamma$ even when $\Gamma \gg J/h$ does not hold, although an analytic proof of this result has eluded us. Several examples are presented in Figure 2.9. This matches the analytical result for finite systems in the Haken-Strobl model that coherence must vanish eventually for any non-zero $\Gamma$ [109].
Chapter 3

Spatial propagation of excitonic coherence enables ratcheted energy transfer

Summary

Experimental evidence shows that a variety of photosynthetic systems can preserve quantum beats in the process of electronic energy transfer, even at room temperature. However, whether this quantum coherence arises in vivo and whether it has any biological function have remained unclear. Here we present a theoretical model that suggests that the creation and recreation of coherence under natural conditions is ubiquitous. Our model allows us to theoretically demonstrate a mechanism for a ratchet effect enabled by quantum coherence, in a design inspired by an energy transfer pathway in the Fenna-Matthews-Olson complex of the green sulfur bacteria. This suggests a possible biological role for coherent oscillations in spatially directing energy transfer. Our results emphasize the importance of analyzing long-range energy transfer in terms of transfer between intercomplex coupling states rather than between site or exciton states.

3.1 Introduction

Mounting experimental evidence for electronic quantum coherence in photosynthetic energy transfer [126, 44, 37, 108, 21] has spawned much debate about both the detailed nature and the biological role of such quantum dynamical features. Quantum coherence is usually encountered in the first, light harvesting stage of photosynthesis. It includes two distinct but not mutually exclusive phenomena that can be differentiated by the choice of basis used to describe the electronic excitations. In the site basis, corresponding to the excitation of individual pigment molecules, coherence emerges in molecular aggregates even in thermal equilibrium, since eigenstates are delocalized over multiple chromophores. Such coherence
between sites can enhance the rate of biological energy transfer by up to an order of magnitude \cite{133,144,78,66}. In contrast, it is coherence in the exciton basis, that is, superpositions of the energy eigenstates, which drives quantum beating via the Schrödinger equation. It is this type of coherence on which we will focus here, and thus in the remainder of this paper, the term ‘coherence’ refers to coherence in the exciton basis. Photosynthetic systems at ambient temperatures have been shown to exhibit this kind of quantum beating when artificially excited \cite{108,37}, but the significance of these discoveries remains unclear. A broad deficiency is the lack of plausible physical mechanisms for how this coherence could arise in and influence biological energy transfer. For example, the suggestion that transport in these systems features speedups reminiscent of quantum search algorithms \cite{44} has been shown to be invalid \cite{68,96}. Experimental observations of long-lasting and delocalized quantum beats alone are not sufficient to determine that they are biologically relevant, since these features arise due to strong inter-chromophoric couplings \cite{129}, which independently yield fast transport rates under almost any theoretical model, even those which entirely neglect quantum coherence.

In this work we address the question of what physical mechanisms lie behind the origin and biological role of electronic coherence in the exciton basis. While our theoretical analysis is general, to make illustrative demonstrations of specific mechanistic features we take physical parameters from a prototypical system, the Fenna-Matthews-Olson (FMO) complex of green sulfur bacteria. FMO is an extensively studied protein-pigment complex \cite{2,9,47} that exhibits excitonic quantum beats \cite{108} and entanglement \cite{125} at room temperature. Biologically, FMO acts as an energy transmitting wire, delivering an electronic excitation created by photon absorption in the chlorosome antenna to a reaction center where it induces charge separation. It exists in the form of a trimer with a protein backbone and $3 \times 7$ bacteriochlorophyll-a molecules, each with different transition energies set by the local electrostatic environment. These pigments and energy transfer pathways are illustrated in Figure 3.1. Several quantitative estimates of the importance of excitonic coherence under particular models suggest that it makes $\sim 10\%$ contribution to transfer energy transfer efficiency in this system \cite{117,154}. The section of the energy transfer path from site 1 to 2 is particularly unusual, since it is energetically uphill while these sites also have the strongest electronic coupling of any pair of sites in the complex. It has been speculated that these factors may indicate a role for quantum coherence in contributing to unidirectional energy flow through this system by avoiding trapping in local minima of the energy landscape \cite{75}. All other steps of the FMO electronic energy transfer pathways in the direction towards the reaction center are energetically downhill, consistent with a pathway that would be optimal for classical energy transport. A key question that is of special importance for the FMO complex, is thus how the system efficiently directs energy transport away from the chlorosome antenna towards the reaction center. Clearly the overall energy gradient in the system plays a role, but does electronic coherence also facilitate unidirectional energy transfer? More generally, can excitonic coherence assist excitation transfer over the uphill steps found in rough energy landscapes?

A striking feature of all experiments showing electronic quantum beatings in photosyn-
Figure 3.1: Energy transfer pathways in a monomer of the FMO complex of *Chlorobaculum tepidum* (*C. tepidum*). (a) Side view of a monomer of the FMO complex [47], showing the primary energy transfer pathways [14] toward the reaction center via site 3 and the inter-complex coupling (ICC) basis states that couple site 8 to the remainder of the complex. Site occupation probabilities for the ICC basis states are proportional to the area of the colored circles. (b) Site energies along the upper energy transfer pathway depicted in panel (a), with the energy of site 8 approximated by the antenna baseplate energy [75]. Lines between sites indicate weak (dashed, $10 \text{ cm}^{-1} < J < 40 \text{ cm}^{-1}$) and strong (solid, $J > 40 \text{ cm}^{-1}$) electronic couplings. Room temperature is approximately 200 cm$^{-1}$.

thesis to date is that they have been performed on small sub-units of light harvesting antenna systems, such as the 7 pigments of the FMO complex [126, 44, 108] or the 14 pigments in LHC II [21, 129]. Yet natural light harvesting antennas are typically composed of hundreds or thousands of pigment molecules organized into many pigment-protein complexes through which energy passes on route to the reaction center [9]. In addition, natural excitation is by sunlight, not ultrafast laser pulses. There is dispute about whether or not coherences can arise after excitation by natural light [30, 92, 73, 19], but many pigment-protein sub-units are actually more likely to receive excitations indirectly, as a result of weak coupling to another complex in the larger network. Clearly, understanding the role of excitonic coherence in a single protein-pigment complex requires placing the energy transfer within and through that system in the context of appropriate initial conditions, as determined by its role in the larger “supercomplex.” Accordingly, a second key question for evaluating the relevance of quantum beats to energy transfer on biological scales is whether or not excitonic coherence could be either arise or be maintained in the process of transfer between different sub-units.

In the remainder of this paper we shall address these two open questions with a general theoretical framework employing a novel basis for analyzing the excitonic dynamics of weakly coupled pigment-protein complexes. First, we develop an analysis of such weakly coupled complexes that suggests a mechanism for how coherence should arise and recur in the process of energy transfer. We find that coherence can continue to be regenerated during long-range energy transport between weakly linked sub-units of a larger excitonic system. This is
the ‘propagation’ of quantum coherence, whereby a process of continual renewal following incoherent quantum jumps may allow non-zero coherence to last indefinitely, despite rapid decay after each jump. This has significant implications for long-range energy transfer in light harvesting supercomplexes composed of multiple units that individually support coherence, such as photosystems I and II [9]. Second, we address the question as to whether such spatially propagated intra-complex quantum coherence enables unidirectional flow of energy, with a specific example that is inspired by the uphill energetic step in FMO. We construct an explicitly solvable ratchet model to show that in this situation, the non-equilibrium nature of even limited quantum beating may allow for qualitatively new types of dynamics. In particular, we show that under biologically plausible conditions, these dynamical features could allow for the operation of a coherently enabled ratchet effect to enhance directed energy flow through light harvesting systems. These analyses provide new understanding of physical mechanisms reliant on quantum coherence that could be relevant to the function of natural photosynthetic systems.

3.2 Spatial propagation of coherence

In photosynthetic energy transfer, excitons typically need to travel through a series of protein-pigment complexes before reaching reaction centers [9]. To accurately understand the role of coherent dynamics between individual sub-units in such a supercomplex, it is first necessary to understand which particular sub-unit states donate or accept excitations for inter-complex transfer. As we shall show in this work, the nature of these states informs us whether or not coherence arises under natural conditions in the process of energy transfer. Moreover, in the context of a light-harvesting complex which is a subcomponent of a larger light-harvesting apparatus, the precise nature of the acceptor states on the complex and the donor states from the complex is paramount to assessing the possible relevance of coherent dynamics in the complex. To draw an analogy to the circuit model of quantum computation [103], these states serve as effective choices of initial states and measurement basis states, respectively, for dynamics on an individual complex. Both of these states need to differ from energy eigenstates in order for strictly unitary dynamics to influence measurement outcomes. The measurement outcomes correspond to observable energy transfer, for which differences in rates or success probabilities could in turn influence biological function.

Since inter-complex couplings are relatively weak, in our analysis we treat them perturbatively, as in multichromophoric generalizations of Förster theory used to calculate overall transition rates between donor and acceptor complexes consisting of multiple chromophores [78, 144, 133]. Our starting point is the equation of motion for the reduced density matrix, which is derived with the following adaptation of the multichromophoric energy transfer rate model [78]. The zeroth order Hamiltonian is $H_0 = H_D + H_A$ where $H_D = H_{eD} + \sum_{ij} B_{Dij} |D_i\rangle\langle D_j| + H_{gD}$, with $H_{eD}$ the electronic Hamiltonian of the donor complex, and corresponding definitions for the acceptor complex $A$. States $|D_j\rangle$ and $|A_k\rangle$ for $j = 1, \ldots, n$ and $k = 1, \ldots, m$ form an arbitrary orthonormal basis for donor and acceptor
single-excitation electronic states and \( B_{D,j} \) are bath operators that couple the electronic chromophore states to environmental states of the pigment-chromophore system. The ground state donor (acceptor) bath Hamiltonian \( H_D^0 \) (\( H_A^0 \)) can be taken without loss of generality to be a set of independent harmonic oscillators. We assume that no bath modes are coupled to both the donor and acceptor so that \([H_D, H_A] = 0\) \cite{78}. The donor and acceptor complexes are coupled by a dipolar interaction for the reduced acceptor and donor density matrix elements, respectively, where \( \sigma = \text{Tr}_B \rho \) to second order in \( H_e \) \cite{78} and Appendix 3.7.1) yields

\[
\frac{d\sigma_{kk'}}{dt} = \sum_{jj''} \frac{J_{jj''}}{4\pi\hbar^2} \int_{-\infty}^{\infty} d\omega \left[ J_{jk} E_D^{jj''}(t, \omega) I_A^{kk''}(\omega) + J_{kj'} E_D^{kj''}(t, \omega) I_A^{kk''}(\omega) \right] \tag{3.1}
\]

\[
\frac{d\sigma_{jj'}}{dt} = -\sum_{kk''} \frac{J_{jj''}}{4\pi\hbar^2} \int_{-\infty}^{\infty} d\omega \left[ J_{jk} E_D^{jj''}(t, \omega) I_A^{kk''}(\omega) + J_{kj'} E_D^{kj''}(t, \omega) I_A^{kk''}(\omega) \right] \tag{3.2}
\]

for the reduced acceptor and donor density matrix elements, respectively, where \( E_D(t, \omega) \) and \( I_A(\omega) \) denote matrices of donor and acceptor lineshape functions (see Eqs. (3.13–3.14)). We emphasize that these results hold for arbitrary system-bath coupling strength, provided that the donor-acceptor coupling is weak: at this point in our analysis we have not yet made any assumption of weak system-bath coupling.

Instead of focusing on the multichromophoric energy transfer rate between complexes that results from summing Eq. (3.1) or (3.2) over all diagonal terms \cite{78}, we focus here on important features relevant to quantum coherence apparent from Eqs. (3.1)–(3.2) directly. These equations indicate that acceptor populations \(| \langle A_k | A_l \rangle \rangle \) will grow and donor populations \(| \langle D_j | D_j \rangle \rangle \) will decay only if there is at least one non-zero coupling term \( J_{jk} = \langle D_j | J | A_k \rangle \) to those states. Accordingly, we argue that the transfer of electronic states is most sensibly described by the “inter-complex coupling” basis in which \( J \) is diagonal, rather than the site or exciton (energy) basis, as is assumed in both the original and generalized Förster theories. This inter-complex coupling (ICC) basis is given by the singular value decomposition \( J = U_D \hat{J} U_A^\dagger \), where \( \hat{J} \) is a rectangular diagonal matrix and \( U_D \) and \( U_A \) are unitary transformations of donor and acceptor electronic states. We can thus write the inter-complex coupling as \( H_e = \sum_l \hat{J}_l (|D_l \rangle \langle A_l | + |A_l \rangle \langle D_l |) \) in terms of the ICC states \(|D_l \rangle = U_D |D_l \rangle \) and \(|A_l \rangle = U_A |A_l \rangle \) for \( l \in \{1, \ldots, \min(n, m)\} \). In the ICC basis, the full electronic Hamiltonian in block-matrix form is

\[
\hat{H}_e = \begin{bmatrix}
U_D^\dagger H_D^0 U_D & U_D^\dagger \hat{J} U_A \\
U_A^\dagger \hat{J}^\dagger U_D & U_A^\dagger H_A^0 U_A
\end{bmatrix}.
\tag{3.3}
\]

Since in general the transformation that diagonalizes \( J \) will not coincide with the (exciton) eigenbases of \( H_D^0 \) and \( H_A^0 \), population growth of an acceptor ICC state \(|A_l \rangle \langle A_l | \rangle \rangle \) thus corresponds to growth of excitonic coherences.

Although in principle Eqs. (3.1)–(3.2) specify all dynamics relevant to inter-complex transfer, the time-dependent donor lineshape \( E_D(t, \omega) \) obscures the specific dependence on donor
density matrix elements. Accordingly, we also derive a time-convolutionless quantum master equation (Appendix 3.7.2) under the additional assumption of weak coupling to the bath relative to the donor electronic Hamiltonian $H^e_D$ [12]. Under this approximation, we see that growth of an acceptor population $\langle \tilde{A}_l | \tilde{A}_l \rangle$ is proportional to populations only of the coupled donor $| \tilde{D}_l \rangle \langle \tilde{D}_l |$. Likewise, decay of a donor population $| \tilde{D}_l \rangle \langle \tilde{D}_l |$ is proportional to populations only of that donor itself (see Eqs. (3.22–3.23) in Appendix 3.7.2). Accordingly, inter-complex transfer rates may show oscillations reflecting donor quantum beats, since the ICC states on the donor which transmit excitations do not necessarily correspond to energy eigenstates. While this part of our argument is only rigorous in the case of weak system-bath coupling, which is not necessarily the case for FMO and other light harvesting systems [75], our simulations find excellent agreement even for moderate strength environmental coupling, as we show below.

To test this analysis of inter-complex energy transfer, we first consider its predictions for the special case in which there is only one non-zero inter-complex coupling in the ICC basis, $H_c = J_s | D^* \rangle \langle A^* | + h.c$. If the acceptor is always initialized in the state $\rho^*_A = | A^* \rangle \langle A^* |$, then when back-transfer to the donor is neglected as is valid in the perturbative limit, the acceptor density matrix should be well described by

$$\rho_A(t) = \int_0^t dt' dp_A(t') G(t - t') \rho^*_A,$$

where $G(t)$ is the Greens function denoting evolution of the acceptor-bath system for time $t$, with the bath initialized at equilibrium. If the predicted donor state is correct, then neglecting temporary bath reorganization effects, the rate of inter-complex transfer should then be proportional to the population of the predicted donor state, for a predicted inter-complex transfer rate

$$\frac{dp_A(t)}{dt} \propto p_{D^*}(t),$$

where $p_{D^*}(t)$ denotes the probability of the donor being in the state $| D^* \rangle$ and $p_A$ the total probability of the excitation being on the acceptor.

For a model system, these predictions show remarkable agreement with results derived from an independent simulation based on a 2nd-order cumulant time-nonlocal (2CTNL) quantum master equation [76]. We consider transfer between two dimer complexes (labelled sites 1, 2 and sites 3, 4), with intra-dimer Hamiltonian parameters matching those of the 1-2 dimer of FMO (Appendix 3.7.5, Eq. (3.43)) and inter-complex coupling $J = J_s | 2 \rangle \langle 3 |$. We perform calculations in the limit $J_s \to 0$ (see Appendix 3.7.4), to ensure accuracy of the perturbative description and eliminate back-transfer effects. The 2CTNL calculations are carried out at 300 K with a bath modeled by a Debye spectral density with reorganization energy 35 cm$^{-1}$ and correlation time 50 fs, with the initial condition on site 1 [75]. Figure 3.2 compares simulated 2CTNL results with the predicted time-dependent inter-complex transfer rate, Eq. (3.5), and acceptor density matrix, Eq. (3.4) (normalized to unity for greater
Figure 3.2: Testing the theory of propagation of coherence via the inter-complex coupling (ICC) basis. Simulations were made for the coupled dimer model described in the text, with ICC donor and acceptor states $|D^*\rangle = |2\rangle$, $|A^*\rangle = |3\rangle$, respectively, and initial condition $|\psi_0\rangle = |1\rangle$. (a) Simulated (solid black, 2CTNL) and predicted (dashed blue, Eq. (3.5)) inter-complex transfer rate as a function of time. (b) Coherence between the two acceptor excitonic eigenstates $\alpha$ and $\beta$ as a function of time. (c) Population of site 3 in the acceptor, i.e., $\rho^*_A = |3\rangle\langle 3|$, as a function of time. (d) Real and (e) imaginary parts of the 3-4 site coherence for the simulated (solid black) and predicted (dashed blue, Eq. (3.4)) acceptor density matrix $\rho_A$, as a function of time. The acceptor density matrix $\rho_A$ was normalized to unit probability at all times in panels (b-e).
clarity), calculated from the 2CTNL results. The results show that estimates based on the dominant elements of the ICC basis provide an accurate representation of both the energy transfer rate (panel a) and acceptor density matrix (panels b-e). We see that transfer of excitation in the ICC basis from $|D^*\rangle$ to $|A^*\rangle$ produces a superposition of acceptor eigenstates (of $H_A$) that gives rise to excitonic coherence (panel b) and hence to oscillatory behavior of both the site populations (panel c) and coherences (panels d-e). Two features are of particular significance, since they show that these ICC-dominated dynamics satisfy the conditions that are necessary for intra-dimer coherence to be relevant to larger scale energy transfer, namely that the dynamics guarantee the preparation and measurement of states which are not energy eigenstates. The first feature is that the inter-dimer transfer rate clearly tracks coherent oscillations of the donor population $|D^*\rangle\langle D^*|$ (panel a). The second feature is that the acceptor is initialized in a state with non-zero excitonic coherence (panel b). Although Fig. 3.2 shows results for only a single initial condition, additional simulations (not shown) show that these features hold for arbitrary initial conditions of the donor. In particular, excitonic coherence in the acceptor (and thus coherent beating) is triggered even when the initial condition in the donor has no such excitonic coherence.

A simple example of the usefulness of the ICC basis is to determine the initial conditions for electronic excitation transfer through the FMO complex. The recently discovered 8th chromophore [7, 148] provides a plausible donor to the remainder of the complex since it sits on the side nearest the chlorosome antenna complex [20]. Since structural information concerning the location of the FMO complex is limited, standard practice to date has been to choose initial and final conditions for simulation of energy transfer in FMO based on approximate orientation and proximity of chromophores. The choice of such initial conditions has varied [2, 20, 96], particularly with regards to whether or not the initial quantum states include any excitonic coherence. Evaluation of the ICC basis between a donor complex consisting solely of site 8 and an acceptor complex consisting of the remainder of the complex (sites 1-7) implies that the acceptor state is mostly localized on site 1 (see Appendix 3.7.5). We illustrate this in Figure 3.1(a). This initial condition is not an energy eigenstate, so the resulting \textit{in vivo} dynamics would necessarily start from a state with coherence in the exciton basis and thus give rise to the quantum beating seen in the laboratory experiments [44].

3.3 Coherent versus thermal transport in a model dimer with an energy gradient

The way in which this coherence regenerating transfer mechanism can yield a non-trivial biological role for coherence can be already illustrated with a simple model dimer complex connected to other complexes. Choosing inter-complex couplings to and from the dimer to be at individual sites as above implies that initialization and transfer in the ICC basis will be at these sites. Consider preferred ‘forward’ excitation transfer to be that from the donor at site 2 onward to the next complex. Then the asymptotic probability of successful transfer
through the complex will be proportional to that population. For a dimer, the electronic Hamiltonian is given by

\[
H = \begin{bmatrix}
\cos \theta & \sin \theta \\
-\sin \theta & \cos \theta \\
\end{bmatrix} \begin{bmatrix} 0 & 0 \\
0 & \Delta E \\
\end{bmatrix} \begin{bmatrix}
\cos \theta & -\sin \theta \\
\sin \theta & \cos \theta \\
\end{bmatrix},
\]

where \( \theta \) is the mixing angle, which measures the intra-dimer delocalization, and \( \Delta E \) the exciton energy difference. A non-zero mixing angle corresponds to non-zero exciton delocalization, as indicated by the inverse participation ratio \( N = 1/(\sin^4 \theta + \cos^4 \theta) \).

The dimer admits two extreme models of energy transfer: quantum beating due to coherent evolution and instantaneous relaxation to thermal equilibrium between excited electronic states. Instantaneous relaxation provides an upper bound on the speed of excitation transfer governed by a classical master equation, since the dynamics governed by such equations are driven toward thermal equilibrium. This is imposed by the requirement of detailed balance which governs classical dynamics, whether between sites as in Förster theory [84] or between exciton populations as in variants of Redfield theory [155]. For instantaneous relaxation to the thermal distribution, the probability that site 2 is occupied is independent of the initial condition:

\[
p_{2\text{th}}^\text{th} \propto \langle 2|e^{-\beta H}|2 \rangle = \cos^2 \theta + e^{\beta \Delta E} \sin^2 \theta,
\]

(3.6)

In contrast, boosts in population due to quantum beating are not restricted by such classical limits [79, 29, 76]. For coherent motion with initialization at site 1, the time-averaged probability of an excitation at site 2 is

\[
p_{1\rightarrow 2}^\text{coh} = \langle |1|e^{-iHt}|2 \rangle_t = 2 \cos^2 \theta \sin^2 \theta,
\]

(3.7)

while for initialization at site 2, we have \( p_{2\rightarrow 2}^\text{coh} = 1 - p_{1\rightarrow 2}^\text{coh} \). Figure 3.3 plots the difference between coherent and thermal population on site 2, as a function of both the intra-dimer delocalization measure \( \theta \) and energy difference \( \Delta E \), for both possible initial conditions. It is evident that regardless of initial conditions, for a sufficiently uphill energetic arrangement (\( \Delta E > 0 \)) intra-dimer quantum beating will be asymptotically more effective than intra-dimer thermalization in enabling transfer onward from the complex via site 2. The location of the FMO parameters in Fig. 3.3 shows that the 1-2 dimer of FMO satisfies such an arrangement at 77 K and is on the borderline for strictly enhanced transfer due to coherence at room temperature.

3.4 Design for biomimetic ratchet

The asymmetry between incoherent and coherent population transfer seen above for a simple model dimer suggests a design principle that could be exploited for enhanced unidirectional transfer [75] and, more generally, a novel type of ratchet based on quantum dynamics [120].
Ratchets and Brownian motors\cite{57} utilize a combination of thermal and unbiased non-equilibrium motion to drive directed transport in the presence of broken symmetry. To take advantage of such a ratchet effect, strongly linked chromophores with coherent transfer not limited by detailed balance should have an uphill energy step relative to the desired direction of transport, whereas weakly linked chromophores with incoherent transfer steps should be arranged downhill.

As a proof of principle, we present an example in which this coherent ratcheting effect results in asymptotic spatial bias of transport. Consider a weakly linked chain of heterodimers breaking spatial inversion symmetry, as illustrated in Figure 3.4(a). In any classical random walk, transition rates must satisfy detailed balance to assure thermal equilibrium. This guarantees that a classical walk along such a chain is unbiased (Appendix 3.7.3). However, we have carried out 2CTNL quantum simulations on small chains of dimers that suggest that including the effects of coherence in each dimer breaks the symmetry of detailed balance to yield a non-zero drift velocity. Since simulations with the 2CTNL approach would be computationally prohibitive for large numbers of dimers, these simulations were carried out on a chain of three weakly linked dimers with parameters for each dimer matching those of the 1-2 dimer of FMO used earlier and an inter-dimer coupling of $15$ cm$^{-1}$. We note that this inter-complex coupling strength is well below the cut-off below which energy transport in light harvesting complexes is usually described by completely incoherent hopping within Förster theory, though without the possibility of coherence regeneration\cite{14,35}. The results of these simulations are used to define left and right inter-dimer transition rates for the central dimer. These are then used together with ICC initial conditions from our analysis of the inter-complex coupling as input into a generalized classical random walk describing

Figure 3.3: Difference between coherent and thermal populations on site 2, $p_{2}^{\text{coh}} - p_{2}^{\text{th}}$, as a function of dimer Hamiltonian parameters for (a) initial site $i = 1$ and (b) initial site $i = 2$. The empty symbols $\Box$ and $\Diamond$ indicate location of parameters for the 1-2 dimer in the FMO complex of \textit{C. tepidum} at 300 K as determined in Refs.\cite{2} and \cite{35} respectively. Filled symbols indicate the corresponding parameters at 77 K.
energy transfer along the chain of dimers. The physical model corresponds to the chain shown in panel (a) of Figure 3.4 with red sites (dimer internal site 1) at energy zero, while blue sites (dimer internal site 2) are at energy $120 \text{ cm}^{-1}$. Full details of the construction of transition rates and of the set up and solution of the generalized random walk are described in Appendix 3.7.4.

Formally, this theoretical approach corresponds to using the microscopic quantum dynamics within and between complexes to define state-specific rates between complexes that generate ‘quantum state controlled’ incoherent energy transfer dynamics over long distances. A feature of this simulation strategy is that we have \textit{a priori} eliminated the possibility of reaching true thermal equilibrium, since we do not include the long range coherence terms between different dimers. However, it is reasonable to expect the long term influence of such coherences to be negligible, since the inter-dimer couplings are very small. We choose this hybrid approach to the excited state dynamics since we wish to base our simulations on numerically exact calculations, made here with the 2CTNL method that is valid in both limits of strong and weak environmental couplings [76].

These quantum state controlled incoherent dynamics can generate a significant bias in the

Figure 3.4: Biased energy transport in an excitonic wire due to spatial propagation of coherence. (a) A weakly linked chain of heterodimers is arranged such that the higher energy state is always to the right, with a typical inter-dimer distance of 3 nm. The arrow indicates the direction of biased transport. (b) Relative asymmetry between left and right inter-dimer transfer rates (Eq. (3.42) of Appendix 3.7.4) as a function of the time before transferring for a dimer excitation initialized in the asymptotic distribution of site populations. (c) Drift velocity vs coherence time as modified by bath correlation time (squares) and cross correlation coefficient between dimer sites (diamonds). The dashed line is a linear fit to guide the eye. Full details of the simulations in panels b and c are in Appendix 3.7.4.
spatial distribution of excitation transfer when the intra-dimer dynamics display long lasting quantum coherence. We analyzed the random walk with both Monte Carlo simulations on long finite chains and an analytic solution \[46\] of the asymptotic mean and variance of the distribution, as detailed in Appendix 3.7.4. Figure 3.4(b) shows that the underlying asymmetry of transfer rates and violation of detailed balance dynamics is due to the non-equilibrium state of the donor. The bias is in the forward direction, corresponding to the uphill step within dimers. Figure 3.4(c) plots the asymptotic drift velocity of the random walk against the timescale of excitonic coherence. We determine this coherence time from a best fit of the timescale of exponential decay of intra-dimer excitonic coherence. The timescale of coherent oscillations was tuned in two ways, (i) by changing the bath correlation time and (ii) by increasing the spatial correlations between the chromophore-bath couplings \[74\]. We see a close correlation between the timescale for quantum beating and the magnitude of the bias, regardless of the underlying physical mechanism used to tune the coherence time. In general, we cannot rule out the possibility that a non-equilibrium/non-Markovian classical model might also yield such biased transport. (We already ruled out such a possibility for a Markovian classical model in Appendix 3.7.3.) However, this strong correlation between the duration of quantum beating, independent of its origin, and the asymptotic transport bias supports our interpretation that in this model system the ratchet effect is due to quantum coherent motion. Indeed, the fact that the drift velocity appears to approach a small or zero value as the coherence time goes to zero in Figure 3.4(c) shows that any contribution deriving from classical non-equilibrium system/non-Markovian bath dynamics here is extremely small relative to that deriving from the quantum coherence maintained in the system degrees of freedom.

Since our results demonstrate a ratchet effect, it is important to consider why this sort of motion is not forbidden by the second law of thermodynamics. The answer is that the system is never allowed to reach thermal equilibrium along the infinite chain of dimers. This feature is shared by the excitations transferred in natural light harvesting systems, which also do not exist for long enough to reach equilibrium. The resulting directed motion shows some similarity to the operation of a quantum photocell \[136\], where coherence can (in principle) allow for enhanced conversion of energy by similarly breaking a limit imposed by detailed balance. In both cases, no additional source of energy is supplied besides that of the non-equilibrium photon which creates the initial excitation. This contrasts with the operation of typical classical and quantum brownian motors \[57\], where detailed balance is broken by applying an additional driving force.

Our results for an infinite chain of heterodimers confirm the effectiveness of our ratchet for energy transfer, which we ascribe to the combination of intra-complex excitonic coherence within dimers and an uphill intra-complex energy gradient. The non-zero drift velocity means that over long distances this ratchet offers a quadratic improvement in transfer times over any corresponding classical walk, which is unbiased (Appendix 3.7.3). However, in contrast to the speedup offered by quantum walks \[68\], this ratchet requires only short ranged and short lived coherences that will be resilient to the static and dynamic disorder of biological environments. This spatial bias constitutes a preferential direction for the energy flow across
CHAPTER 3. SPATIAL PROPAGATION OF EXCITONIC COHERENCE

Figure 3.5: Simulations of FMO dynamics at room temperature. (a) Population of dominant ICC donor state at site 2 in the 1-2 dimer \(|\tilde{D}_2\rangle\langle\tilde{D}_2|\), solid line) compared with the rate of population change of its ICC acceptor state in the 3-7 complex \(|\tilde{A}_2\rangle\langle\tilde{A}_2|\), dashed line) and the rate of population change of the other ICC acceptor state not coupled to this donor state \(|\tilde{A}_1\rangle\langle\tilde{A}_1|\), dash-dotted line), for the initial condition is \(|\psi_0\rangle = |1\rangle\). The time derivatives have been scaled to aid comparison of correlations. (b) Population of site 2 relative to the total 1-2 dimer population, \(p_2/(p_1 + p_2)\), for both choices of initial conditions.

3.5 Role of coherent energy transport in the Fenna-Matthews-Olson complex

We now specifically consider the role of the coherent dynamics in the uphill step energy of the FMO complex, which corresponds to the 1-2 dimer in the usual notation (see Fig. 3.1). Since the 1-2 dimer is relatively weakly coupled to the other chromophores in the complex, we may consider transfer to and from this dimer on the basis of our perturbation analysis using ICC states. By performing a singular value decomposition of the appropriate coupling matrices (see Appendix 3.7.5), we find that the dominant couplings to and from this dimer are from site 8 to site 1, and from site 2 to site 3. This suggests the relevance of our dimer model from Section 3.3, where site 8 acts as a donor to the 1-2 dimer, and site 2 in turn acts as a donor to the 3-7 complex. Figure 3.5(a) presents results of a 2CTNL simulation on sites 1-7 of FMO, partitioning FMO between donor state on the 1-2 dimer and acceptor states on the remaining sites 3-7 (i.e., neglecting the prior donation from the 8th site to the 1-2 dimer). The corresponding ICC donor/acceptor states are given in Appendix 3.7.5 (Eqs. 3.47–3.48). We see that the ICC donor population \(|\tilde{D}_2\rangle\langle\tilde{D}_2|\approx |2\rangle\langle2|\) is positively correlated with the rate of growth of its coupled ICC acceptor \(|\tilde{A}_2\rangle\langle\tilde{A}_2|\), but negatively correlated with the growth of
the other ICC acceptor state $|\tilde{A}_1\rangle\langle\tilde{A}_1|$, to which it is not coupled. This is in agreement with the predictions of our theory from Section 3.2. (The small deviations arise because FMO is not quite in the regime of validity for the perturbation theory and because Eq. (3.5) is not strictly valid for the situation with two acceptor states $|\tilde{A}\rangle$.) The simulation is performed at 300 K for a bath correlation time of 50 fs as described previously [75].

As indicated by the location of the FMO 1-2 dimer Hamiltonian parameters in Figure 3.3, this particular chromophore dimer appears to be optimized to have an uphill energy gradient just large enough so that excitonic coherence enhances transfer if initialized at site 2 (panel a) without also suppressing transfer initialized at site 1 (panel b). In Figure 3.5(b) we compare the portion of dimer population on site 2 from 2CTNL calculations with the classical upper bound of the thermal average, for initial conditions in both of the ICC states $|1\rangle$ and $|2\rangle$. The populations show quantum beating deriving from partially coherent motion. The populations also agree with the predictions of our simple dimer model (Section 3.3): the population at site 2 averaged over quantum beats (Eq. (3.7)) is nearly equal to the thermal average (Eq. (3.6)) for initialization at site 1 and greater than the thermal average for initialization at site 2.

As evident from Fig. 3.5, these temporary boosts in population at site 2 due to coherence should correspond to enhanced biological function, since they drive excitations preferentially toward site 3 instead of backwards toward the antenna complex. The 1-2 dimer in the FMO complex thus appears to act as one link of our proposed ratchet for energy transport, thereby enhancing unidirectional energy flow through this pathway of the FMO complex. Consistent with previous numerical estimates of the contribution of coherent energy transfer to transfer efficiency in photosynthetic systems [117, 154], we expect that any quantitative enhancement to the speed of energy transfer through FMO due to such a limited ratchet effect will be relatively small compared to the contribution of incoherent energy relaxation. Refining such estimates is not the purpose of this work. Rather, our new dynamical model of transport between ICC states allows us to propose specific physical advantages that the electronic coherence provides for general light harvesting systems. In particular, we established the ability to propagate excitonic coherence between weakly coupled sub-units and to use the ratchet effect to enhance unidirectional transport. It is also conceivable that the cumulative contribution of many such small contributions from propagating coherence through the entire photosynthetic apparatus of green sulphur bacteria (of which FMO is only a small part) could indeed make a major contribution to the speed of energy transfer, as in the full ratchet example.

## 3.6 Conclusions

We have proposed a microscopic mechanism for the propagation of excitonic coherence in energy transfer between photosynthetic complexes. The mechanism allows coherence to be propagated between sub-units of a large light harvesting “supercomplex” that is composed of multiple complexes that individually support coherence. Our analysis shows that the
key role in the inter-complex transfer is played by the inter-complex coupling (ICC) basis, rather than energy or site bases employed by prior analyses. By utilizing ICC donor and acceptor states, we showed that coherence can enable biased energy flow through a ratchet mechanism. We provided evidence that this same principle acts to ensure unidirectional energy flow in the FMO complex. Since one-way transmission of electronic energy from the antenna complex to the reaction center constitutes the main function of the FMO protein in the light harvesting apparatus of green sulfur bacteria, this supports a biological role for the electronic quantum coherence in this particular light harvesting system.

Propagating coherence provides both a mechanism by which coherent motion can influence transfer rates and photosynthetic efficiency in light harvesting systems of arbitrary size (a possible quantum advantage), and a scalable method for multi-scale modeling of such excitonic systems without neglecting the contributions of coherence (practical simulations). Our example and analysis of a coherently enabled ratchet effect along a chain of heterodimers demonstrates both of these features. This proof of principle model shows that even short-lived excitonic coherence can, since it propagates spatially, lead to large scale dynamics that are incompatible with any completely classical description. We also demonstrated how fully quantum models need only to be used for tightly coupled sub-complexes, while transfer between sub-complexes may take the form of classical hops with connections between states of different sub-complexes constrained by the ICC basis.

Similar techniques should allow us to assess the role of coherence in natural photosynthetic super-complexes with hundreds of chlorophyll molecules, such as arrays of LH1 and LH2 rings in purple bacteria, and the photosystem I and II super-complexes of higher plants [9]. For example, direct calculation of ICC states should help us evaluate the significance of long lasting coherences in bacterial reaction centers [86, 87], since these systems are also usually unlikely to absorb light directly [9] and thus might be benefitting from recurrence of coherence propagated from light harvesting complexes. Some bacterial reaction centers also feature an uphill step opposing the direction of desired energy flow [147], resembling the energetic arrangement in the uphill step of the FMO complex.

Finally, the dynamics in our chain of heterodimers model constitute a novel type of ratchet that utilizes spatial propagation of quantum coherence in place of a driving force and as such are also of more general interest. Thus, in addition to excitonic systems, we expect that a similar ratchet effect could be demonstrated in other experimental systems described by spin-boson Hamiltonians, such as cold atoms in optical lattices [137, 119].

3.7 Appendices

3.7.1 Extending multichromophoric Förster theory

In this Appendix, we provide additional technical details of the derivation of Eqs. (3.1–3.2). Consider a system under zeroth order Hamiltonian $H_0$ with perturbation Hamiltonian $V$. In
the interaction picture \( \rho_I(t) = e^{iH_0 t/\hbar}\rho(t)e^{-iH_0 t/\hbar} \) the von Neumann equation is

\[
\frac{d\rho_I}{dt} = -\frac{i}{\hbar}[V_1(t), \rho_I(t)],
\]

which can be formally integrated to yield,

\[
\rho_I(t) = \rho_I(0) - \frac{i}{\hbar} \int_0^t dt'[V_1(t'), \rho_I(t')].
\]

Inserting Eq. (3.9) into Eq. (3.8), keeping all terms second order in \( V \) and transforming back to the Schröedinger picture yields the second order contribution to the time-convolutionless equation of motion

\[
\frac{d\rho}{dt} = -\frac{1}{\hbar^2} \int_0^t d\tau \left[ V, \left[ e^{-iH_0 \tau/\hbar} V e^{iH_0 \tau/\hbar}, \rho(t) \right] \right],
\]

where we approximated \( e^{-iH_0 \tau/\hbar} \rho(t - \tau)e^{iH_0 \tau/\hbar} \approx \rho(t) \) (valid to this order in \( V \)).

We are interested in the lowest order contribution to the donor and acceptor electronic states from a perturbative treatment of the inter-complex coupling terms with the zeroth order Hamiltonian given by that of the otherwise independent donor and acceptor complexes. Since a first order treatment of \( H_c \) gives coherences between the donor and acceptor but no population transfer, we thus consider the second order contribution. Note that our perturbation parameter is this inter-complex coupling \( H_c \) rather than the usual coupling to the bath, so our results will apply to any bath coupling strength. Substituting our perturbation \( V = H_c \) into Eq. (3.10) and tracing over the bath yields the equation of motion for acceptor states,

\[
\frac{d\sigma_{kk'}}{dt} = \sum_j \sum_{j'k''} \frac{J_{jk'}^{j'k''}}{\hbar^2} \int_0^t d\tau \text{Tr}_B \left[ J_{jk} \langle D_j | \rho_D^0 \rho_A^0 e^{-iH_0 \tau/\hbar} | D_j' \rangle \langle A_{k'} | e^{iH_0 \tau/\hbar} | A_{k'} \rangle \right.
\]

\[
\left. + \langle A_k | e^{-iH_0 \tau/\hbar} | A_{k''} \rangle \langle D_j' | e^{iH_0 \tau/\hbar} \rho_D^0 | D_j \rangle J_{jk'} \right],
\]

where we used the initial condition \( \rho = \rho_D^0 \rho_A^0 \) for a general excited donor state with the acceptor in the ground state at thermal equilibrium \[78\]. The donor equation is similar and thus omitted for conciseness. To simplify these equations, we use the following identity, which follows from the substitution \( H_0 = H_A + H_D \), by employing the cyclic properties of the trace as well as the assumptions that the donor and acceptor baths are independent and that all strictly donor and strictly acceptor terms commute,

\[
\text{Tr}_B \left[ \langle D_j | \rho_D^0 \rho_A^0 e^{-iH_0 \tau/\hbar} | D_j' \rangle \langle A_{k'} | e^{iH_0 \tau/\hbar} | A_{k'} \rangle \right] = \text{Tr}_B \left[ e^{iH_D \tau/\hbar} \langle D_j | \rho_D^0 e^{-iH_D \tau/\hbar} | D_j' \rangle \right] \text{Tr}_B \left[ e^{-iH_D \tau/\hbar} \langle A_{k'} | e^{iH_D \tau/\hbar} | A_{k'} \rangle \rho_A^0 \right].
\]
Substitution of this identity and its Hermitian conjugate into Eq. (3.11) gives a form amenable to substitution by products of acceptor and donor lineshape functions \[78\], given by

\[
I_{Ak}'(\omega) = \int_{-\infty}^{\infty} dt e^{i\omega t} \text{Tr}_B \left\{ e^{iH_A^t/\hbar} \langle Ak' | e^{-iH_A t/\hbar} | Ak \rangle \rho_A^g \right\} \tag{3.13}
\]

\[
E_{Dj}'(t, \omega) = 2 \int_0^t dt' e^{-i\omega t'} \text{Tr}_B \left\{ e^{-iH_D^t/\hbar} \langle Dj' | e^{iH_D t/\hbar} \rho_D^g | Dj \rangle \right\}. \tag{3.14}
\]

Inserting these lineshapes yields Eqs. (3.1–3.2). Explicit dependence upon \(t\) in the donor lineshape can be removed by applying the Markov approximation, that is, allowing the upper limit of this integral to be extended to infinity and assuming that the donor \(\rho_D^g\) is stationary. This would give rate expressions corresponding to those of equilibrium multichromophoric Förster theory \[78\].

We note that the result in Eqs. (3.1–3.2) shows that these equations do not necessarily conserve positivity, a feature hidden by the sum over states to determine an overall transfer rate \[78\]. This is an intrinsic limitation of the perturbative approach to inter-complex transfer. In particular, these expressions may predict the creation of non-physical acceptor coherences of the form \(\langle A_k | A_{k'} \rangle\) even without necessarily increasing both of the corresponding population terms \(\langle A_k | A_k \rangle\) and \(\langle A_{k'} | A_{k'} \rangle\). For this reason, in determining ICC states, we explicitly only consider those states which will experience population growth or decay.

### 3.7.2 Weak system-bath coupling

Under an approximation of weak system-bath coupling relative to the electronic Hamiltonian of the isolated donor \(H_D^e\), the full density matrix can be factorized in the form \(\rho(t) = \rho_B^eq\sigma(t)\) between the equilibrium state of the bath \(\rho_B^{eq} = \rho_B^gD\rho_A^g\) and the electronic state of the system \(\sigma(t)\). We do not need to assume weak system-bath coupling for the acceptor, since it is already in factorized form in the electronic ground state. Likewise, we do not need to assume weak system-bath coupling relative to the inter-complex coupling \(H_c\), since \(H_c\) does not enter into lineshape expressions for either the donor or the acceptor. Accordingly, Eq. (3.10) becomes,

\[
\frac{d\sigma}{dt} = -\frac{1}{\hbar^2}[V, [K(t), \sigma]], \tag{3.15}
\]

\[
K(t) = \int_0^t d\tau \text{Tr}_B[e^{-iH_0\tau/\hbar}Ve^{iH_0\tau/\hbar}\rho_B^{eq}], \tag{3.16}
\]

where the explicit perturbation \(V\) is still the inter-complex coupling \(H_c\). The Markov approximation is given by taking \(t \to \infty\), in which case we write \(K = \lim_{t \to \infty} K(t)\). Since \(V\) and \(K\) are not in general equal, the Markovian expression is not in Lindblad form and thus does not necessarily conserve positivity, a standard limitation of perturbative derivations of quantum master equations \[12\].
For convenience, from now on we apply the Markov approximation. Similar conclusions hold in the more general case. We then can write Eq. (3.15) in terms of the evolution of each density matrix element as

$$\frac{d\sigma_{ab}}{dt} = \frac{1}{\hbar^2} \sum_{cd} R_{abcd}\sigma_{cd}$$

(3.17)

by defining Redfield-like tensor elements

$$R_{abcd} = -\sum_e \left[ \delta_{db} V_{ae} K_{ec} + \delta_{ac} K_{de} V_{eb} \right] + K_{ac} V_{db} + V_{ac} K_{db}.$$

(3.18)

To evaluate our particular model of inter-complex transfer, it is useful to define an acceptor lineshape that only depends upon the bath state in the same form as the donor lineshape (Eq. (3.14)),

$$E_{D}^{j'j}(\omega) = \int_{-\infty}^{\infty} dt e^{i\omega t} \text{Tr}_B \left\{ e^{iH_D^t/\hbar} |D_j'\rangle \langle D_j| e^{-iH_D^t/\hbar} \rho_D^g \right\}.$$  

(3.19)

For weak system-bath coupling and in this Markov limit, we can write the general donor lineshape $E_D(t,\omega)$ (Eq. (3.14)) in terms of this modified lineshape,

$$E_{D}^{j'j}(\infty,\omega) = \sum_{j''} E_{D}^{j'j}(\omega)\sigma_{jj''}.$$  

(3.20)

Since $K$ is Hermitian, to evaluate the model of Section 3.2 it suffices to calculate $K_{jk} = \langle D_j|K|A_k\rangle$. Using the cyclic property of the trace and inserting the donor and acceptor lineshapes, we find

$$K_{jk} = \frac{1}{4\pi} \sum_{j'k'} J_{jk'} \int_{-\infty}^{\infty} d\omega E_{D}^{j'j}(\omega) I_{A}^{k'k}(\omega).$$  

(3.21)

We can now evaluate the tensor elements in Eq. (3.18) that specify the influence of donor density matrix elements on inter-complex transfer, either by using the matrix elements for $K$ given in Eq. (3.21) or by using the equivalence in Eq. (3.20) to insert the modified donor lineshape into Eqs. (3.1–3.2). The relevant tensor elements for the change of the acceptor elements due to the donor are given by,

$$R_{kk'j'o} = \sum_{j''k'} J_{jk''} \int_{-\infty}^{\infty} d\omega \left[ J_{jj'k''} E_{D}^{j'o}(\omega) I_{A}^{k'k''}(\omega) + J_{j'k} E_{D}^{j'o}(\omega) I_{A}^{k'k''}(\omega) \right].$$

(3.22)

and for the change of the donor itself due to donating an excitation,

$$R_{jj'j'o} = -\sum_{kk'j''} J_{j'k'} \int_{-\infty}^{\infty} d\omega \left[ \delta_{jj'o} J_{jk} E_{D}^{j''o}(\omega) I_{A}^{k'k}(\omega) + \delta_{jj'o} J_{j'k} E_{D}^{j''o}(\omega) I_{A}^{k'k}(\omega) \right].$$

(3.23)
Since these tensor elements are given in terms of an arbitrary basis for the donor and acceptor electronic states, we may write them in terms of the ICC states for which $J$ is diagonal. Considering the elements that affect populations ($k = k'$ for acceptor, $j = j'$ for donor), it is then evident that in the ICC representation, the factors $J_{j_0k}$ restrict nonzero contributions from donor states $j$ to only those deriving only from the coupled donor ICC state $|D_{j_0}\rangle \langle D_{j_0}|$. Each of these terms also includes a sum over other inter-complex coupling matrix elements and lineshapes, but these only affect the magnitude of the allowed transitions. In the case where there is only a single nonzero ICC coupling, Eq. (3.17) thus reduces to Eq. (3.5) of the main text.

Note that since our donor and acceptor lineshapes (Eq. (3.19) and Eq. (3.13)) take identical forms under weak environmental coupling, resulting forward and backward transfer rates will be equal and thus may not necessarily respect detailed balance. Therefore we do not calculate actual rates using Eq. (3.19).

### 3.7.3 Proof that classical Markovian transport is unbiased

Consider a classical Markov process that models transport along a chain of dimers like the chain we used for the quantum coherent ratchet model (Figure 3.4). We impose only one requirement on the transition rates in this model: thermal equilibrium must be a steady state. For a Markov process, this implies that the transition rates satisfy detailed balance. On each dimer, we consider two states in the single excitation subspace, which could equally well be sites or excitons. For simplicity, consider excitation transfer only between nearest-neighbor states (similar symmetry constraints guarantee unbiased transport even in the general case). Then an excitation initially at the lower energy state of each dimer has two possible moves: with probability $p$ to the higher energy state of the same dimer, or with probability $1 - p$ to the higher energy site of the neighboring dimer to the left (the non-zero coupling guarantees that eventually the excitation will move). For an excitation at the higher energy state of a dimer, detailed balance requires that the rate of transitions to each neighboring state (at the lower energy) is the rate from those states scaled by the Boltzmann factor $e^{\beta \Delta E}$. The relative intra- vs inter-dimer transition rates are still the same, so the probability of an intra-dimer jump is still $p$, and $1 - p$ for the inter-dimer jump, now to the right. Since every jump alternates between high and low energy states, and these intra- and inter-dimer transitions are alternatively to the left and to the right, on average the random walk must be stationary.

### 3.7.4 Ratchet methods

**Propagation of coherence** With weak coupling between different dimers, inter-dimer transfer should follow the principles of our theory of propagated coherence described in Section 3.2. Here we restrict the inter-dimer coupling to be between nearest neighbors, to simplify the singular value decomposition. This is a reasonable approximation for realistic dipole-dipole couplings in light harvesting arrays because the $1/r^3$ scaling ensures a rapid fall-off with inter-chromophore distance. Accordingly, an ICC analysis tells us that after
an inter-dimer transfer the dynamics will be reset with the initial condition on the site in the dimer nearest the side from which the excitation was received. Thus if an excitation is received from the dimer to the left (right), we restart dynamics the initial condition is on the left (right) site of the new dimer. For the complex consisting of the \( n \)th dimer, this corresponds to the explicit inter-complex coupling matrix (in the ICC basis)

\[
J = \sum_{\epsilon \in \{-1, +1\}} J|n, \epsilon\rangle\langle n - \epsilon, -\epsilon|,
\]

where \( J \) is an arbitrary inter-dimer coupling strength and \( |n, \epsilon\rangle \) is the state corresponding to occupation of the right (\( \epsilon = -1 \)) or left (\( \epsilon = +1 \)) site of dimer \( n \). We also assume that upon excitation at a site in a new dimer, the baths of the donating chromophore will instantaneously revert to thermal equilibrium. Accordingly, since the chain of dimers is periodic, we can build overall dynamics in this manner from full quantum calculation of just four time-dependent transfer rates corresponding to left or right transfer to a neighboring dimer from each of the two initial conditions on sites.

**Scaled 2CTNL calculations** For computational feasibility, we based our calculations of transfer rates on scaling the results of 2CTNL simulations on a three dimer (six site) system. We may denote the left, central and right dimers as \(-1, 0, +1\), respectively. We use the 2CTNL method because it accurately models dynamics under both strong and weak environmental coupling \[76\]. Since we need to calculate rates neglecting back-transfer while these simulation methods describe full system dynamics, we calculate the dynamics here with the inter-dimer coupling \( J_0 \) set to be very small so that back-transfer was negligible.

To begin, we need cumulative transition probabilities \( F_{\epsilon\delta}^0(t) \) for the transition from initial conditions \( \epsilon \in \{+1, -1\} \) to neighboring dimer \( \delta \in \{+1, -1\} \) at time \( t \). From our simulations on the three dimer chain, the quantity \( F_{\epsilon\delta}^0(t) \) is simply the total population at time \( t \) on dimer \( \delta \) obtained by starting with initial condition on site \( \epsilon \) of the central dimer. The probability density as a function of \( t \), which is the transition rate, is then given by \( f_{\epsilon\delta}^0(t) = \frac{\partial}{\partial t} F_{\epsilon\delta}^0(t) \) and evaluated numerically. We then scale the transfer rate to obtain the rescaled rate \( f_{\epsilon\delta}(t) = (J/J_0)^2 f_{\epsilon\delta}^0(t) \) corresponding to the coupling \( J \). The rescaled cumulative transition probability is obtained by numerical integration, \( F_{\epsilon\delta}(t) = \int_0^t d\tau f_{\epsilon\delta}(\tau) \). This scaling of the transfer rate assumes that to lowest order in \( J \) the transfer rate is proportional to \( J^2 \), as given by Eq. (3.1). For our parameters, we found that the scaled transfer rate \( f_{\epsilon\delta}(t) \) does indeed converge as \( J_0 \rightarrow 0 \) and that using a value \( J_0 = 1 \text{ cm}^{-1} \) was sufficiently small to make any error negligible. This method neglects the effects of excitation loss on the dynamics of the donating dimer, which is reasonable to lowest order in \( J \). We simulated the three dimer chain using two such 2CTNL calculations, one for each initial condition on a specific site of the central dimer. Calculations including spatially correlated baths on each dimer were performed as described previously \[74\]. In principle, one could perform calculations taking into account static disorder, but we do not expect static disorder would influence our qualitative findings since the primary effect of disorder is to limit delocalization and our scaling procedure already constrains exciton delocalization to individual dimers.
CHAPTER 3. SPATIAL PROPAGATION OF EXCITONIC COHERENCE

Figure 3.6: Inter-complex transfer rates $f_{\epsilon \delta}(t)$ with initial conditions (a) $\epsilon = +1$ and (b) $\epsilon = -1$ for steps $\delta = +1$ (solid lines) and $\delta = -1$ (dashed lines). These rates are derived from 2CTNL simulations for a chain of three dimers with correlation time 50 fs and no spatial correlations, as described in the text. The transfer rates oscillate, corresponding to quantum beatings in the donor, but eventually converge to the same equilibrium rate, as required to satisfy detailed balance. However, at early times, the left ($\delta = +1$) and right ($\delta = -1$) transfer rates are not equal, oscillating out of phase. When averaged over the limiting distribution $\pi_{\epsilon}$ of the initial condition this gives rise to the marked short time asymmetry in the left and right inter-dimer transfer rates that is shown in Figure 3.4(b) of the main text. This asymmetry, although small in absolute terms, is amplified by being repeated over many hops between dimers and is responsible for the asymptotic bias of the random walk.

Figure 3.6 gives an example of these transfer rates $f_{\epsilon \delta}(t)$. The transfer rates oscillate, corresponding to quantum beatings in the donor, but eventually converge to the same equilibrium rate, as required to satisfy detailed balance. However, at early times, the left ($\delta = +1$) and right ($\delta = -1$) transfer rates are not equal, oscillating out of phase. When averaged over the limiting distribution $\pi_{\epsilon}$ of the initial condition this gives rise to the marked short time asymmetry in the left and right inter-dimer transfer rates that is shown in Figure 3.4(b) of the main text. This asymmetry, although small in absolute terms, is amplified by being repeated over many hops between dimers and is responsible for the asymptotic bias of the random walk.

**Generalized random walk** With each transition to a neighboring dimer only depending on the initial conditions at each dimer, the dynamics constitute a type of Markov chain controlled random walk known as a semi-Markov process [134]. In each step of the random walk, we start with a state of the form $|n, \epsilon\rangle$ denoting occupation of the right ($\epsilon = -1$) or left ($\epsilon = +1$) site of the $n$th dimer. The cumulative transition probabilities $F_{\delta \epsilon}(t)$ for transitioning from $|n, \epsilon\rangle$ to the left or right dimer ICC acceptor state $|n + \delta, \delta\rangle$ for $\delta = \pm 1$ (see Eq. (3.24)) are determined by the rescaled 2CTNL calculations as described above. The
update $\epsilon' = \delta$ is the initial condition for the excitation on the new dimer following from our ICC analysis. The walk is memory-less in terms of a two-dimensional clock variable $(n, t)$ denoting “space-time” position, but the initial condition at each dimer nevertheless functions as an additional “coin” degree of freedom $\epsilon$ that controls the likelihood of jumps to a new clock state $(n', t')$.

**Monte-Carlo algorithm** Given the transition probabilities $F_{\epsilon\delta}(t)$ for this random walk, we used two techniques to calculate the long time behavior of the overall random walk. First, we performed Monte-Carlo simulations of the evolution for a total time $T$ by averaging over trajectories of many jumps. We start by setting the clock to the state $(n, t) = (0, 0)$ and the coin to $\epsilon = +1$. We sample from the distribution of possible space-time shifts $\xi_{\epsilon\delta} = (\delta, t_{\epsilon\delta})$ by choosing a pair $(u_1, u_2)$ of independent uniformly distributed random numbers between 0 and 1. For convenience, we define the final transition probability $p_{\epsilon\delta} \equiv \lim_{t \to \infty} F_{\epsilon\delta}(t)$. If $u_1 \leq p_{\epsilon,+1}$, we choose $\delta = +1$ for this jump; otherwise, $\delta = -1$. The time $t_{\epsilon\delta}$ it takes for this jump is determined by numerically solving the equation $u_2 = F_{\epsilon\delta}(t_{\epsilon\delta})/p_{\epsilon\delta}$ for $t$. We then update the clock $(n', t') = (n + \delta, t + t_{\epsilon\delta})$ and the coin $\epsilon' = \delta$. This process is repeated until time $t + t_{\epsilon\delta} > T$, at which point we record the location of the previous dimer $n$ as the final state of that trajectory. The probability density of the final distribution over dimers is derived by binning over many such trajectories ($\sim 5000$). Empirically, our Monte-Carlo simulations suggest that the distribution converges to a normal distribution characterized by its mean and variance, as expected from a central limit theorem for weakly dependent variables [42].

**Analytic model** Second, we calculated the mean and variance of final distribution analytically in the asymptotic limit of the total walk time $T \to \infty$, using the method suggested in Ref. [46]. Since the results of these calculations agreed with the Monte-Carlo simulations but were much faster, we use this second method for the plots in Figure 3.4. To begin, we calculate the moments of the transition time $t_{\epsilon\delta}$ for each jump $\epsilon \to \delta$,

\[
E(t_{\epsilon\delta}) = \frac{1}{p_{\epsilon\delta}} \int_0^\infty t f_{\epsilon\delta}(t) dt \tag{3.25}
\]

\[
E(t_{\epsilon\delta}^2) = \frac{1}{p_{\epsilon\delta}} \int_0^\infty t^2 f_{\epsilon\delta}(t) dt \tag{3.26}
\]

by numerical integration. Now, note that transitions between coin states can be described as a Markov chain with transition matrix $P$ with entries given by the final transition probabilities $p_{\epsilon\delta} = \lim_{t \to \infty} F_{\epsilon\delta}(t)$ as defined above, i.e.,

\[
P = \begin{pmatrix} p_{+1,+1} & p_{+1,-1} \\ p_{-1,+1} & p_{-1,-1} \end{pmatrix}. \tag{3.27}
\]

Accordingly, the limiting distribution $\pi_{\epsilon}$ over the coin space is given by the left eigenvector of $P$ with eigenvalue 1, that is, the solution $\pi$ of the equation $\pi' = \sum_{\epsilon} \pi_{\epsilon} p_{\epsilon\epsilon'}$. The quantity
\[ \pi_{\epsilon} p_{\epsilon\delta} \] gives the probability of the step \( \epsilon \rightarrow \delta \) in the limiting distribution. Recalling the definition of the space-time shift \( \xi_{\epsilon\delta} = (\delta, t_{\epsilon\delta}) \) associated with the step \( \epsilon \rightarrow \delta \), we obtain an average space-time shift \( \bar{\xi}_{\epsilon\delta} = (\delta, \mathbb{E}(t_{\epsilon\delta})) \) for this step. Since the coin will converge to the limiting distribution \( \pi_\epsilon \), we now obtain the average space-time shift over all steps as

\[ \bar{\xi} = \mathbb{E}(\xi) = \sum_{\epsilon\delta} \pi_{\epsilon} p_{\epsilon\delta} \bar{\xi}_{\epsilon\delta} \equiv (\bar{n}, \bar{t}). \] (3.28)

Now let \( n_T \) denote the spatial position of the random walk after a total time \( T \). This random walk is the sum of \( T/\bar{t} \) independent steps on average, each of which has an average spatial shift \( \bar{n} \). Since the expectation adds linearly, we then obtain the average position of the overall walk as

\[ \mathbb{E}(n_T) = \bar{n}T/\bar{t}. \] (3.29)

Figure 3.4 plots the corresponding drift velocity \( v = \mathbb{E}(n_T)/T \).

Given that our random walk appears to converge to a normal distribution, we can fully characterize the distribution with its mean, calculated above, and its variance. As a practical matter, the variance indicates the width of the distribution and thus determines whether or not a non-zero drift velocity would be observable experimentally. To calculate the variance, we consider two sources of space-time deviations,

\[ \eta_{\epsilon\delta} = \xi_{\epsilon\delta} - \bar{\xi}_{\epsilon\delta} \] (3.30)
\[ \mu_{\epsilon\delta} = \bar{\xi}_{\epsilon\delta} - \bar{\xi}, \] (3.31)

corresponding to deviations \( \eta_{\epsilon\delta} \) of the space-time shift of a particular transition from its average value, and deviations \( \mu_{\epsilon\delta} \) of the average space-time shift for a particular transition from the average space-time shift over all transitions. Since successive steps are weakly correlated by the ICC conditions, the latter quantity must be averaged over all possible steps in all possible trajectories. We therefore define \( \bar{\mu} \) as the single step average obtained by summing \( \mu_{\epsilon\delta} \) over all possible sequential steps:

\[ \bar{\mu} = \lim_{n \to \infty} \frac{1}{n} \sum_{i=1}^{n} \mu_{\epsilon_i \delta_i}. \] (3.32)

Note that for a standard Markov chain with no correlation between steps, this single step average reduces to \( \mu \). Assuming the covariation between \( \eta_{\epsilon\delta} \) and \( \bar{\mu} \) is small, we can combine them to calculate the overall space-time covariance matrix,

\[ \text{Var}(\xi) = \text{Var}(\xi - \bar{\xi}) \]
\[ = \text{Var}(\eta + \bar{\mu}) \] (3.34)
\[ = \text{Var}(\eta) + \text{Var}(\bar{\mu}). \] (3.35)
Averaging over the limiting distribution \( \pi_\epsilon \), we find for the first contribution to the variance,
\[
\text{Var}(\eta) = \sum_{\epsilon \delta} \pi_\epsilon p_{\epsilon \delta} \text{Var}(\eta_{\epsilon \delta})
\] (3.36)
where
\[
\text{Var}(\eta_{\epsilon \delta}) = \begin{pmatrix}
0 & 0 \\
0 & \text{Var}(t_{\epsilon \delta})
\end{pmatrix},
\] (3.37)
with \( \text{Var}(t_{\epsilon \delta}) = E(t_{\epsilon \delta}^2) - [E(t_{\epsilon \delta})]^2 \). Now consider the second contribution to the variance, \( \text{Var}(\bar{\mu}) \). The variance of the single step average \( \bar{\mu} \), Eq. (3.31), introduces a double sum over products of deviations \( \mu_{\epsilon \delta} \). With a correlated random walk, the products of deviations at different space-time values are also correlated and hence evaluation of these requires enumeration of all possible jumps connecting them, where these are determined by the transition probability matrix \( P \), Eq. (3.27). This enumeration, which constitutes a multi-state generalization of the variance for weakly dependent processes [42], is given explicitly by
\[
\text{Var}(\bar{\mu}) = \sum_{\epsilon \delta} \pi_\epsilon p_{\epsilon \delta} \mu_{\epsilon \delta}^T \mu_{\epsilon \delta} + \sum_{\epsilon \delta \rho \sigma \ m \geq 0} \pi_\epsilon p_{\epsilon \delta} p_{\delta \rho}^{(m)} p_{\rho \sigma} \left[ \mu_{\epsilon \delta} \mu_{\rho \sigma} + \mu_{\rho \sigma}^T \mu_{\epsilon \delta} \right],
\] (3.38)
where \( p_{\delta \rho}^{(m)} = (P^m)_{\delta \rho} \) and we sum each variable \( \epsilon, \delta, \rho, \sigma \) over \( \pm 1 \). The second term in Eq. 3.38 sums up all contributions that \( m \)-steps apart, where these are specified by the Chapman-Kolmogorov equation [12]. We note that for convenience, instead of explicitly performing the sum over \( m \), one can equivalently replace the term \( \sum_{m} p_{\delta \rho}^{(m)} \) in the equation above with \( Q_{\delta \rho} \), where \( Q = (1 - P^*)^{-1} \) and \( P^* \) is the non-equilibrium portion of \( P \), that is, with entries \( P^* = P_{\epsilon \delta} - \pi_\epsilon \). Combining Eqs. (3.36) and (3.38) into (3.36) yields a space-time covariance matrix \( \text{Var}(\xi) \) for the two dimensional shift variable \( \xi \). This covariance matrix has explicit entries,
\[
\text{Var}(\xi) = \begin{pmatrix}
\text{Var}(n) & \text{Cov}(n,t) \\
\text{Cov}(n,t) & \text{Var}(t)
\end{pmatrix},
\] (3.39)
To calculate the final spatial variance \( \text{Var}(n_T) \), we must take into account the uncertainty associated with the number \( m \) of discrete hops that happened in time \( T \), in addition to the uncertainty over \( n \). To correctly incorporate both contributions, we calculate the variance of the spatial displacement \( n \) over a single coin shift over the full two-dimensional coin space,
\[
\text{Var}(n_{t})(n) = \text{Var}(n_{t})(n - \bar{n}/\bar{t})
\]
\[
= \text{Var}(n) - 2(\bar{n}/\bar{t}) \text{Cov}(n, t) + (\bar{n}/\bar{t})^2 \text{Var}(t)
\]
\[
= (1, -\bar{n}/\bar{t}) \text{Var}(\xi)(1, -\bar{n}/\bar{t})^T,
\] (3.40)
where in the first step we subtracted the average value of \( n \) over the coin space. We write the variances over the full coin space \( (n, t) \) to emphasize that they are distinct from terms like
Var(n), which is only over the spatial degree of freedom n. Since the variance adds linearly over \( m \approx T/\bar{t} \) independent steps, we obtain the variance of the distribution after time \( T \) as

\[
\text{Var}(n_T) = (1, -\bar{n}/\bar{t}) \text{Var}(\xi)(1, -\bar{n}/\bar{t})^T T/\bar{t}.
\]

(3.41)

The diffusion coefficient for the walk is then given as \( D = \text{Var}(n_T)/2T \).

Figure 3.7 plots the full results of scans over correlation time and cross-correlation coefficients used to create Figure 3.4 of the main text. We see that the width of the excitation transfer distribution is approximately constant over all parameter choices at about 60 nm after 1 ns, and that the asymmetry between initial conditions \( \Delta \pi = \pi^+ - \pi^- \) accounts for most of the variation in drift velocity. Figure 3.4(b) of the main text is a plot of the relative transfer rate asymmetry for the limiting distribution of the initial condition \( \pi_{\epsilon} \),

\[
A(t) = \frac{\sum_{\epsilon,\delta} \pi_{\epsilon} \delta f_{\epsilon,\delta}(t)}{\sum_{\epsilon,\delta} \pi_{\epsilon} f_{\epsilon,\delta}(t)},
\]

(3.42)

where the sums are over \( \epsilon, \delta \in \{-1, +1\} \) as usual.

3.7.5 FMO Hamiltonian and singular value decompositions

The FMO complex exists in a trimer arrangement, where each monomer contains 7 bacteriochlorophyll molecules, and three additional BChl molecules (termed the 8th BChl for each of the three monomers) are each located between a distinct pair of monomers [148]. In this paper, we use a Hamiltonian for a monomer of the FMO complex of \( C. \ tepidum \) calculated by Adolphs and Renger [2], augmented by dipole-dipole couplings to the 8th BChl site calculated using their same methodology with the crystal structure of Tronrud et al. [148]. We assign each of the three BChl 8 pigments to the monomers with which they have the strongest dipole-dipole coupling. The Hamiltonian matrix is given below in units of \( \text{cm}^{-1} \) above 12210 cm\(^{-1} \), where elements of the matrix are indexed according to site from 1 to 8:

\[
\begin{bmatrix}
200 & -87.7 & 5.5 & -5.9 & 6.7 & -13.7 & -9.9 & 37.5 \\
-87.7 & 320 & 30.8 & 8.2 & 0.7 & 11.8 & 4.3 & 6.5 \\
5.5 & 30.8 & 0 & -53.5 & -2.2 & -9.6 & 6. & 1.3 \\
-5.9 & 8.2 & -53.5 & 110 & -70.7 & -17. & -63.3 & -1.8 \\
6.7 & 0.7 & -2.2 & -70.7 & 270 & 81.1 & -1.3 & 4.3 \\
-13.7 & 11.8 & -9.6 & -17. & 81.1 & 420 & 39.7 & -9.5 \\
-9.9 & 4.3 & 6. & -63.3 & -1.3 & 39.7 & 230 & -11.3 \\
37.5 & 6.5 & 1.3 & -1.8 & 4.3 & -9.5 & -11.3 & ?
\end{bmatrix}
\]

(3.43)

The energy of site 8 is marked with a question mark to indicate that it is unknown, since it has not been calculated. Accordingly, our simulations of the full FMO complex use only the portion of this Hamiltonian for sites 1-7, as in previous studies [75].

To determine donor and acceptor ICC states for a given coupling matrix \( J \), we perform the singular value decomposition \( J = U_D J U_A = \sum_l \hat{A}_l \langle \hat{D}_l | \rangle \langle \hat{A}_l | \) as described in Section 3.2.
Here are the results of two examples we use with our FMO Hamiltonian. Let the notation $J^A_D$ denote the coupling matrix from the donor (D) rows and the acceptor (A) columns of Eq. (3.43). As plotted in Figure 3.1 for the coupling from site 8 to sites 1-7, we have $J^D_A = J_s |D^*\rangle \langle A|$ with

$$J_s = 41.9 \quad |D^*\rangle = |8\rangle \quad |A^*\rangle = \begin{bmatrix} -0.912 \\ -0.158 \\ -0.031 \\ 0.043 \\ -0.105 \\ 0.229 \\ 0.275 \end{bmatrix}, \tag{3.44}$$

with entries $\langle i|A^*\rangle$ for states $|i\rangle = |1\rangle, \ldots, |7\rangle$. With only a single donor site, the ICC acceptor (donor) state from the singular value decomposition is as simple as the normalized vector corresponding to the dipole-dipole matrix. Since occupation probabilities correspond to these amplitudes squared, the acceptor among sites 1-7 is mostly (83%) on site 1, as shown in Fig. 3.1(a).

A less trivial example is given by considering the 1-2 dimer as a donor to and acceptor from the remainder of the complex 3-8. In this case, we have $J^{3\rightarrow 8}_{1\rightarrow 2} = \sum_{i=1,2} \tilde{J}_i |\tilde{D}_i\rangle \langle \tilde{A}_i|$ with

$$\tilde{J}_1 = 43.6 \quad |\tilde{D}_1\rangle = \begin{bmatrix} -0.969 \\ -0.247 \end{bmatrix} \quad |\tilde{A}_1\rangle = \begin{bmatrix} -0.297 \\ 0.085 \\ -0.153 \\ 0.238 \\ 0.196 \\ -0.887 \end{bmatrix}, \tag{3.45}$$

$$\tilde{J}_2 = 34.3 \quad |\tilde{D}_2\rangle = \begin{bmatrix} 0.247 \\ -0.969 \end{bmatrix} \quad |\tilde{A}_2\rangle = \begin{bmatrix} -0.832 \\ -0.274 \\ 0.028 \\ -0.432 \\ -0.193 \\ 0.089 \end{bmatrix}, \tag{3.46}$$

with entries corresponding to states $|i\rangle$ in ascending order. Thus the coupling in the ICC basis is mostly from site 8 (78%) to site 1 (94%), and from site 2 (94%) to site 3 (69%). If
we omit site 8 from the acceptor, these acceptor and donor states are modified as follows:

\[
\tilde{J}_1 = 19.7 \quad |\tilde{D}_1\rangle = \begin{bmatrix} 0.995 \\ 0.099 \end{bmatrix} \quad |\tilde{A}_1\rangle = \begin{bmatrix} 0.433 \\ -0.257 \\ 0.342 \\ -0.633 \\ -0.479 \end{bmatrix},
\]

(3.47)

\[
\tilde{J}_2 = 34.4 \quad |\tilde{D}_2\rangle = \begin{bmatrix} 0.099 \\ -0.995 \end{bmatrix} \quad |\tilde{A}_2\rangle = \begin{bmatrix} -0.876 \\ -0.254 \\ -0.001 \\ -0.381 \\ -0.153 \end{bmatrix}.
\]

(3.48)

We use these ICC states in Fig. 3.5 since only sites 1-7 are included in the 2CTNL simulation, as the site energy of the 8th BChl is unknown (see Eq. (3.43)), and as it is furthermore unclear whether this 8th BChl is present in all cases in the natural system [148].
Figure 3.7: Full results of simulations used for analysis of the unidirectional random walk, as used to create Figure 3.4 of the main text. The parameters of each dimer match that of sites 1-2 in FMO, as described in the main text. We used a Debye spectral density with a reorganization energy of $35 \text{cm}^{-1}$ and variable bath and spatial correlations, as indicated on the figure. For the left panels we have variable time correlation and no spatial correlations. For the right panels we vary the spatial correlation (see Ref. [74]) and fix the correlation time at $50 \text{fs}$. (a,b) Drift velocity, from Eq. (3.29). (c,d) Standard deviation $\sigma = \sqrt{\text{Var}(n_T)}$ of the walk at 1 ns, from Eq. (3.41). (e,f) Coherence time $\tau$, from a least squares fit of the exponential decay of excitonic coherence, $|\rho_{e_1e_2}| \sim Ae^{-t/\tau} + B$: we evaluate this here and in Figure 3.4 for $t > 100 \text{fs}$ to exclude non-exponential decay. (g,h) Asymptotic transfer asymmetry $\Delta \pi = \pi_+ - \pi_-$ indicating the overall preference for right over left transfer.
Part II

Probing and controlling quantum coherence
Chapter 4

Inverting pump-probe spectroscopy for state tomography of excitonic systems

Summary

We propose a two-step protocol for inverting ultrafast spectroscopy experiments on a molecular aggregate to extract the time-evolution of the excited state density matrix. The first step is a deconvolution of the experimental signal to determine a pump-dependent response function. The second step inverts this response function to obtain the quantum state of the system, given a model for how the system evolves following the probe interaction. We demonstrate this inversion analytically and numerically for a dimer model system, and evaluate the feasibility of scaling it to larger molecular aggregates such as photosynthetic protein-pigment complexes. Our scheme provides a direct alternative to the approach of determining all Hamiltonian parameters and then simulating excited state dynamics.

4.1 Introduction

Ultrafast nonlinear spectroscopy allows us to experimentally observe excited state dynamics in molecular aggregates, and in particular, energy transfer essential to the function of natural light harvesting systems [98, 9, 93]. The existence of these experimental tools prompts a natural question: is it possible to use spectroscopic measurements to directly infer the excited state of such systems? A complete answer to this question would be a procedure for quantum state tomography (QST), that is, for reconstruction of the full density matrix describing the quantum state [103, 145]. State tomography is a technique that has found widespread application for validating and characterizing quantum devices designed as components for quantum computation. Such full characterization of an exciton state over multiple pigments, beyond a mere classical probability distribution, would offer information essential to understanding the explicitly quantum features of energy transport, which include coherence [44], entanglement [123] and possibly other types of non-trivial quantum dynamics [68, 67, 11]
In this work, we show that under appropriate conditions and assumptions, QST of excited states can be performed from the results of a series of pump-probe type ultrafast spectroscopies.

The most sophisticated non-linear technique for resolving energy transfer dynamics is the two-dimensional (2D) photon-echo, in which the time delays between three ultrafast pulses are manipulated to provide a 2D map between pump and probe frequencies at fixed time delays \[30, 1\]. These two-dimensional maps allow for direct visualization of the relationship between excitation and emission energies as a function of delay time. More formally, 2D spectroscopy is usually interpreted in the limit of impulsive interactions. In this approximation, it provides snapshots of the 3rd-order response function \[98\]. Important applications of 2D spectroscopy to photosynthetic systems have included resolving energy transfer pathways \[14\] and the dynamics of electronic quantum beats \[44, 129, 107, 37\]. In contrast, pump-probe spectroscopy (also known as transient absorption) is a simpler type of 3rd-order spectroscopy that historically predates 2D. In a pump-probe setup, a pump pulse excites the system, which is probed at some time later by a probe pulse. Because of its relative ease of experimental implementation, pump-probe was used to follow ultrafast energy transfer dynamics in photosynthesis long before 2D spectroscopy. For example, it provided the first evidence of electronic quantum beats in photosynthetic pigment-protein complexes, in 1997 \[126\]. Pump-probe provides less information than the 2D photon echo, because the pump-probe signal can be obtained by integrating over the excitation axis in a 2D spectra \[130\]. However, for the purposes of this work, pump-probe has a clear advantage, namely, that it can be directly interpreted as a measurement of the state created by the pump pulse. Formally, the pump dependence is entirely contained within the change in the density matrix of the system after interacting with the pump \[80\].

Recently, it was shown that a combination of photon-echo measurements of excitonic systems can be combined to perform quantum process tomography of excitonic dimers, either by using differently colored pulses \[157\] or by combining peak amplitudes from a set of 2D spectra \[156\]. Process tomography \[103, 95\] is more general than state tomography, because it specifies the full set of possible quantum evolutions for a system given any initial condition. This makes it well suited to characterizing gates for quantum computation, which are by definition designed to handle any possible input state. However, determining the full process matrix is expensive: it requires at least \(d^4 - d^2\) real parameters for a \(d\)-dimensional Hilbert space, in contrast to \(d^2\) parameters for state tomography. Moreover, for analysis of complex
molecular dynamics in condensed phases, such information, although potentially helpful, is not necessary, because most trajectories contained in the process matrix start from initial conditions that are implausible for a molecular aggregate. Indeed, typical theoretical investigations of dynamics in light harvesting systems \cite{75,142} follow dynamics after excitation for only a limited set of plausible initial states, such as the states which absorb sunlight or excitations from neighboring antenna complexes. Finally, the relative simplicity of state tomography helps to simplify consideration of new theoretical approaches to tomography, particularly because process tomography is often based on a series of state tomographies \cite{95}.

In this paper, we present a new approach to state tomography of excitonic systems based on pump-probe spectroscopy. Our approach is based on a two stage protocol that separates the easy (field based) and hard (system based) parts of the inversion process. This yields several advantages over prior approaches \cite{157,156}, including the ability to use arbitrarily shaped laser pulses and to perform the first inversion even when the second inversion is not possible. After presenting the details of each of these inversions, we demonstrate their feasibility by applying them to invert the simulated spectra of a model dimer with a Markovian environment. We close with a consideration of the conditions under which state inversion would be feasible for a natural light-harvesting system, the FMO complex of green sulfur bacteria.

4.2 Recipe for pump-probe spectroscopy

We begin by presenting the specific theoretical formalism for pump-probe spectroscopy that we propose to invert. The measured signal in any 3rd-order spectroscopy experiment, including pump-probe, is a function of the 3rd-order polarization \cite{98}. This 3rd-order polarization depends on three interactions between the applied fields and the sample, with the time-ordering of these interactions enforced by time delays of the pulses and by looking at the signal emitted in a particular phase-matched direction. For a pump-probe experiment, the first two interactions happen with the same pulse, the pump, and the last interaction is with the probe pulse. The phase-matched condition is that the signal is observed in the direction of the probe. Based on this phase-matched geometry and the response function formalism \cite{1} (see Appendix 4.7.1), we can combine the allowed time orderings to write the nonlinear polarization for a pump-probe experiment under the rotating wave approximation as

\[ P^{(3)}(t) = \int_0^\infty dt_3 R_{PP}(t_3, \rho_{PP}^{(2)}(t - t_3)) E_{mp}^+(t - t_3), \]

in terms of the pump-probe response

\[ R_{PP}(t, \rho_{PP}^{(2)}) = \frac{i}{\hbar} \text{Tr} \left[ \mu(-) G(t) V^{(+)} \rho_{PP}^{(2)} \right]. \]

This pump-probe response is of identical form to the linear response function \cite{98}, but with the electronic ground-state density matrix \( \rho_0 \) replaced by the second-order contribution to the
density matrix $\rho_{PP}^{(2)}$ that contributes to the phase-matched signal observed in a pump-probe experiment (that is, with signal wave-vector $k_S = k_{pr}$). The quantities $E_{pu}^+(t)$ and $E_{pr}^+(t)$ denote the complex envelopes of the pump and probe pulses, respectively, with $E^- \equiv (E^+)^*$. The dipole operators $\mu(-) = \sum_n d_n a_n$ and $\mu(+) = (\mu(-))^\dagger$, with $a_n$ as the annihilation operator for an electronic excitation on pigment $n$ and $d_n$ the corresponding dipole moments. The Liouville space operator $G(t)$ is the retarded material Green function for evolution for time $t$ and $V^{(\pm)} \cdot \equiv [\mu^{(\pm)}, \cdot]$. Formally, the portion of the second order contribution to the density matrix which contributes to the signal is given by

$$
\rho_{PP}^{(2)}(t) = \left( \frac{i}{\hbar} \right)^2 2 \sum_{\pm} \int_0^\infty dt_2 dt_1 G(t_2)V^{(\pm)}G(t_1)V^{(\mp)} \rho_0 E_{pu}^+(t-t_2)E_{pu}^-(t-t_2-t_1).
$$

(4.3)

In deriving Eqs. (4.1–4.3), we employed the rotating wave approximation (accurate for resonant excitation [1]) and neglected those terms from the double-quantum-coherence contribution ($k_S \neq k_{pr}$). Accordingly, we can safely neglect the possibility of multiple excitations in the calculation of $\rho_{PP}^{(2)}$. In Appendix 4.7.2 we prove that the excited state portion of $\rho_{PP}^{(2)}$ is both equal to the excited state portion of the full density matrix and is itself a valid (but unnormalized) density matrix.

The core of our proposed quantum state tomography is the sequential inversion of Eqs. (4.1), (4.3). The remainder of this section discusses additional details relevant to simulating experimental signals to test our inversion procedure. We emphasize that these expressions hold under the very general conditions, requiring only the rotating wave approximation, that all applied fields are weak and negligible overlap between pump and probe pulses. No assumptions were made concerning the shapes of these pump and probe pulses. Our decomposition here is similar to the window-doorway picture for the pump-probe signal [98], but here we have separated out the influence of the control fields, even when not in the impulsive “snapshot” limit. Related expressions in terms of a convolution of pump and probe components have been shown to facilitate analysis of pump-probe experiments with shaped probes [112].

### 4.2.1 Detection scheme and probe convolution

In a typical pump-probe experiment, the probe pulse has a fixed time-envelope, subject to a variable delay time $T$ between the two pulses. Accordingly, we may substitute $E_{pr}^+(t) = E_{pr}(t - T)$. Likewise, experimental signals are most directly interpreted in the frequency domain, so we now consider the Fourier transform of the nonlinear polarization, $P^{(3)}(\omega) = \int dt \ e^{i\omega (t - T)} P^{(3)}(t)$, calculated relative to the probe delay $T$. We can also write the pump-probe response in the Fourier domain, $R_{PP}(\omega, \rho_{PP}^{(2)}) = \int dt \ e^{i\omega t} R_{PP}(t, \rho_{PP}^{(2)})$. In terms of these quantities in the frequency domain with the explicit probe delay $T$, we can then replace Eq. (4.1) with a one-dimensional convolution,

$$
P^{(3)}(\omega, T) = \int_{-\infty}^\infty d\tau \ R_{PP}(\omega, \rho_{PP}^{(2)}(\tau)) E_{pr}^-(\tau - T) e^{i\omega (\tau - T)}.
$$

(4.4)
To obtain this relation, we substituted $t_3 = t - \tau$ and extended the lower limit of the integral in Eq. (4.1) to $-\infty$, because by definition $G(t) = 0$ for $t < 0$. We cannot simply turn this convolution into a multiplication by taking the Fourier transform of these quantities with respect to $T$, because for small or negative delay times $T$, there are contributions from signals where the pump does not necessarily interact before the probe. If $R_{PP}(\omega, \rho^{(2)}_{PP}(\tau))$ does not vary appreciably over the duration of the probe pulse, then the equation above is the Fourier transform of the probe field envelope, so we can approximate

$$P^{(3)}(\omega, T) \approx E_{pr}(\omega)R_{PP}(\omega, \rho^{(2)}_{PP}(T)). \quad (4.5)$$

In the limit of a completely impulsive probe, $E_{pr}(t) \approx E_0 \delta(t)$ and thus $E_{pr}(\omega)$ is constant, so the nonlinear polarization and the pump-probe response are equal up to a constant of proportionality.

We measure the non-linear polarization $P^{(3)}(t)$ by detecting the corresponding signal field $E_S(t) \propto iP^{(3)}(t) [98]$. Here we consider heterodyne detection, either with the probe pulse as in a standard “self-heterodyned” pump-probe setup, or with a separate local-oscillator (LO) pulse. The use of a separate local-oscillator is possible in a transient-grating setup, in which the pump pulse is replaced by two otherwise identical pumps with different wavevectors $k_1$ and $k_2$, so that the signal wavevector $k_S = -k_1 + k_2 + k_3$ does not match the probe wavevector $k_3$. Mathematically, this transient-grating signal yields the same non-linear polarization as in pump-probe, although it raises experimental complications by requiring phase-stability with an additional pulse. In heterodyne detection, the absolute value squared of the sum of the signal and local-oscillator (or probe) fields can be spectrally dispersed and measured in the frequency domain [131]. Typically, the signal field is much smaller than than of the local oscillator, so upon subtracting away the local oscillator contribution, the measured signal $S(\omega)$ is proportional to $\text{Re}[E_S(\omega)E_{LO}^*(\omega)]$, and thus

$$S(\omega, T) \propto \text{Im}[P^{(3)}(\omega, T)E_{LO}^*(\omega)]. \quad (4.6)$$

This equation is a multiplication in the frequency domain. Hence it is a convolution, and takes on similar form to Eq. (4.4) when expressed in the time-domain. In the pump-probe setup, $E_{LO} = E_{pr}$, so the signal for a fast probe given by inserting Eq. (4.5) yields

$$S(\omega, T) \propto |E_{pr}(\omega)|^2 \text{Im}R_{PP}(\omega, \rho^{(2)}_{PP}(T)). \quad (4.7)$$

In this case, the signal only depends on the imaginary (absorptive) part of the non-linear polarization $P^{(3)}$ and the pump-probe response. In the alternative transient grating setup, as long as one is still in the limit of a fast probe, applying a $\pi/2$ phase shift to the now distinct local oscillator pulse allows for obtaining the real (dispersive) part of the pump-probe response function in a similarly direct manner [131]. More generally, heterodyne detection with and without a $\pi/2$ phase shift allows for obtaining both real and imaginary parts of the non-linear polarization, respectively.
4.2.2 Pump-probe response function

To isolate the effect of the probe, the pump-probe response function given by Eq. (4.2) can be written as

$$R_{PP}(t, \rho_{PP}^{(2)}) = \text{Tr} \left[ \mathcal{P}(t) \rho_{PP}^{(2)} \right],$$  \hspace{1cm} (4.8)

with the pump-probe response operator $\mathcal{P}(t)$ defined as

$$\mathcal{P}(t) = \frac{i}{\hbar} \mu(-) G(t) V^{(+)}.$$  \hspace{1cm} (4.9)

When inserted in Eq. (4.8), the action of $\mathcal{P}(t)$ is equivalent to the action of $i/\hbar[\mu^(-)(t), \mu^{(+)}(0)]$, where $\mu^{(\pm)}(t)$ denotes $\mu^{(\pm)}$ in the Heisenberg picture. This is similar but not equivalent to a family of quantum measurements parametrized by the continuous time variable $t$ (or frequency $\omega$ in the Fourier domain), since $R_{PP}$ can be complex valued. Accordingly, the pump-probe response can be interpreted as the projection of $\rho_{PP}^{(2)}$ onto $\mathcal{P}(t)$, where these are viewed as vectors in Liouville space.

$$R_{PP}(t, \rho_{PP}^{(2)}) = \langle \mathcal{P}(t) | \rho_{PP}^{(2)} \rangle.$$  \hspace{1cm} (4.10)

Individual components $\langle \mathcal{P}(\omega) | \alpha \rangle$ of the pump-probe response operator are equivalent to the species associated spectra of the state $| \alpha \rangle$.

In most spectroscopy experiments, the signal is an ensemble measurement summed over all possible molecular orientations and static disorder of Hamiltonian parameters (inhomogeneous broadening). Accordingly, the pump-probe response in Eq. (4.2) should be replaced by its average over molecular orientations and static disorder. The orientational average can be handled elegantly using the expression for the pump-probe response in Eq. (4.8): in the magic angle $\theta \approx 54.7^\circ$ (MA) relative polarization configuration between the pump and probe pulses, the quantities $\mathcal{P}(t)$ and $\rho_{PP}^{(2)}$ can simply be replaced by their independent isotropic averages,

$$\langle R_{PP}(t, \rho_{PP}^{(2)}) \rangle_{\text{MA}} = \langle \mathcal{P}(t) \rangle_{\text{iso}} \langle \rho_{PP}^{(2)} \rangle_{\text{iso}}.$$  \hspace{1cm} (4.11)

By virtue of the properties of isotropically averaged tensors, these independent isotropic averages are equal to the average of the quantities obtained from the $xx$, $yy$ and $zz$ configurations. In contrast, the ensemble average over static disorder cannot be factorized this way in general, because under static disorder the pump-probe operator and density matrix are correlated, and altering the system Hamiltonian (e.g., to shift transition energies) changes both quantities systematically.
CHAPTER 4. INVERTING PUMP-PROBE SPECTROSCOPY

4.3 Inversion protocols

4.3.1 Deconvolution of the pump-probe signal

The first stage of our inversion protocol is a double-deconvolution to determine the complex valued pump-probe response function \( R_{PP}(T, \rho_{PP}^{(2)}) \) from the results of a series of heterodyne measurements, i.e., the signal \( S(\omega, T) \). We need such a double-deconvolution procedure because the results of heterodyne detection depend on a (trivial) convolution over the nonlinear polarization, which in turn depends on a convolution over the response function [see Eqs. (4.4) and (4.6)]. Since the excited state density matrix is entirely contained in the pump-probe response function (Appendix 4.7.2), this inversion retains all information about the quantum state. However, it is not immediately clear that the real (dispersive) part of the response function contains useful information independent of the imaginary (absorptive) part, which is the portion measured by usual pump-probe experiments.

Inverting the signal to obtain the pump-probe response function is a non-trivial but important task, since, as pointed out above, the signal is directly proportional to the response only when the probe pulse is much faster than all energy transfer dynamics. Such pulses can be difficult to realize experimentally. The need for a full inversion to obtain the response function is particularly relevant for understanding experiments which show fast oscillations due to quantum beats, whether these are of electronic, vibrational or mixed origin. In such cases, the fast probe assumption of Eq. (4.5) is not valid. We shall refer to the use of this approximate description for inversion as the “naive” approach. In contrast, a proper treatment of this inverse problem would attempt to undo the convolution in Eq. (4.4).

To address this challenge, we suggest the use of standard deconvolution techniques [60] based on general-form Tikhonov regularization (also known as ridge regression), which we describe in detail in Appendices 4.7.3 and 4.7.4. The response function can then be obtained from two sequential 1D deconvolutions. First, we invert the measured signal \( S(\omega, T) \) recorded at each choice of delay time \( T \) to obtain the nonlinear polarization \( P^{(3)}(\omega, T) \). The relationship between these signals is simple multiplication by the probe (or local oscillator) field in the frequency domain, so this step only uses the deconvolution to smooth the reconstruction along the \( \omega \)-axis. Second, we invert the nonlinear polarization \( P(\omega, T) \) with a one-dimensional deconvolution for each fixed value of \( \omega \) to obtain the response function \( R_{PP}(\omega, \rho_{PP}^{(2)}(T)) \). For this inversion, we only use experimental data with the delay between pump and probe pulses long enough so that we can ignore pulse overlap effects. Otherwise, we would be including non-pump-probe contributions to the signal. However, we nevertheless also reconstruct the pump-probe response at shorter times in order to appropriately handle boundary conditions, since the probe convolution means that these values for the response function contribute to the nonlinear polarization inside our region of interest.

This first stage in the inversion of pump-probe experiments requires only the detection results, i.e., the signal \( S(\omega, T) \), and an excellent characterization of the probe and local oscillator fields. No system information is required at all. Likewise, we have sacrificed no information from our measurement about the internal system information, including its
quantum state. Thus in principle this stage can be performed with high accuracy for any system, no matter how complex its internal degrees of freedom.

4.3.2 Obtaining the quantum state

The second step to complete the state tomography is to invert the pump-probe response function $R_{PP}(\omega, \rho_{PP}^{(2)}(T))$ to obtain the quantum state $\rho_{PP}^{(2)}(T)$. This is certainly the harder step, since it requires the ability to construct the pump-probe response of arbitrary states. The necessary information is contained in the pump-probe operator $\mathcal{P}(t)$ given by Eq. (4.9); calculating this requires both the transition dipole moments and a model for dynamics of the 1-exciton coherences between the probe and signal interactions. Essentially the same information is necessary to implement proposed algorithms for quantum process tomography [157, 156]. However, we emphasize that we do not need to know the nature of the initial state created by the pump pulse nor any details of the energy transfer dynamics in the 1-exciton subspace. The lack of required microscopic dynamical information is significant, since exact energy transfer dynamics are non-trivial to calculate from first principles [106].

Here we consider a simple protocol for state tomography, based on an assumed model for calculating the pump-probe response. It is by no means the only such possible state tomography protocol: we choose it because it is straightforward to implement, and turns out to be relatively robust to imperfections such as static disorder. To perform the inversion, we propose to extract an estimate of the excited-state electronic density matrix $\hat{\rho}_e(\tau)$ from the estimated response function $\hat{R}_{PP}(\omega_i, \tau)$ at that delay time $\tau$, for each frequency $\omega_i$ matching the single-exciton transition energies. The relationship between the vector of pump-probe response measurements and the density matrix elements at any fixed time delay is linear [see Eq. (4.10)], so as long as this map is non-singular, we can solve for the density matrix by simply applying the matrix inverse to the vector formed by these estimated response function points. It is possible that in some circumstances this reconstruction will not yield a valid density matrix, since we did not include the constraint that the reconstruction be positive semi-definite. In this case, then a best estimate to minimize the mean-squared-error of the reconstruction should be obtained using techniques based on maximum likelihood [77], although we do not encounter this issue for the examples we consider in this paper.

An additional important practical step is the choice of Liouville space in which the extracted state lies. Our results so far hold for transition dipole operators and time evolution without any particular restrictions concerning electronic vs vibrational states or the Hamiltonian we use to describe our system. However, as a practical matter for excitonic energy transfer in light harvesting systems, we are most interested in determining the electronic degree of freedom. The electronic portion of $\rho_{PP}^{(2)}$ has useful structure: namely, it only includes nonzero elements in two blocks, the 0- and 1-excitation subspaces. We denote the projection of the density matrix $\rho$ onto these subspaces by $\rho_g$ and $\rho_e$, respectively. There is only one electronic state in the 0-excitation subspace (the ground state $g$), so the electronic portion of $\rho_g$ must be in that state, $|g\rangle\langle g|$. In the Markov limit, or for delay times much longer than the bath relaxation time, the vibrational portion of $\rho_g$ will be in thermal equilibrium $\rho_{eq}^B$. 
These facts determine $\rho_g$, up to a constant of proportionality: the ground state population. Because total probability is conserved in the process of laser excitation, $\text{Tr} \rho^{(2)}_{PP} = 0$, so the ground state population is related to the excited state population by $\text{Tr} \rho^{(2)}_g = -\text{Tr} \rho^{(2)}_e$. Accordingly, we can write

$$\rho^{(2)}_{PP} = - (|g\rangle\langle g| \otimes \rho^{B}_{\text{eq}}) \text{Tr} [\rho^{(2)}_e] + \rho^{(2)}_e. \quad (4.12)$$

In this case, the pump-dependence in the pump-probe signal [Eq. (4.3)] is entirely contained in the excited state portion of the density matrix. Since for weak fields $\rho_e \approx \rho^{(2)}_e$, with Eqs. (4.10) and (4.12) we have a linear map from any excited state density matrix $\rho_e$ to the corresponding pump-probe response. For a system with $n$ electronic states, we can parameterize this unnormalized density matrix in terms of a linear combination of $n^2$ real parameters [145], since the excited state density matrix is positive (see Appendix 4.7.2) and thus Hermitian.

A brief discussion of the scalability of this approach is in order. Based on the real and imaginary parts of the pump-probe response function in the magic angle configuration, our state tomography protocol in principle has $2n$ independent real parameters from which to extract the $n^2$ real parameters (including normalization) necessary to describe an arbitrary excited state density matrix of $n$ electronic states [145]. Accordingly, we cannot necessarily expect this procedure to scale beyond a dimer ($n = 2$), for which we numerically demonstrate the success and stability of this inversion procedure in the next section. The recently proposed quantum process tomography algorithm based on peak and cross-peak amplitudes in 2D spectroscopy [156] has similar scaling difficulties. It requires determining $n^4 - n^2$ real parameters in the process matrix from at most $12n^2$ possible experimental measurements: the real and imaginary signals, $n$ coherence and $n$ rephasing frequencies, at most 3 independent polarization configurations and 2 phase-matched geometries. These estimates, however, hold only for this specific approach and with a randomly oriented ensemble. Oriented or single molecule measurements offer a much larger number of independent polarization measurements, a point we will return to Section 4.5.

### 4.4 Example: dimer model

To understand in more detail how the quantum state determines the pump-probe signal, we consider the case of the signal for a dimer of coupled pigments. In general, we can write an effective Hamiltonian for the electronic excited states of a dimer in the form

$$H_{el} = E_1 a_1^\dagger a_1 + E_2 a_2^\dagger a_2 + J(a_2^\dagger a_1 + a_1^\dagger a_2). \quad (4.13)$$

The terms $E_1$ and $E_2$ are the transition energies of sites 1 and 2, and $J$ is the pigment-pigment coupling energy. We restrict the system to at most one excitation on each site, so our state space is spanned by the set $\{|g\rangle, |e_1\rangle, |e_2\rangle, |f\rangle\}$, denoting the ground state, excitation of the first or second site, and excitation of both sites. We further assume the usual linear coupling
to a bath of phonons. Details of the bath are specified below. The electronic part of this Hamiltonian can be diagonalized by applying a unitary rotation $U$ to the single-excitation subspace, given by

$$
U = \begin{bmatrix}
\cos \theta & \sin \theta \\
-\sin \theta & \cos \theta
\end{bmatrix},
$$

(4.14)

where we defined the mixing angle $\theta = \frac{1}{2} \arctan(2J/\Delta)$ with $\Delta = E_1 - E_2$. These single excitation eigenstates are denoted $|\alpha\rangle$ and $|\beta\rangle$. The transition dipole moments for each pigment are $d_1$ and $d_2$, oriented with relative angle $\phi$.

### 4.4.1 Analytical calculation of pump-probe response

To begin, we choose a parametrization for the excited state density matrix of a dimer. In general, any valid density matrix for a two-level system can be written in any basis in form $\frac{1}{2}(I + \mathbf{r} \cdot \mathbf{\sigma})$, in terms of the Pauli matrices $\mathbf{\sigma} = \{\sigma_x, \sigma_y, \sigma_z\}$ and the Bloch vector $\mathbf{r} = \{r_1, r_2, r_3\}$, with $r_i$ real and $|\mathbf{r}|^2 \leq 1$ \[103\]. This can be straightforwardly generalized to unnormalized density matrices by adding the normalization $r_0$ and defining $\sigma_0 = I$, in which case the set of valid but unnormalized states are those that can be written in the form $\frac{1}{2}(\mathbf{r} \cdot \mathbf{\sigma})$, where $\mathbf{r}$ is now the 4-dimensional vector $\{r_0, r_1, r_2, r_3\}$ with constraints $r_1^2 + r_2^2 + r_3^2 \leq r_0^2$ and $r_0 > 0$. We will use these four real parameters to parametrize the excited state electronic density matrix $\rho_e$ for our tomography protocol, since it has population $r_0 \ll 1$. Using this representation, the total second-order correction to the electronic density matrix from Eq. (4.12) is given by

$$
\rho^{(2)}_{PP} = -r_0 |g\rangle\langle g| + \frac{\mathbf{r} \cdot \mathbf{\sigma}}{2}.
$$

(4.15)

For convenience, we suppose the state is written in terms of the eigenbasis expansion of the excited states $\{|\alpha\rangle, |\beta\rangle\}$, so the parameters $r_1$ and $r_2$ correspond to excitonic coherences and $r_3$ corresponds to the balance of population between excitonic states. In practice, the experimental signal is only known up to a constant factor, so we can only hope to be able to reliably determine the normalized excited-state density matrix, given by the usual Bloch-vector elements $\{r_1/r_0, r_2/r_0, r_3/r_0\}$.

It is now straightforward (if tedious) to write down the exact pump-probe response function in terms of microscopic parameters. For illustrative purposes, we do so here for a dimer with a Markovian bath described by Redfield theory in the secular approximation \[93\]. The time-evolution contained directly in the pump-probe response function is for times following the probe interaction, so the relevant part of the system density matrix for this evolution includes coherences between ground and singly excited states and between singly and doubly excited states. In secular-Redfield theory, coherences in the excitonic basis only evolve with exponential decay, $G(T)|a\rangle\langle b| = e^{-\gamma_{ab}T\Theta(T)}|a\rangle\langle b|$, where $G(T)$ is the retarded material Green function denoting evolution for time $T$, $\Theta$ is the Heaviside step function, and $\gamma_{ab}$ is
some complex number with positive real part. Since the formulas for the response function will accordingly be most compact in the exciton basis, we consider the excitonic transition dipole moments given by,

\begin{align}
\mu_{g\alpha} &= \mu_1 \cos \theta + \mu_2 \sin \theta, \\
\mu_{g\beta} &= -\mu_1 \sin \theta + \mu_2 \cos \theta, \\
\mu_{\alpha f} &= \mu_1 \sin \theta + \mu_2 \cos \theta, \\
\mu_{\beta f} &= \mu_1 \cos \theta - \mu_2 \sin \theta,
\end{align}

(4.16a)

(4.16b)

(4.16c)

(4.16d)

with \( \mu_i = d_i a_i \), where \( d_i \) is the component of the dipole-transition vector parallel to the probe polarization. For convenience, we define \( f_\alpha \) and \( f'_\alpha \) to denote the Fourier transform of the time evolution operator that leads to a peak in the pump-probe spectrum at frequency \( \omega_\alpha \), with decay constant \( \gamma \) or \( \gamma' \), where the prime indicates the decay constant for the transition between the 1- and 2-exciton manifolds instead of between the 0- and 1-exciton manifolds:

\[
\begin{align*}
f_\alpha &= \frac{1}{i(\omega_\alpha - \omega) - \gamma}, & f'_\alpha &= \frac{1}{i(\omega_\alpha - \omega) - \gamma'},
\end{align*}
\]

(4.17)

We define \( f_\beta \) and \( f'_\beta \) analogously, for the components peaked at \( \omega_\beta \).

Using Eq. (4.10), the calculation of the pump-probe response function for an arbitrary state is determined by the vectorized version of the pump-probe operator, \( \langle\langle P(\omega) | \rangle\rangle \). For this dimer problem, we define the pump-probe bra vector such that \( R_{PP} = \langle\langle P | r \rangle\rangle \), where \( |r\rangle = \{r_0, r_1, r_2, r_3\} \). Such a relation still holds upon substitution of \( |r\rangle \) for \( \rho_{PP}^{(2)} \), since the relation between the two given by Eq. (4.15) is linear. With this convention, evaluating the pump-probe operator in Eq. (4.9) for this dimer model described by secular-Redfield theory yields the general result (see Appendix 4.7.7),

\[
\langle\langle P \rangle\rangle \propto \begin{pmatrix}
-3\mu_{g0}^2 f_\alpha + \mu_{g3}^2 f'_\alpha - 3\mu_{g3}^2 f_\beta + \mu_{o3}^2 f'_\beta \\
-\mu_{g0}^2 \mu_{g3} (f_\alpha + f_\beta) + \mu_{o0} \mu_{o3} (f'_\alpha + f'_\beta) \\
-3\mu_{g0}^2 f_\alpha + \mu_{g3}^2 f'_\alpha - 3\mu_{g3}^2 f_\beta + \mu_{o3}^2 f'_\beta \\
-3\mu_{g0}^2 f_\alpha + \mu_{g3}^2 f'_\alpha - 3\mu_{g3}^2 f_\beta + \mu_{o3}^2 f'_\beta
\end{pmatrix}^T,
\]

(4.18)

This equation holds for each single molecule that would contribute to the pump-probe signal. We can also calculate the exact isotropic average of Eq. (4.18) over an ensemble of randomly oriented molecules. In terms of the original Hamiltonian parameters, it is given by

\[
\langle\langle P \rangle\rangle_{iso} \propto \begin{pmatrix}
(cos^2 \theta + \delta^2 \sin^2 \theta) (f'_\alpha - f_\alpha) + (\sin^2 \theta + \delta^2 \cos^2 \theta) (f'_\beta - f_\beta) + \delta \sin 2\theta \cos \phi (f'_\alpha + f_\alpha - 3f_\beta + 3f_\beta) + \delta \cos 2\theta \cos \phi (f'_\alpha + f_\alpha - 3f_\beta + 3f_\beta) \\
-\frac{1}{2} (\delta^2 - 1) \sin 2\theta (f'_\alpha + f_\alpha - f_\beta + f_\beta) + \delta \cos 2\theta \cos \phi (f'_\alpha + f_\alpha - f_\beta + f_\beta) + \delta \sin 2\theta \cos \phi (f'_\alpha + f_\alpha - f_\beta + f_\beta) \\
- \frac{1}{2} (\delta^2 - 1) \sin 2\theta (f'_\alpha + f_\alpha - f_\beta + f_\beta) + \delta \cos 2\theta \cos \phi (f'_\alpha + f_\alpha - f_\beta + f_\beta) + \delta \sin 2\theta \cos \phi (f'_\alpha + f_\alpha - f_\beta + f_\beta)
\end{pmatrix}^T,
\]

(4.19)

where \( \theta \) is the excitonic mixing angle, \( \delta = |d_2|/|d_1| \) is the ratio of the two site transition dipole moments and \( \phi \) is the angle between them. Note that neither of these equations
includes the effects of static disorder, which could be accounted for by averaging the pump-probe response function over each member of the ensemble. Formally, it does not suffice to separately average $\langle \langle P \rangle \rangle$, since under static disorder the state $| r \rangle$ also varies in correlated way (see Sec. 4.2.2).

Equation (4.19) makes it possible to determine some cases in which solving for the isotropically averaged state cannot possibly be successful, regardless of the exact inversion protocol. We can identify these cases because successful inversion requires that the elements of $\langle \langle \langle P \langle \rangle \rangle \rangle_{iso}$ be linearly independent. For example, in the homodimer case with both pigments fixed to have the same transition energies ($\theta = \pi/4$ or $\theta = 3\pi/4$) and equal transition-dipole moment magnitudes ($a = 1$), the pump-probe signal does not depend on the coherence terms, so it will be impossible to determine them ($r_1$ and $r_2$). Likewise, the coherence terms do not contribute if the transition dipole moments have identical magnitude ($\delta = 1$), and either these are oriented perpendicularly ($\cos \phi = 0$) or there are matching dephasing rates for the 0-1 and 1-2 coherences ($f_\alpha = f_\alpha'$ and $f_\beta = f_\beta'$, as occurs in the high-temperature limit). As Yuen-Zhou et al. found for the same dimer model [157], quantum process tomography also fails under similar but not identical conditions.

### 4.4.2 Numerical example

For a numerical example, we consider the dimer model used in a prior investigation of quantum process tomography [157]. We model excitation by a resonant 40 fs full-width-at-half-maximum (FWHM) pump centered at 12 800 cm$^{-1}$. The parameters in the electronic Hamiltonian are $E_1 = 12 881$ cm$^{-1}$, $E_2 = 12 719$ cm$^{-1}$ and $J = 120$ cm$^{-1}$, and the experiment is performed on an ensemble with normally distributed static disorder of standard deviation 40 cm$^{-1}$ added to each site energy. The transition dipole moments are fixed with ratio $\delta = |d_2/d_1| = 2$ and orientation angle $\phi = 0.3$. Each pigment is assumed to be coupled to an independent bath of phonons, with spectral density of the form $J(\omega) = \frac{\lambda}{\omega_c} \omega e^{-\omega/\omega_c}$ with $\omega_c = 120$ cm$^{-1}$ and $\lambda = 30$ cm$^{-1}$. The bath is assumed to be at thermal equilibrium at $T = 273$ K and is modeled by secular Redfield theory [93], including only the real (dissipative) part of the Redfield tensor.

To simulate an experimental dataset, we first calculate the non-linear polarization $P^{(3)}(\omega, T)$ for a probe of the same shape as the pump pulse, on a grid of 181 probe frequencies $\omega$ (intervals of 3.33 cm$^{-1}$ between 12 500 cm$^{-1}$ and 13 100 cm$^{-1}$) and 140 central time-delays $T$ between pump and probe pulses (intervals of 6.81 fs between 50 fs and 1 ps). From this non-linear polarization, we then calculate the results of a hypothetical heterodyne detection with a local oscillator matching the probe pulse, with and without a $\pi/2$ phase shift. Finally, we accounted for noise in detection by including additive noise with uniformly random phase and amplitude drawn from a standard deviation with width equal to $10^{-2}$ times the maximum amplitude over all delay times and frequencies of the heterodyne detected signal $S(\omega, T)$. These simulated measurements, generated for comparison both with and without detection noise, are shown in Fig 4.1 together the response function from which they are calculated.
Figure 4.1: Absorptive (left) and dispersive (right) parts of the pump-probe response function $R_{PP}(\omega, \rho_{PP}^{(2)}(\tau))$ (top) and the corresponding heterodyne detected signal $S(\omega, \tau)$ (bottom) for our dimer model system. The dashed line indicates the two exciton transition energies in this system. Only the absorptive part (left) is revealed directly by a pump-probe experiment. Obtaining the dispersive part (right) requires a transient grating setup with heterodyne detection, as described in Sec. 4.2.1.

### 4.4.3 Response function inversion

Figure 4.2 illustrates the performance of the completed double Tikhonov regularization based deconvolution algorithm for typical noisy and noise free examples of our test problem. We compare with the “naive” approach of assuming that the probe is impulsive and using Eq. (4.5) to obtain the response function by simply dividing the signal by absolute value squared of the probe field $|E_{pr}(\omega)|^2$. Table 4.1 summarizes the results of the simulated inversion for the noise free case and 1000 such noisy examples. In addition to the double Tikhonov and naive methods, we also consider the alternatives of substituting the naive approach individually for each of the two Tikhonov steps. Recall that in the first stage of the inversion ($S \rightarrow P^{(3)}$), the Tikhonov regularization serves only to smooth the data. It is not surprising then that Table 4.1 shows that the specific method chosen for this first stage (i.e., naive or Tikhonov) makes no difference for the noise free case. In the second stage
Figure 4.2: (a) Example reconstruction of the pump-probe response at fixed probe-frequency $\omega_\alpha$ for an instance of the high-noise test problem. (b) Errors in the estimated pump-probe response obtained by the direct and Tikhonov inversion methods for a single example of the low and high noise test problems. The error is given by the absolute value squared of the difference between the estimated and actual response function, $|\hat{R}_{pp}(\omega, \tau) - R_{PP}(\omega, \tau)|^2$. 
(\(P^{(3)} \rightarrow R_{\text{PP}}\)), the Tikhonov regularization also performs a deconvolution over the probe envelope.

The results in Fig. 4.2 and Table 4.1 show that the Tikhonov based inversion is a clear improvement over the naive approach, reducing the root-mean-squared-error (RMSE) by a factor of 12 for our noisy example and 1300 for our noise-free example. The noisy and noise free examples allow us to observe that the Tikhonov regularizations remove two types of errors inherent in the naive inversion: (1) errors from noisy measurements and (2) errors associated with the convolution of the pump-probe response over the finite probe duration. In the noisy case, both errors are large; in the noise free case, there are only errors from the second source. Clearly, reducing the experimental noise associated with measurement alone does not suffice to accurately estimate the pump probe response, as the double Tikhonov inversion of the noisy signal outperforms naive inversion of the noise free signal by a factor of 7 in RMSE.

As Figure 4.2 shows, the errors in the estimate of the response function are not uniformly distributed, revealing structure relevant to our specific example and also to more generic systems. The largest errors are associated with smallest delay times. This makes sense, since the smallest delay times are those at which the response function (shown in Fig. 4.1) varies most rapidly. For almost any system, the pump-probe spectrum will change fastest at short delay times, but this is especially true for our example system, where the pump-probe signal includes contributions from quickly oscillating coherences. The Tikhonov estimates face an additional stability challenge at short delays times, since, as discussed above, the reconstruction cannot use measurements from the pulse overlap regime.

### Table 4.1: Summary of deconvolution performance over 1000 instances of simulated experimental noise. RMSE (root-mean-squared-error) is given by the sum of the absolute difference between the estimated and actual response functions, \(\sqrt{\sum_{\omega,\tau} |\hat{R}_{\text{pp}}(\omega, \tau) - R_{\text{PP}}(\omega, \tau)|^2}\). Improvement is the multiple of the reduction in RMSE compared to the naive approach. Uncertainties indicate one standard deviation in the empirical distribution.

<table>
<thead>
<tr>
<th>Noise</th>
<th>Naive (P^{(3)})</th>
<th>Naive</th>
<th>RMSE</th>
<th>Improvement</th>
</tr>
</thead>
<tbody>
<tr>
<td>(10^{-2})</td>
<td>Naive</td>
<td>Naive</td>
<td>12.12 ± 0.07</td>
<td>—</td>
</tr>
<tr>
<td>(10^{-2})</td>
<td>Tikhonov</td>
<td>Naive</td>
<td>7.78 ± 0.05</td>
<td>1.6 ± 0.0</td>
</tr>
<tr>
<td>(10^{-2})</td>
<td>Naive</td>
<td>Tikhonov</td>
<td>3.34 ± 0.08</td>
<td>3.6 ± 0.1</td>
</tr>
<tr>
<td>(10^{-2})</td>
<td>Tikhonov</td>
<td>Tikhonov</td>
<td>0.98 ± 0.06</td>
<td>12.5 ± 0.7</td>
</tr>
<tr>
<td>0</td>
<td>Naive</td>
<td>Naive</td>
<td>7.110</td>
<td>—</td>
</tr>
<tr>
<td>0</td>
<td>Tikhonov</td>
<td>Naive</td>
<td>7.110</td>
<td>1.0</td>
</tr>
<tr>
<td>0</td>
<td>Naive</td>
<td>Tikhonov</td>
<td>0.005</td>
<td>1301</td>
</tr>
<tr>
<td>0</td>
<td>Tikhonov</td>
<td>Tikhonov</td>
<td>0.005</td>
<td>1301</td>
</tr>
</tbody>
</table>
4.4.4 State tomography

Since we have demonstrated that the first, response function inversion can be performed with vanishing error, we now consider inverting the exact pump-probe response function to obtain the state of our model dimer. Despite the presence of static disorder in our example, we use the factorization of the response function in Eq. (4.11). We are obliged to do so even though strictly speaking the relationship does not hold, because the alternative of reconstructing the density matrix for each member of the ensemble from a bulk measurement is unrealistic. Accordingly, even without adding noise associated with the measurement, when carried out for an ensemble, our inversion faces potential stability issues because of the static disorder.

The degeneracies and near degeneracies in Eq. (4.19) mean that for most Hamiltonian choices our inversion algorithm can only robustly extract at most three of the four parameters necessary to fully characterize the dimer excited state, since the reconstruction matrix will be poorly conditioned. The condition number of a linear transformation gives a bound on the multiplicative increase in the relative error after performing the linear transformation [59]. For our specific numerical example, the condition number drops from 3700 to 3.1 when we include only three parameters. One source of these stability issues for a dimer is evident from Eq. (4.19): since our numerical example has well separated transition energies, the main contribution to the peaks in the dispersive part of the signal is to the imaginary part of the coherence term, $r_2$. This leaves our inversion to recover three parameters ($r_0$, $r_1$ and $r_3$) from the two peak amplitudes in the absorptive signal. Since recovering three unknowns from two equations is not possible, we need to fix one of these values in order to make the inversion stable. The obvious choice is to fix the normalization $r_0$, since the total excited state population should remain constant after the end of the pump pulse until spontaneous decay, on timescales approaching 1 ns for natural pigment-protein complexes [9]. To determine the normalization, we solve for it at a moderately long delay time (e.g., $\tau = 10$ ps) at which point we can safely assume (at least under secular Redfield dynamics) that the real part of the coherence $r_1 \to 0$, but very few excitations have been lost. If these timescales are not easily separable, then this normalization term could be fit to an exponential decay.

The results of applying this state tomography procedure to our numerical example with varying levels of static disorder are shown in Fig. 4.3. The fidelity, ranging from 0 to 1, provides a numerical summary of the quality of the state reconstruction [103]. For the level of static disorder chosen by Yuen-Zhou et al. (40 cm$^{-1}$), the reconstruction [panel (a)] has a worst-case fidelity of 99.5% over delay times $T$ shorter than 1 ps, and an average-case fidelity of 99.9%. However, we see that both the worst-case and average-case fidelities drop sharply as the static disorder is increased above this level [panel (b)], since our assumption that the pump-probe response can be factorized between the pump-probe projection and the second order density matrix becomes increasingly unrealistic.
Figure 4.3: Results of quantum state tomography for our dimer test problem. (a) Original (solid) and reconstructed (dotted) values for each element of the Bloch state vector for the reconstruction with static disorder of standard deviation 40 cm\(^{-1}\). Normalization is omitted since the state vector elements are rescaled such that \(r_0 = 1\) fixed for all times following initial excitation. (b) Worst- and average-case fidelities for the reconstructions \(\rho_e(\tau)\) for delay times \(\tau\) in the range 50 fs to 1 ps as a function of the width (standard deviation) of the distribution of static disorder. Results are obtained from an ensemble average over \(10^6\) samples for each point.
4.5 Scaling to larger systems

Can state tomography scale to systems larger than an excitonic dimer? In particular, can we apply it to precisely reveal the excitonic state in a natural light-harvesting system? Any scaling difficulties will be encountered in the second step of our inversion protocol, to determine the quantum state from the response function, since the relationship between the response function and measured signal does not directly depend on system parameters. Successful state tomography certainly requires both knowledge of how each density matrix element contributes to measurements and appropriate conditions such that each element, at least in principle, makes an independent and non-zero contribution. By construction, these conditions were satisfied for our hypothetical dimer example. We found that the primary limitation on solving for the state was ensemble disorder, which can in principle be avoided by single molecule techniques. Now, to explore the limits of state tomography, we relax these assumptions in order to consider the feasibility of state tomography in an actual protein-pigment complex.

As a model light-harvesting system, we focus on a monomer of the Fenna-Matthews-Olson (FMO) complex of green sulfur bacteria, which consists of 7 pigment molecules \cite{2, 126}. The FMO complex is a widely used model system for understanding photosynthetic energy transfer and is thus one of the best characterized natural protein-pigment complex. The crystal structure for the FMO complex is known, which combined with input from spectroscopy experiments, has allowed for general agreement on an electronic Hamiltonian \cite{2, 62}. Because the arrangement of pigments is fairly disordered, each excited state in a monomer of the FMO complex is bright, although they overlap in the presence of homogeneous and inhomogeneous broadening. This is important, since full state tomography would certainly not be possible on a system with multiple dark states, because no optical probes could reveal the distribution of energy among those states. However, typical of the situation for other natural pigment-protein systems, there is little consensus on the magnitude of the static disorder or the spectral density of the electronic-vibrational coupling \cite{142}. These difficulties are compounded by the theoretical and computational challenge of modeling dynamics in a system as large as FMO exactly for arbitrary system-bath interaction strength \cite{75}. For our concrete example, we use the electronic Hamiltonian for FMO of \textit{Chlorobaculum tepidum} from Ref. \cite{2}, with the spectral density and computational model of secular Redfield theory matching those used in for the dimer example. This model includes only one electronic state per pigment and assumes Gaussian distributed static disorder with standard deviation 42.5 \text{cm}^{-1} (100 \text{cm}^{-1} \text{FWHM}).

Our formalism for the pump-probe response function allows us to place bounds on the feasibility of any state tomography procedure, since the relationship between system information and the resulting pump-probe spectra is entirely contained in the pump-probe response operator. By looking at the ensemble average of this operator, we implicitly consider inversion under the scenario that the average over static disorder can be factorized between the pump-probe operator and the density matrix,. This assumption was successful in the dimer example above when the magnitude of static disorder was not too large. As
discussed in Section 4.2.2, the pump-probe operator at each frequency can be interpreted as a Liouville space bra-vector \( \langle \langle P(\omega) | \rangle \rangle \). Accordingly, it is possible to interpret the calculation of a pump-probe response as the act of applying the linear operator

\[
P = \int d\omega |\omega\rangle \langle P(\omega)|
\]  

(4.20)

to the state \( |\rho_e\rangle \). We now consider the properties of the linear operator \( P \) in the limit of effectively continuous sampling of probe frequencies \( \omega \). To represent states in Liouville space, we use a basis set that allows us to represent each state with \( n^2 \) real values, in terms of populations \( |n\rangle \langle n| \) and coherences \( |n\rangle \langle m| + |m\rangle \langle n| \) and \( i|n\rangle \langle m| - i|m\rangle \langle n| \). This allows us to construct a real-valued version of the map \( P \) that takes real valued state vectors to real valued spectra by concatenating the real and imaginary parts of \( P \).

To begin, in Figure 4.4 we plot the elements of the absorptive (real) part of the pump-probe operator for our model of the FMO complex in the isotropic average (magic angle configuration). We represent the operator in terms of the species associated spectra \( \langle \langle P(\omega)|\alpha\rangle \rangle \) of each exciton population and the real \( (\alpha = |n\rangle \langle m| + |m\rangle \langle n|) \) and imaginary \( (\alpha = i|n\rangle \langle m| - i|m\rangle \langle n|) \) part of each coherence, so that the pump-probe spectra of any excited state \( \rho_e \) is equal to the linear combination of the plotted spectra weighted by the indicated density matrix elements,

\[
\langle \langle P(\omega)|\rho_e\rangle \rangle = \sum_{\alpha} \langle \langle P(\omega)|\alpha\rangle \rangle |\langle \alpha|\rho_e\rangle|.
\]  

(4.21)

In addition to the unperturbed spectra, we also plot the range of possible spectra given current uncertainty about the best fit parameters. We conservatively estimate the uncertainty in the electronic Hamiltonian by sampling over additive independent Gaussian noise of width \( 20 \text{ cm}^{-1} \) for each site energy and 10% of the value of each off-diagonal coupling. This uncertainty is in addition to the static disorder, which we leave with fixed magnitude. The most striking feature of these spectra is that, at least in the isotropic average, the dominant contribution to the pump-probe spectra is from the population terms. The smaller contribution of most coherence terms, compounded by the already smaller values of the coherences in the density matrix due to dephasing, explains why it is difficult to observe oscillations due to electronic coherence in pump-probe spectra [126]. Even for extremely precise measurements, the uncertainty in some of these species associated spectra suggests that our current Hamiltonian characterization does not suffice to reliably obtain most density matrix elements. Indeed, the dominance of the diagonal terms suggests that a practical scheme for partial state tomography could consist of entirely ignoring the off-diagonal terms.

Another approach to estimating the feasibility of inversion for arbitrary states is to look at the spectral properties of the operator \( P \) as revealed by the singular value decomposition, \( P = USV^\dagger \), where \( U \) and \( V \) are unitary and \( S \) is diagonal with positive elements. In particular, we focus on the singular values \( \sigma_i \), given by the diagonal elements of \( S \) in descending order and normalized to the highest singular value \( \sigma_1 \). To compare the feasibility of inversion
Figure 4.4: Species associated spectra, defined by the contribution of the marked density matrix elements to the pump-probe response, for the FMO complex at 77 K (blue) and 300 K (red), obtained as the average of 1000 samplings over static disorder. Labels indicate the contributing density matrix element in the excitonic basis. Shaded regions indicate central 95% confidence intervals obtained from 1000 additional samplings over Hamiltonian uncertainty, as described in the text.
under various conditions, we plot these singular values in Figure 4.5. The singular values reveal significant information about the feasibility of an inversion: in general, inversion is more feasible when the singular values $\sigma_i$ decay more slowly [60]. For example, the condition number, which gives an upper bound on the ratio by which the relative error can increase in an inversion, is equal to the ratio of the largest to the smallest singular values. In Figure 4.5, the condition number is one over the value shown for $i = 49$.

Figure 4.5 provides an indication of the relative significance of different experimental constraints to state tomography. We see two major changes that reduce the condition number of the inversion by around two orders of magnitude each. First, reducing temperature from 300 K to 77 K improves the conditioning because spectral features in the species associated spectra are sharpened. Second, changing from a randomly ori-
CHAPTER 4. INVERTING PUMP-PROBE SPECTROSCOPY

Figure 4.6: Maximum amplitude over probe frequencies of the species associated spectra for an FMO monomer at 77 K for (a) the isotropic average and (b) each independent polarization configuration of the probe and local oscillator, including the ensemble average over static disorder. The labeling of each species matches that used in Figure 4.4: all entries including and above the diagonal correspond to the real part of the matching density matrix element (in the excitonic basis), and all entries below the diagonal correspond to the imaginary part. The cartesian coordinates were chosen arbitrarily, matching those used in an assignment of the crystal structure.

entend (isotropic) to an oriented sample helps because in principle 9 times more independent measurements are possible than in the magic angle configuration, one for each combination of $x$, $y$ and $z$ polarizations for the probe and signal interactions. This is illustrated in Figure 4.6 which plots the peak amplitudes of each of the species associated spectra. In some cross-polarization configurations, coherences give contributions of similar magnitude to populations. Single molecule measurements do offer an important advantage over oriented ensembles that is not seen in this figure, since their analysis does not require any assumption that the average over static disorder can be factorized between pump and probe. Finally, this figure suggests that the dispersive component of the signal, which as discussed in Section 4.2.1 requires a transient grating experiment, offers little additional information compared to the absorptive component that is provided directly by the pump-probe signal.

4.6 Conclusions

What information does an ultrafast spectroscopy experiment tell us about an excitonic system? How can we best design these experiments? We believe that a powerful way to answer these questions is to treat ultrafast spectroscopy as a hierarchy of statistical inverse problems,
as we have demonstrated here for estimating the electronic excited state. By dividing our analysis into many smaller steps—from experimental signal to response function to excited state and eventually on to dynamics, equations of motion and Hamiltonian parameters—we can see exactly how and where our models and experiments fall short. In this regard, our approach contrasts strongly with the established procedure of “forward simulation” for determining Hamiltonian parameters in complex excitonic systems by simultaneously fitting many experiments with an assumed theoretical model for calculating spectra from first principles \[2,105\]. Moreover, to identify the time-evolving excited state or another intermediate quantity in our approach, we do not need to introduce additional errors by recalculating from first principles.

Our multi-stage inversion has clear extensions to more general non-linear spectroscopies beyond QST and pump-probe. As we describe in Appendix \[4.7.3\], we could apply essentially the same inversion procedure to a photon-echo experiment to determine the phase-matched component of the 2nd-order density matrix that contributes to the observed signal \[Eq. (4.24)\]. If it is possible to construct a full set of independent phase-matched initial conditions, our state tomography procedure could be used for process tomography, along the lines of a previous proposal \[157\]. More generally, this suggests a new indirect approach for process tomography: first, field information should be used to obtain the 3rd-order response function (as outlined in Appendix \[4.7.6\]); second, system information should be used to extract the process matrix. Determining the response function as an intermediate quantity allows us to be sure we have obtained the maximum information from experiments before considering the harder theoretical problem of extracting system parameters, such as the state, process matrix or underlying Hamiltonian. Such extensions will be pursued in future work.

More immediately, our approach is particularly well suited to evaluating the benefits of employing colored pulses or an ultrafast pulse shaper, because our formalism makes no assumptions about the shape of pump and probe pulses: they are only required not to overlap in time. In contrast, prior proposals for process tomography relied on the assumption that interactions with laser pulses are much faster than the timescale of dissipative system dynamics \[157,156\]. Accordingly, we envision potentially using our scheme for verification of state preparation following shaped pump pulses \[15,24\], scenarios for which single molecules or oriented samples are similarly helpful. Indeed, pump-probe spectroscopy has been used to experimentally verify ultrafast coherent control \[115\]. The deconvolution step in our inversion protocol also made no assumptions about the shape of the probe pulse. Although our extensive numerical simulations found no cases in which a shaped probe pulse was preferable to the corresponding time-frequency limited pulse, our inversion protocol can just as easily obtain the non-linear response from, say, pump-probe measurements where the probe has residual chirp. This suggests the possibility of improving pulse characterization for better time resolution instead of or in addition to efforts to further compress pulses in time \[112\].

Finally, we point out that we have demonstrated state tomography in this work mostly for ensemble systems, including averaging over molecular orientations and static disorder. These features inevitably reduce the performance of the inversion. However, both oriented
and single molecule experiments may be possible in the near future, given recent advances of preforming ultrafast spectroscopy on crystallized proteins [70] and the possibility of using non-linear fluorescence measurements with phase-cycling [89] to scale non-linear spectroscopy to single molecules. For such single molecule experiments, we expect the present inversion will provide a powerful analytical tool.

4.7 Appendices

4.7.1 Derivation of pump-probe signal
Rearranging the terms that result from inserting Eq. (1.13) into Eq. (1.12) yields Eqs. (4.1–4.3).

4.7.2 Positivity of $\rho^{(2)}$
We consider the system density matrix $\rho$ in the presence of weak fields of strength $\epsilon \ll 1$. Let $\rho^{(n)}$ denote the contribution to the density matrix of strength $O(\epsilon^n)$. Thus we can write $\rho = \rho^{(0)} + \rho^{(1)} + \rho^{(2)} + \rho^{(3)} + O(\epsilon^4)$. Since the temperature is typically several orders of magnitude smaller than the electronic energy gap, the system starts in a tensor product of the electronic ground state $|g\rangle \langle g|$ and the equilibrium vibrational state $\rho_{\text{eq}}$, $\rho^{(0)} = |g\rangle \langle g| \otimes \rho_{\text{eq}}$.

We are interested in the excited state portion of $\rho_{\text{PP}}^{(2)}$, the component of $\rho^{(2)}$ that contributes to the phase-matched signal $k_S = k_{\text{pr}}$ given by Eq. (4.3). We write this excited state density portion as $\rho_e^{(2)} = Q\rho_{\text{PP}}^{(2)}$, where $Q$ denotes the projection onto the 1-excitation manifold. Since the non-phase-matched components involve 2-excitation states, we also have $\rho^{(2)} = Q\rho^{(2)}$. This projection is given by $Q\rho = I_1 \rho I_1^\dagger$, where $I_1 = \sum_m |m\rangle \langle m|$ is the identity operator restricted to the 1-excitation manifold and $|m\rangle$ denotes the state where only pigment $m$ is excited. Since the map $Q$ is written in the appropriate form and $\sum_n I_n I_n^\dagger = I$, $Q$ is completely positive, with $0 \leq \text{Tr} Q\rho \leq 1$.

Moving from the ground state to the 1-excitation manifold requires at least two applications of the creation/annihilation operators contained in the dipole transition operators $\mu^{(\pm)}$, and a dipole operator must be applied an even number of times. Accordingly, $Q\rho^{(n)} = 0$ for $n = 0, 1, 3$, which leaves $Q\rho = \rho_e^{(2)} + O(\epsilon^4)$. Since we proved $Q\rho$ is positive and $\rho^{(2)}$ itself is $O(\epsilon^2)$, we have shown that $\rho_e^{(2)}$ is positive, up to relative errors of $O(\epsilon^2)$. Any positive operator is a valid density matrix if it has trace one.

4.7.3 Tikhonov regularization
The convolution of the pump-probe response with the probe pulse in Eq. (4.4) and the non-linear polarization with the local-oscillator in Eq. (4.6) are both particular cases of a Fredholm integral equation of the first kind. An extensive literature exists on numerical
inversion of such equations, known as discrete inversion problems [60]. In general, the discretization of such an integral equation can be written as

$$ b = Ax + \epsilon, \quad (4.22) $$

where $b$ is the measured signal [e.g., the nonlinear polarization $P^{(3)}(\omega, T)$], $x$ is the desired quantity to obtain [e.g., the response function $R_{PP}(\omega, T)$], $A$ is a linear operator representing the integral equation with appropriate coefficients (determined here by the probe field $E_{pr}$) and $\epsilon$ denotes some additive experimental error inherent in the data collection. The obvious solution to estimating $x$ from $A$ and $b$ is to calculate $\hat{x} = A^{-1}b$. However, in practice $A$ may not be invertible. This is the case for our inversion, since we ignore the experimental signal for times in the pulse overlap regime but still attempt to reconstruct the pump-probe response at those times, which guarantees that $b$ has a lower dimensionality than $x$. In addition, the presence of even a vanishingly small amount of experimental noise $\epsilon$ makes exact least-squares minimization unsuitable; it will over-fit the noise component $\epsilon$.

Accordingly, to calculate a robust estimate $\hat{x}$ of $x$ we use general form Tikhonov regularization [60],

$$ \hat{x} = \arg\min_{x} \{ ||Ax - b||^2 + \lambda^2||Lx||^2 \} \quad (4.23) $$

Tikhonov regularization can be derived formally from the perspective of Bayesian inference, given normally distributed errors and priors [150]. It can be equivalently be expressed as the linear least-squares problem, $\min ||[A_L^0]x - [b_0]^T||^2$, and thus the exact solution is given by $\hat{x} = [A_L^0]^+[b_0]$, where $+$ denotes the Penrose-Moore pseudoinverse [60]. Ideally, the linear operator $L$ and (real) regularization parameter $\lambda$ are chosen so that $\lambda^2||Lx||^2$ is an optimally weighted penalty on undesirable features of the solution $x$, reflecting our prior knowledge of the general form of $x$. Common choices of $L$ include the identity matrix $I$ and finite-difference approximations to the first or second derivative given by $(D_1x)_n = x_n - x_{n-1}$ and $(D_2x)_n = x_{n+1} - 2x_n + x_{n-1}$. We compare different techniques for selecting $\lambda$ and $L$ in Appendix 4.7.4.

There are a number of powerful techniques for calculating efficient approximate solutions to Eq. (4.23), especially in cases where the linear operator $A$ is structured [59], such as in our case, where $A$ is a Toeplitz matrix. For several hundred time-delays or probe frequencies, we find that we can solve each deconvolution with Eq. (4.23) exactly and quickly ($\sim$1s on a modern CPU) by calculating the singular value decomposition of the matrix $[A_L^0]$. In principle, it would be possible to solve both steps in the inversion of the pump-probe response in a single two-dimensional Tikhonov regularization. Such 2D inversions are routinely performed in image processing [60], but would require slower, more approximate techniques than the exact solution we used here. Since we find significant improvement without invoking these more complicated methods, we do not use them here.
### Noise Penalty Selection

<table>
<thead>
<tr>
<th>Noise</th>
<th>Penalty</th>
<th>Selection</th>
<th>$\lambda_{\text{opt}}$</th>
<th>Improvement</th>
</tr>
</thead>
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<tr>
<td>$10^{-2}$</td>
<td>$I$</td>
<td>Exact</td>
<td>$0.151 \pm 0.007$</td>
<td>$2.3 \pm 0.2$</td>
</tr>
<tr>
<td>$10^{-2}$</td>
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</tr>
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<td>$6.2 \pm 1.2$</td>
</tr>
<tr>
<td>$10^{-2}$</td>
<td>$D_2$</td>
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<td>$5.7 \pm 1.2$</td>
</tr>
<tr>
<td>$10^{-2}$</td>
<td>$D_2$</td>
<td>NCP</td>
<td>$2.57 \pm 0.36$</td>
<td>$2.3 \pm 0.4$</td>
</tr>
<tr>
<td>$10^{-3}$</td>
<td>$I$</td>
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<td>$5.9 \pm 0.5$</td>
</tr>
<tr>
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<td>$30 \pm 5$</td>
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<tr>
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<td>$D_2$</td>
<td>Exact</td>
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<td>$56 \pm 12$</td>
</tr>
<tr>
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<td>$D_2$</td>
<td>GCV</td>
<td>$0.103 \pm 0.019$</td>
<td>$52 \pm 12$</td>
</tr>
<tr>
<td>$10^{-3}$</td>
<td>$D_2$</td>
<td>NCP</td>
<td>$0.449 \pm 0.039$</td>
<td>$19 \pm 2$</td>
</tr>
</tbody>
</table>

Table 4.2: Regularization performance for different penalty operators and parameter selection techniques for 1000 instances of random noise with relative magnitude $10^{-2}$ or $10^{-3}$. Numbers are the mean plus or minus one standard deviation. Improvement is the multiple of the reduction in mean-squared-error for the reconstructed response function using Tikhonov regularization over the error associated with the naive impulse-probe estimate.

### 4.7.4 Parameter selection for Tikhonov regularization

To perform deconvolutions using Eq. (4.23), we need to choose a procedure to select the regularization parameters $\lambda$ and $L$. In practice, there are a wide variety of techniques for making these selections and the best choice depends on the particular problem at hand [60]. Here we compare the performance of different techniques on simulations matching the dimer problem we analyze in Section 4.4.

To begin, we compared the performance of general form Tikhonov regularization with $L$ equal to $I$, $D_1$ and $D_2$, with $\lambda$ chosen optimally so as to minimize the exact mean-squared-error $||\hat{x} - x||^2$. A summary of reconstructions of $R_{PP}(\omega, \rho_{PP}^{(2)}(T))$ for 1000 instances of low and high noise is shown in Table 4.2. As a benchmark, we consider the ratio of the mean-squared-error from the Tikhonov estimate to the mean-square-error of our naive estimate $\hat{R}_{PP}(\omega, \rho_{PP}^{(2)}(T)) \propto P(\omega, T)/E_{pr}(\omega)$, which holds in the limit of an instantaneous probe pulse [Eq. (4.5)]. For our state inversion algorithm, reconstruction of the response function is most important at frequencies matching the exciton transition energies, so we picked $\omega = \omega_\alpha$, the transition frequency of the higher energy exciton state. We found qualitatively similar results for $\omega = \omega_\beta$ and other choices of $\omega$ as well. As Table 4.2 shows, with exact selection of the best regularization parameter $\lambda$, we found consistently best performance with $D_2$, the linear operator approximating the second derivative of the response function with respect to the delay time $T$. This is an intuitively reasonable choice, since plausible response functions should be smooth.

With the choice for $L$ determined, we also need a realistic procedure for selecting the regularization parameter $\lambda$. In a true inversion problem the response function $x$ is unknown,
so we cannot choose $\lambda$ to minimize the exact mean-squared-error. There are a variety of standard techniques for making this choice, with performance that can vary widely depending on the problem being solved, so selection of an appropriate method requires more tests on simulated data. We considered two such methods for $L = D_2$: generalized cross-validation (GCV) and the normalized cumulative periodogram (NCP). We calculate the GCV error using the exact pseudoinverse solution $[150]$ and the NCP error by adding together the errors for the real and imaginary parts of the spectra $[60]$. We then minimize these error estimates as a function of $\lambda$ using a 1-dimensional search with the downhill simplex method $[102]$. We also impose the additional restriction $\lambda \geq 5 \times 10^{-11}$ to avoid convergence failures with our SVD implementation that we encountered when performing deconvolutions on noise-free simulated spectra. The results, also shown in Table 4.2, show that GCV is the best choice for our test problem, with performance nearly matching that of exact selection technique. In contrast, NCP systematically overestimated the noise, as indicated by regularization parameters about four times larger than the exact selection method. However, NCP still offered an improvement in the reduction of the mean-squared-error compared to the naive approach.

### 4.7.5 Alternative formulation

There are several obvious extensions or alternatives to the recipe described in section 4.2. For example, the exact same relations in Eqs. (4.1–4.3) hold for a general photon-echo (or non-rephasing) experiment with two distinct pump pulses, except that in this situation the sum in Eq. (4.3) to determine the portion of $\rho^{(2)}$ that contributes to the signal should be removed to leave only one of the two phase-matched contributions. Instead, the photon-echo (PE) signal depends on the second-order density matrix given by

$$
\rho^{(2)}_{\text{PE}}(t) = \left( \frac{i}{\hbar} \right)^2 \int_0^\infty dt_2 dt_1 G(t_2) V^{(+)} G(t_1) V^{(-)} \rho_0 E_2^+(t - t_2) E_1^- (t - t_2 - t_1).
$$

However, unlike the case for the state $\rho^{(2)}_{\text{PP}}$ that contributes to the pump-probe signal, the excited state portion of $\rho^{(2)}_{\text{PE}}$ is not necessarily either hermitian or equivalent to the total excited state density matrix. This makes its interpretation less clear but presents no additional technical difficulties for our inversion procedure.

### 4.7.6 Triple deconvolution to obtain the full 3rd-order response function

The deconvolution procedure demonstrated in Chapter 4 has an interesting application for more general 3rd-order spectroscopy experiments, beyond pump-probe. In particular, we envision applying it to estimate the full 3rd-order response function $R^{(3)}_{k_0}(t_3, t_2, t_1)$ from a series of ultrafast measurements. This would formalize the standard interpretation of 2D photon-echo as snapshots of the 3rd-order response function, even in cases where the laser
pulses cannot be accurately described as fully impulsive, and allow for quantitative comparisons between different experimental setups and theory independent of the particular laser setup. Indeed, since this response function contains all possible system-information, such determination of the third order response function would arguably constitute the “ultimate” 3rd-order spectroscopy experiment, because all other possible third-order experiments could be calculated from numerical integration of the response function over the applied fields.

To illustrate this proposal, we rewrite the equation for the non-linear polarization given by Eq. (I.12) in terms of the central times $\tau_i$ for each laser pulse $i$ and the delay times between each pulse, $T_3 = t - \tau_3$, $T_2 = \tau_3 - \tau_2$ and $T_1 = \tau_2 - \tau_1$:

$$P_{k_s}^{(3)}(T_3, T_2, T_1) = \iiint_{0}^{\infty} dt_3 \, dt_2 \, dt_1 \, R_{k_s}^{(3)}(t_3, t_2, t_1) \times \mathcal{E}(T_3 - t_3)\mathcal{E}(T_3 + T_2 - t_3 - t_2)\mathcal{E}(T_3 + T_2 + T_1 - t_3 - t_2 - t_1).$$

(4.25)

Here we use the fixed laser envelope $\mathcal{E}(t) \equiv E_i(t + \tau_i)$ for each pulse and assumed that $E_i(t)$ is strictly real-valued in the rotating frame. We also assumed a definite time-ordering between each system-field interaction; in general, this equation should be replaced by a sum over all six possible time-orderings. In the impulsive limit $\mathcal{E}(t) \approx \delta(t)$, each integral drops away and we have $R_{k_s}^{(3)}(T_3, T_2, T_1) \approx P_{k_s}^{(3)}(T_3, T_2, T_1)$. More generally, this equation provides a linear map from the response function to the non-linear polarization, which holds even if all possible time-orderings are considered.

Because a typical 3D spectrum requires $\sim 10^2$ measurements along each time axis, $R_{k_s}^{(3)}$ is a $\sim 10^6$ dimensional vector, and thus the transformation matrix for this linear relation would have $\sim 10^{12}$ elements and be too large to fit in memory on most modern computers. To efficiently invert this relation, we write it as a series of three nested one-dimensional convolutions,

$$P_{k_s}^{(3)}(T_3, T_2, T_1) = \int dt_3 S_2(t_3, T_3 + T_2, T_1)\mathcal{E}(T_3 - t_3)$$

(4.26)

$$S_2(t_3, T_2, T_1) = \int dt_2 S_1(t_3, t_2, T_2 + T_1)\mathcal{E}(T_2 - t_3 - t_2)$$

(4.27)

$$S_1(t_3, t_2, T_1) = \int dt_1 R_{k_s}^{(3)}(t_3, t_2, t_1)\mathcal{E}(T_1 - t_3 - t_2 - t_1),$$

(4.28)

in terms of the intermediate quantities $S_1$ and $S_2$. Since each of these relations specifies a set of one-dimensional convolutions, we should be able to independently invert each of them using the same generalized Tikhonov regularization technique that we demonstrated for Eq. (4.4). Note that this decomposition into a hierarchy of three convolutions requires a definite time ordering between the pulses. In fact, in the usual setup for 2D spectroscopy, it turns out that only a definite time ordering between the second and third pulse is important; overlap between the first two pulses can be accounted for exactly by the convention that negative times $t_1$ refer to the non-rephasing instead of the photon-echo direction. Fortunately, this
constraint of no pulse overlap between the second and third pulses is not insurmountable, since it restricts only the last convolution and thus can be dealt exactly as demonstrated in Sec. 4.3.1 by restricting the deconvoluted signal to population times no smaller than some minimum delay.
4.7.7 Mathematica code for derivation in Sec. 4.4.1

- Initial conditions and operators in Liouville space:

\[
\mu = \begin{pmatrix}
0 & \mu g & \mu b & 0 \\
0 & 0 & 0 & \mu af \\
0 & 0 & 0 & \mu bf \\
0 & 0 & 0 & 0
\end{pmatrix}
\]

\[
\rho_0 = \begin{pmatrix}
-\frac{1}{2} (r_0 + r_0) & 0 & 0 & 0 \\
0 & \frac{1}{2} (r_0 + r_0) & 0 & 0 \\
0 & 0 & \frac{1}{2} (r_1 + r_1) & 0 \\
0 & 0 & 0 & 0
\end{pmatrix}
\]

\[
G_t = \begin{pmatrix}
0 & 0 & 0 & 0 \\
f_a & 0 & 0 & 0 \\
f_b & 0 & 0 & 0 \\
0 & f_p b & f_p a & 0
\end{pmatrix}
\]

sitedipoles = 
\{ \mu g \to \cos[\theta], \} \{ d_1 \to \sin[\theta], d_2 \to \mu b \to -\sin[\theta], d_1 \to \cos[\theta], d_2 \to \mu af \to \sin[\theta], d_1 \to \cos[\theta], d_2, \mu bf \to \cos[\theta], d_1 - \sin[\theta], d_2 \};

- Derivation of Eq. (18):

\[
\begin{aligned}
S &= \text{Tr}[\mu . (G_t (\mu^* . \rho_0 - \rho_0 . \mu^* ) )] // \text{FullSimplify}
\end{aligned}
\]

\[
\frac{1}{2} \left( -3 f_a \mu g \mu a^2 - 3 f_b \mu b \mu b^2 + f_p b \mu a \mu f^2 + f_p a \mu b \mu f^2 \right) r_0 + (- (f_a + f_b) \mu a \mu g \mu a \mu f^2) r_1 +
\]

\[
\begin{aligned}
&\frac{1}{2} \left( (-3 f_a \mu g \mu a^2 - 3 f_b \mu b \mu b^2 + f_p b \mu a \mu f^2 + f_p a \mu b \mu f^2) r_0 + (- (f_a + f_b) \mu a \mu g \mu a \mu f^2) r_1 +
\end{aligned}
\]

Table[CoefficientList[\{2 S, \{r_1\}\}]//\text{FullSimplify}, \{1, 0, 3\}] /. \{\text{\textbackslash}1 \to \text{\textbackslash}1\} // \text{MatrixForm}

\[
\begin{pmatrix}
-3 f_a \mu g \mu a^2 - 3 f_b \mu b \mu b^2 + f_p b \mu a \mu f^2 + f_p a \mu b \mu f^2 \\
- (f_a + f_b) \mu a \mu g \mu a \mu f^2 \\
- (f_a + f_b) \mu a \mu g \mu a \mu f^2 \\
- (f_a + f_b) \mu a \mu g \mu a \mu f^2
\end{pmatrix}
\]

Note the switched sign assigned to i because of the complex conjugate when turning this from a ket- to a bra-vector.

- Derivation of Eq. (19):

\[
\begin{aligned}
S_2 &= \text{Collect}[2 S \text{ sitedipoles, \{1, 2\}] /. \{d_2 \to 1, d_2 \to \delta^2, d_1 d_2 \to \delta \cos[\theta]\}
\end{aligned}
\]

\[
\begin{aligned}
f_p a \cos[\theta] r_0 &= 3 f a \cos[\theta] r_0 + 3 f a \sin[\theta] r_0 + 3 f a \sin[\theta] r_0 + (f_b + f_p) \cos[\theta] r_1 + (f_b + f_p) \cos[\theta] r_1 +
\end{aligned}
\]

\[
\begin{aligned}
&\frac{1}{2} \left( (f_b + f_p) \cos[\theta] r_0 + 2 f_b \cos[\theta] r_0 + 6 f a \cos[\theta] r_1 + 6 f a \cos[\theta] r_1 +
\end{aligned}
\]

Table[CoefficientList[\{S_2, \{r_1\}\}]//\text{FullSimplify}, \{\cos[\theta], \sin[\theta] \to -\sin[2 \theta]\}] /. \{\text{\textbackslash}1 \to \text{\textbackslash}1\} // \text{MatrixForm}

\[
\begin{pmatrix}
(f_p a - 3 f a + \delta^2) \cos[\theta] r_0 \\
(f_p a - 3 f a + \delta^2) \sin[\theta] r_0 \\
(f_p a + f_p b + f_b + f_p a + f_b + f_p a + f_b) \cos[\theta] r_0 \\
(f_p a + f_p b + f_b + f_p a + f_b + f_p a + f_b) \cos[\theta] r_0
\end{pmatrix}
\]

\[
\begin{pmatrix}
(f_p a + f_p b + f_b + f_p a + f_b + f_p a + f_b) \cos[\theta] r_0 \\
(f_p a + f_p b + f_b + f_p a + f_b + f_p a + f_b) \cos[\theta] r_0 + 1/2 \left( (f_p a + f_p b + f_b + f_p a + f_b + f_p a + f_b) \left( -1 + \delta^2 \right) \sin[2 \theta] \right)
\end{pmatrix}
\]

\[
\begin{pmatrix}
(f_p a + f_p b + f_b + f_p a + f_b + f_p a + f_b) \cos[\theta] r_0 + 1/2 \left( (f_p a + f_p b + f_b + f_p a + f_b + f_p a + f_b) \left( -1 + \delta^2 \right) \sin[2 \theta] \right) \\
(f_p a + f_p b + f_b + f_p a + f_b + f_p a + f_b) \cos[\theta] r_0 + 1/2 \left( (f_p a + f_p b + f_b + f_p a + f_b + f_p a + f_b) \left( -1 + \delta^2 \right) \sin[2 \theta] \right)
\end{pmatrix}
\]
Chapter 5

Realistic and verifiable coherent control of excitonic states in a light harvesting complex

Summary

We explore the feasibility of coherent control of excitonic dynamics in light harvesting complexes despite the open nature of these quantum systems. We establish feasible targets for phase and phase/amplitude control of the electronically excited state populations in the Fenna-Mathews-Olson (FMO) complex and analyze the robustness of this control. We further present two possible routes to verification of the control target, with simulations for the FMO complex showing that steering of the excited state is experimentally verifiable either by extending excitonic coherence or by producing novel states in a pump-probe setup. Our results provide a first step toward coherent control of these systems in an ultrafast spectroscopy setup.

5.1 Introduction

The control of atomic and molecular processes using coherent sources of radiation is a well established experimental technique. Particularly successful have been implementations that aim to control the non-equilibrium dynamics of highly coherent quantum systems, e.g. internal and external states of cold atoms [36], and ones that aim to control the equilibrium states resulting from controlled mixed (coherent and incoherent) dynamics such as those dictating chemical reactions [139]. On the other hand, few experiments have attempted to control the non-equilibrium states of systems undergoing mixed dynamics. Indeed, recent theoretical work in the field of quantum control has actively investigated questions related to such open quantum systems (e.g. [13, 132, 39]). Formulating optimal control protocols can be challenging for such systems. In fact, it is usually difficult to even decide whether or not an
open quantum system is controllable (i.e., whether all states are reachable from an arbitrary initial state), given a model of its dynamics and control [39]. Theoretical treatment of such systems is complicated by the fact that one cannot exploit a clear separation of timescales to restrict the dynamical model to purely coherent or incoherent dynamics. Instead one must incorporate both coherent dynamics and decoherence processes in a unified manner, e.g., using quantum master equation models.

In this paper we examine a paradigmatic open quantum system, electronic excited states in photosynthetic light harvesting complexes (LHCs) [8], and investigate strategies for controlling the non-equilibrium dynamics of these excited states. Photosynthetic light harvesting complexes are typically composed of dense arrangements of pigment molecules, such as chlorophyll, embedded within protein backbones. Electronic excited states result from the absorption of photons by pigments in such pigment-protein structures. These states – termed excitons – can be either localized on single pigments or delocalized across multiple pigments due to the strong electronic coupling between pigments. The excitation energy carried by these states is funneled to regions of the light harvesting complex that can initiate the decomposition of such excitons into separated free charge carriers. This energy transfer process, which is dictated by the dynamics of excitons, is extremely complex and has recently been shown to have significant quantum coherent character [41, 37, 108]. Subsequent modeling and theoretical study [96, 111, 75, 117, 26, 125, 121, 33, 27, 34, 25] have determined that the energy transfer process is described by a finely tuned balance of coherent and incoherent dynamical processes. Due to this partially coherent nature of the excitonic dynamics, the control of the energy transfer process in LHCs using laser fields is expected to be sensitive to both the temporal and spatial phase coherence of the controlling laser fields. For these reasons, we regard the control of energy transfer in LHCs as a paradigmatic example of coherent control of mixed quantum dynamics in open quantum system dynamics. Achieving control of excitonic dynamics in photosynthetic systems is a first step towards active control of energy transfer dynamics in complex organic molecular assemblies, a potentially important capability for artificial light harvesting technologies [124]. The ability to control excitonic dynamics in LHCs is also a potentially useful tool in the quest to develop a complete understanding of energy transfer in these complex systems.

Several previous studies have already addressed the coherent control of excitonic dynamics in LHCs. Herek et al. performed an early experiment demonstrating moderate control over energy transfer pathways in the LH2 light harvesting complex using shaped femtosecond laser pulses [63]. Theoretical modeling of this same LHC and calculation of optimal control fields to achieve enhanced fluorescence was performed in Ref. [85]. These studies demonstrated coherent control of chemical products of light harvesting system, but not control of femtosecond electronic dynamics themselves. In contrast, Brüggemann, May and co-workers performed a series of theoretical studies focusing on the formulation of optimal femtosecond pulses to control the excitonic dynamics of the Fenna Matthews Olson (FMO) complex [16, 18, 17]. These studies aimed to localize excitation energy in regions of the FMO complex using shaped pulses with and without polarization control. Recently, Caruso et al. [24] performed a theoretical study that focused on preparing various localized and prop-
agating excitonic states of the FMO complex using shaped femtosecond pulses determined with the recently introduced CRAB optimization algorithm [40].

In this work, we extend the studies of optimal control of excitonic dynamics in FMO by systematically analyzing the limitations to achievable control that are imposed by practical constraints for bulk, small ensemble and single complex experiments. As an important complement, we also identify schemes for authentication of any such coherent control of excitonic dynamics by prediction of the signatures of coherent control in pump-probe spectra. We close with a discussion of the outlook for further development of coherent control and its applications for analysis of excitonic coherence in biological systems.

5.2 Model for laser excitation of FMO

We use the Heitler-London model Hamiltonian given by Eq. (1.1–1.6).

We focus our investigations on the FMO complex of green sulfur bacteria, an extensively studied protein-pigment complex. Biologically, a monomer of the FMO complex serves as a "quantum wire" with seven chlorophyll pigments that transfers excitation energy from the chlorosome antenna towards the reaction center in a partially coherent manner [44, 37]. The crystal structure of the FMO protein is known, and the system has been subject to a large number of linear and non-linear spectroscopic measurements [94]. Accordingly, the Hamiltonian of the system is quite well established. Here we use the electronic Hamiltonian determined by Adolphs and Renger that includes Gaussian static (ensemble) disorder of full-width-at-half-maximum $100 \, \text{cm}^{-1}$ for each transition energy $E_n$ [2]. We model the system-reservoir coupling by assuming that each pigment is coupled to an independent reservoir with identical Debye spectral densities $J_n(\omega) = J(\omega)$ of the form $\omega^2 J(\omega) = \frac{2 \gamma \omega}{\omega^2 + \gamma^2} \Theta(\omega)$, where $\Theta$ denotes the Heaviside function and with reorganization energy $\lambda = 35 \, \text{cm}^{-1}$ and bath relaxation rate $\gamma = 1/(50 \, \text{fs})$ tuned to experimental values as in Ref. [75]. Because for FMO all of the key energy scales in the problem coincide ($\hbar \lambda \sim \hbar \gamma \sim J_{nm}$), the Hamiltonian given by Eqs. (1.1)-(1.6) does not fall in the range of validity of the standard perturbative approaches of either Förster or Redfield theories [75]. This has made photosynthetic systems, and in particular the FMO complex, prototypes for alternative methods to solve open quantum systems [76, 122, 72, 146, 114, 33]. These methods provide significant improvement in accuracy, including, for example, representation of non-Markovian effects.

Nonetheless, in this work we use Redfield theory in the secular approximation, because we can evaluate Redfield dynamics for a single molecule of FMO in $\sim 100 \, \text{ms}$ on a single modern CPU, compared to up to hours for more accurate methods [75, 122, 72, 146, 114, 33]. Such rapid evaluation of dynamics solutions is a necessary trade-off to ensure we can optimize candidate control pulses in a reasonable time. However, we do not expect our optimally shaped pulses would show qualitative differences for controlling exciton dynamics when evaluated on more realistic models. The approach of secular Redfield theory is to treat the system-reservoir coupling $H_{S,R}$ to second order and to apply the Markov and secular approximations [93]. This allows us to write an equation of motion for the electronic reduced
density matrix $\rho$,
\[
\frac{d\rho}{dt} = -\frac{i}{\hbar}[H_S + H_{S-L}(t), \rho] + D\rho
\]  
(5.1)
where the dissipation superoperator $D$ can be written as a sum of components in the standard Lindblad form. We include the explicit time-dependence in $H_{S-L}$ to indicate that this is the only non-constant term (aside from $\rho$), which holds under the assumption that we can neglect modification of the dissipative dynamics due to strong field excitation \[128\]. This description gives rise to qualitatively reasonable dynamics including quantum beats and relaxation to the proper thermal equilibrium, unlike other efficient simplified quantum master equations such as the Haken-Strobl or pure dephasing model \[55, \ 23\]. Employing the secular approximation guarantees completely positive dynamics, at the price of neglecting environment induced dynamical coherence transfer \[107\].

To efficiently simulate light-matter interactions, we use the rotating wave approximation, which allows us to ignore the contribution of very quickly oscillating and non-energy conserving terms \[140\]. To do so, we switch to a rotating frame with frequency $\omega_0$, typically chosen to match the carrier frequency of the applied field. The dynamics are given by replacing each Hamiltonian $H$ with its rotating equivalent $\tilde{H}$. The only terms in Eqs. (1.1)-(1.6) which are not equivalent to those in the non-rotating frame is the system Hamiltonian $\tilde{H}_S$, which in the rotating frame has the transition energies $\tilde{E}_n = E_n - \hbar\omega_0$, and the system-light interaction
\[
\tilde{H}_{S-L} = \sum_n (d_n \cdot \hat{e}) a_n \tilde{E}(t) + h.c.
\]  
(5.2)
The electric field in the rotating frame, $\tilde{E}(t)$, is related to the full electric field by $E(t) = \hat{e}\tilde{E}(t)e^{i\omega_0 t} + c.c.$, where $\hat{e}$ is a unit vector in the direction of the polarization of the field. Since the Redfield dissipation superoperator $D$ is time-independent, to determine the electronic density matrix $\rho$ resulting from a control field we may numerically integrate Eq. (5.1) upon substituting $\tilde{H}_S$ and $\tilde{H}_{S-L}$ for $H_S$ and $H_{S-L}$, respectively. Weak fields also allow us to perform efficient averages over all molecular orientations \[38\].

### 5.3 Optimal control methods

We focus here on optimizing state preparation under weak field excitation, the experimentally relevant regime for ultrafast spectroscopy. Spectroscopic measurements usually cannot determine the fraction of an ensemble sample that is excited, so we employ the normalized excited state density matrix given by
\[
\rho' = \frac{\rho_e}{\text{Tr}\rho_e},
\]  
(5.3)
where $\rho_e$ denotes the projection of the density matrix onto the single excitation subspace. In the weak field regime, $\rho'$ will not be sensitive to the overall pump amplitude, since the total excited state population will remain small.
Our control objectives can all be expressed in terms of this normalized excited state density matrix $\rho'$. Our first state preparation goal is localization of the excitation on a pigment $n$:

$$\max C_{\text{site}}(t) \equiv \max \langle n | \rho'(t) | n \rangle$$

for $n \in \{1, 2, \ldots, 7\}$, with $a_n^\dagger a_n | m \rangle = \delta_{mn} | m \rangle$. The second goal we consider is the preparation of an excitonic state:

$$\max C_{\text{exc}}(t) \equiv \max \langle \alpha | \rho'(t) | \alpha \rangle$$

for $\alpha \in \{1, 2, \ldots, 7\}$, where the excitonic states $| \alpha \rangle$ are the eigenstates of $H_S$, and we choose to order them by energy so that exciton $\alpha = 1$ is the lowest energy one. The third goal is the maximization of an excitonic coherence:

$$\max C_{\alpha,\beta}^{\text{coh}}(t) \equiv \max | \langle \alpha | \rho'(t) | \beta \rangle |$$

for $\alpha, \beta \in \{1, 2, \ldots, 7\}$. The time $t$ in all these cost functions is restricted to times following the end of the shaped control pulse. In addition to these state population targets, in section 5.5 we describe and carry out optimization of another cost function of $\rho'(t)$ that is directly related to experimentally measurable spectroscopic signatures.

We employ two types of pulse parameterizations in this work, optimizing the parameterized control fields in each case with standard numerical optimization techniques (see below). To first determine the theoretical limits of control without taking any constraints on physical realization of the control fields, we use an adaptation of the chopped random basis (CRAB) scheme \cite{22}, which was recently used to optimize state preparation for FMO \cite{24}. This control field is defined in the time domain and is of the form

$$E(t) = f_{\text{cutoff}}(t) \sum_k^N (A_k + iB_k) e^{i\omega_k t},$$

for $N$ fixed frequencies $\omega_k$ and $2N$ real valued optimization parameters $A_k$ and $B_k$. This parameterization allows variation of both amplitude and phase of the control field components. In our case, we choose $N = 19$ frequencies $\omega_k$ at equal intervals spanning the FMO absorption spectrum. The cutoff function $f_{\text{cutoff}}(t)$ is chosen as a step function that restricts the control fields to a particular total pulse duration $T$. For complexes with fixed orientation (in contrast to optimization over an ensemble of orientations), we also include parameters $\phi$ and $\theta$ to choose the optimal polarization $\hat{e}$ of the control field. These optimization parameters are illustrated in Figure 5.1.

The parametrization given by Eq. (5.7) creates pulses with different overall energies and energy distributions, but “coherent control” is in some cases understood as referring to exploiting the coherent nature of the laser light itself \cite{140}. For this reason, some initial experimental demonstrations of coherent control have stressed the sensitivity of control to
Figure 5.1: Parameters used in the first parameterization [Eq. (5.7)] for controlling excitation of FMO, superimposed over the FMO linear absorption spectrum. The vertical red lines indicate the chosen frequencies $\omega_k$.

the phase of the control field. Thus, we also consider a second pulse parametrization suited for coherent control within an experimentally constrained phase-only control scenario. Here we define the control field in the frequency domain and each frequency is assigned a variable phase term which is parameterized as a polynomial function of the frequency:

$$E(\omega) = A(\omega) \exp \left[ i \sum_{k=2}^{N+1} C_k (\omega - \omega_0)^k \right].$$  \hspace{1cm} (5.8)$$

The quantity $A(\omega)$ denotes the unshaped amplitude profile of the control field, which is fixed by the laser setup, $\omega_0$ is the central frequency of the laser and $C_k$ is a real valued optimization parameter. We neglect terms with $k < 2$, in order to remove global phase shifts ($k = 0$) as well as time-translations ($k = 1$). The surviving terms $k \geq 2$ correspond to linear ($k = 2$) and higher-order ($k > 2$) chirps in the frequency domain. In this work we have chosen the amplitude $A(\omega)$ to be represented by a Gaussian function, with amplitude fixed to $\sim 10^7 \text{ V m}^{-1}$ in the time-domain and standard deviation 225 cm$^{-1}$, corresponding to a full-width-at-half-maximum of 55 fs in the time domain. In this paper, we restrict ourselves to $N = 10$ terms. To simulate hypothetical pulses matching those produced by an ultrafast pulse shaper, we apply this field in the frequency domain to 600 points stretching between ±3 standard deviations, and obtain the time-domain pulse in the rotating frame from the inverse Fourier transform. Cutting off frequencies more than 3 standard deviations away from the central frequency does result in some small artifacts visible in the time-domain. We then use the following two-step heuristic to determine the final time for the pulse: we set to zero the pulse field at all times with amplitude less than 0.005 times the maximum amplitude and then set the final time as the point at which 99% of the overall
integrated total pulse amplitude has passed. For optimization of oriented complexes, the relative polarization \( \hat{e} \) is specified by angles \( \theta \) and \( \phi \) as above.

To optimize our pulses over the parameters in Eqs. (5.7) and (5.8) we use two optimization routines, the Subplex direct search algorithm \[123\] and the Covariance Matrix Adaptation Evolution Strategy (CMA-ES) \[58\] genetic algorithm. Subplex is a local, derivative free search algorithm that has been previously used with control fields using the CRAB parametrization \[22, 24\]. CMA-ES is a genetic algorithm designed for solving difficult continuous optimization problems while employing only a few tunable hyper-parameters (here we set the population size to 50 and the initial standard deviation to 1). We limited each optimization algorithm to a maximum of 10,000 function evaluations with a single initial condition, \( A_k = B_k = 1 \) for Eq. (5.7) and \( C_k = 0 \) for Eq. (5.8). Interestingly, we found that the best optimization algorithm depended on the particular optimization target (e.g., Subplex worked better than CMA-ES for 69% of the cases depicted in Fig. 5.3), so we used the best result from optimizations with both algorithms. With more function evaluations available, more random initial conditions could be used with Subplex (as in Ref. \[24\]) and population sizes could increased for CMA-ES. Because both algorithms struggle to optimize over very rough control landscapes, when implementing using the pulse parameterization in Eq. (5.7), we choose the total pulse duration with a separate optimization, by performing a grid search over all pulse durations between 100 fs and 500 fs at increments of 50 fs. In practice, we find this significantly increases the consistency and quality of our optimization results compared to including the pulse duration as a search parameter. In addition, to guarantee that our optimal pulses are still in the weak field regime with Eq. (5.7), we subtract from each objective function a smooth cutoff function of the form \( \Theta(x - \alpha)(x - \alpha)^2 \), where \( x \) is the total excited state population and \( \alpha = 0.01 \) is set as the maximum acceptable excited state population. Note that for an unshaped Gaussian pulse (i.e., Eq. (5.8) with all \( C_k = 0 \)), this maximum excited state population of 1% corresponds to a maximum electric field amplitude in the time domain of no more than \( 1.2 \times 10^7 \text{ V m}^{-1} \).

To match experimental conditions, in addition to optimizing over pulse parameters, in most of our optimizations we average over ensembles of complexes characterized by orientational and/or energetic (static) disorder. For these calculations, we use two approaches. To average over the orientations, we use the fact that the isotropic average of the excited state density matrix under weak fields is equal to the average of the x, y and z polarization orientations (see Appendix 5.7.1). Accordingly, we can obtain the exact orientational average at the cost of only a factor of 3 times more function evaluations. Unfortunately, there is no such shortcut for averages over energetic disorder. In such cases, we perform optimizations on the average of 10 randomly (but consistently) chosen samples, and still limit ourselves to the fixed computational cost of 10,000 function evaluations by now allowing for no more than 1000 function evaluations. To determine final optimal results in the presence of static energetic disorder, we average over ensembles of 1000 samples. For these simulations, we average the excited state density matrix \( \rho_e \) in the site basis before inserting it into the objective functions given by Eqs. (5.3–5.6).
5.4 Limits of coherent control for initial state preparation in FMO

An interesting question to consider before investigating control pulses designed for specific target states, is whether or not the FMO system can be prepared in any arbitrary state, i.e., whether FMO is controllable. Formally, a closed quantum system is completely controllable if control fields can be used to generate any arbitrary unitary operation \([127]\). Complete controllability implies that it is possible to prepare arbitrary pure states starting from any initial pure state, which in our case is the ground state. The controllability of a closed quantum system can be analyzed algebraically, by examining the Lie algebra generated by the system and control Hamiltonians. Accordingly, we consider the following highly idealized scenario: the electronic degree of freedom for a single FMO molecule without coupling to vibrations and restricted to at most one electronic excitation. Inter-pigment and pigment-protein interactions break the degeneracy of the excited states, so for the system without dissipation there actually is a constructive algorithm for determining arbitrary unitary controls \([116]\). We confirmed this by running the algorithm of Ref. \([127]\) to verify that we do indeed have complete controllability for formation of exciton states in the FMO complex under the combination of the electronic system Hamiltonian \(H_S\) and the light-matter interaction \(H_{S-L}\) with any arbitrarily chosen single polarization of light.

In contrast, there are few rigorous results known for determining the controllability of open quantum systems \([39]\). Accordingly, in our calculations below for realistic experimental conditions (weak fields, bulk samples with orientational and static disorder, finite temperatures) we assess the feasibility landscape of both arbitrary (amplitude/phase) and phase-only control in a brute-force manner, namely by evaluating the effectiveness of candidate control pulses for various targets. Our constraints are chosen to reflect the current experimental situation and include the use of weak fields, averaging over all orientations, averaging over static disorder and decoherence at \(77\,\text{K}\). Averaging over orientations and over static disorder would not be necessary in single complex spectroscopy experiments, which may become feasible in the foreseeable future (see below). We have carried out optimizations to both maximize and to minimize population on specific sites and excitonic states.

The results of these optimizations with amplitude and phase control [Eq. (5.7)] and with phase-only control [Eq. (5.8)], are summarized in Figure 5.2 and compared with the corresponding populations achieved using unshaped pulses. The latter is the set of populations realized by a fixed “unshaped” Gaussian pulse with a variable time-delay after the end of the pulse. The variable time-delay simply allows incorporation of the inherent relaxation in the system, which can aid in optimizing some goals (e.g., preparation of the lowest energy exciton, or of site 3, on which the lowest exciton is mostly localized). These results show that under experimental conditions corresponding to bulk samples of FMO complexes in solution at liquid nitrogen temperatures, we are in a coherent control situation where fidelity values are more similar to those achieved in typical reactive chemical control situations than the values required for quantum information processing, underscoring once again the critical role
CHAPTER 5. REALISTIC AND VERIFIABLE COHERENT CONTROL

Figure 5.2: Population control results for all targets (site and exciton populations). Blue and red bars indicate the minimum-to-maximum populations achievable with phase only control and with phase plus amplitude control, respectively. The white bars indicate the minimum-to-maximum achievable by using unshaped pulses together with a variable time delay following the pulse (see text). Phase only control is a special case of phase and amplitude control, and unshaped pulses are a special case of shaped pulses, so the red area is actually inclusive of the entire range shown and the blue area is inclusive of the white bar. Exciton 1 has the lowest energy and exciton 7 the highest energy.

of the open quantum system dynamics.

We now consider the effect of each of three major constraints on the achievable fidelity of control, both singly and in all possible combinations. We identify these three primary constraints as the following: the isotropic average over all molecular orientations, the ensemble average over static disorder of the transition energies $\mathcal{E}_n$ and the effects of decoherence due to the interaction with the environment (represented by a bath of phonon modes) at 77 K. The independent and cumulative effect of these constraints are illustrated by the Venn diagrams in Figure 5.3 and the values are given in Table 5.1. We have restricted the depictions here to just the results for maximizing each exciton or site population and for joint phase and amplitude control using Eq. (5.7).

Although it is clear from the lower panels of Figure 5.3 that the precise results of optimization are different for each target state, we can nevertheless extract a number of striking trends. For example, for most targets, the single largest limiting factor to controllability is decoherence. Also, in general, it is easier to achieve single exciton rather than site localized target states, as indicated by the average control fidelities over all sites or all excitons in Table 5.1. Site 3 is an exception to both these trends, which is readily rationalized by recognizing that the lowest energy exciton (exciton 1) is primarily localized on site 3. Indeed, it is notable that optimization both of population on site 3 and in exciton 1 are relatively robust to all three of the constraints. We can also see that averaging over orientations without
Site 1: Isotropic average Ensemble disorder Decoherence (at 77 K) Closed system, oriented, single molecule 100% 84.8% 72.4% 63.9% 57.4% 50.7% 44.9% 32.9% 0.2 0.4 0.6 0.8 1.0 Target fidelity

Figure 5.3: Venn diagrams indicating control fidelity for optimization under different experimental constraints with joint phase and amplitude control. The outer region refers to the closed quantum system constituted by the excitonic Hamiltonian without coupling to the protein environment. Here the excitonic system is completely controllable and the fidelity of preparing any state is 100%. The circles enclosed by colored lines indicate the fidelity achieved when we add averaging over orientation of the FMO complex (red circles), averaging over site energy disorder (green circles) and adding the coupling to the protein environment at a finite temperature (blue circles). (Above) Venn diagram for maximum population on site 1. (Below) Venn diagrams for all site and exciton targets.
decoherence is evidently a more severe constraint for localized site target states than for single exciton target states. This can be rationalized as reflecting a simple physical strategy for targeting excitonic states, namely, to drive the system for a long time at the proper transition energy. In most cases, it is clear that the difficulty of control under realistic conditions stems from the combination of two or more of these limiting factors, which together rule out many intuitive control strategies.

The optimal pulse shapes for selected instances of site and exciton target states, with and without ensemble averaging over static disorder, are shown in Figure 5.4. We illustrate these pulses by plotting their Wigner spectrograms [99], given by the expression

\[ W(t, \omega) = \int_{-\infty}^{\infty} d\tau E^*(t - \tau/2)E(t + \tau/2) \exp(i\omega\tau), \]  

where \( E(t) \) is the pump field and * denotes the complex-conjugate. The Wigner spectrogram can be interpreted as a type of joint time-frequency distribution, with the desirable properties,

\[ |E(t)|^2 = \int \frac{d\omega}{2\pi} W(t, \omega) \]  

\[ |E(\omega)|^2 = \int dt W(t, \omega). \]
Figure 5.4: Optimal pulses to maximize the population of the isotropic average on exciton 6 (top) or site 1 (bottom) in the presence of decoherence, both without (left) and with (bottom) static disorder. The central plot of each pulse is of the Wigner spectrogram. Red (blue) indicates positive (negative) values. Top and right plots show the marginal time and frequency distributions $|E(t)|^2$ and $|E(\omega)|^2$. 
Recall that because we are in the weak-field regime and normalize all objective functions by the excited state population, our results are independent of the overall amplitude of the pump pulse, so there is no need to provide an absolute scale for the control field amplitude. As Figure 5.4 shows, optimal pulses for targeting states in the presence of static disorder generally require a more complicated frequency distribution and a broader band of excitation frequencies. This is particularly evident from the optimal pulses for creating an excitation in a single excitonic state, where the optimal pulses are generally peaked at the transition energy of the desired state. The optimal pulses for preparing an excitation in exciton 6 (top panels) illustrates also the complementary trend that in the presence of static disorder the optimal pulses are usually shorter in time. Not surprisingly, pulses designed with optimal polarizations (i.e., without the average over all orientations), are even shorter since these optimizations can make use of polarization in addition to or instead of excitation frequency to selectively target specific states.

To explore the influence of decoherence in more detail, we consider the independent effects of adjusting the temperature of the bath and the reorganization energy. Figure 5.5 shows the error for maximizing population in one specific site, as a function of the reorganization energy (left panel) and as a function of the bath temperature (right panel). We see that although lowering the bath temperature to near zero does make it easier to target site 1, this is not as powerful a control knob as removing the system-bath coupling (i.e., setting the bath reorganization energy to zero).
5.5 Authentication of coherent control in pump-probe spectra

To experimentally verify the excited state that is created by a control pulse, we propose to use ultrafast pump-probe spectroscopy. In pump-probe spectroscopy, a pump pulse excites the system, followed by a probe pulse at a controlled delay time. Although there are a number of ultrafast spectroscopies that may be used for probing light harvesting systems [98], pump-probe spectroscopy is particularly well suited for verifying state preparation since its signal can be formally interpreted as a function of the full excited state created by the pump pulse [69]. In the limit of an impulsive probe pulse, provided that we are in the weak field regime and that there is no time overlap between the pump and probe pulses, the frequency resolved pump-probe signal is given by

\[ S(\omega, T) \propto \text{Re} \{ \text{Tr}[\mu G(\omega)[\mu^\dagger, \rho_{pu}^{(2)}(T)]] \} \]  

(5.12)

where \( \omega \) is the probe frequency and \( T \) is the time delay of the probe relative to the end of the pump probe [69]. We emphasize that one cannot verify state preparation with this approach before the end of the pump pulse. The operator \( G(\omega) \) is the Fourier transform of the retarded material Green function, \( \mu \) is the annihilation component of the dipole operator \( \mu \) in the direction of the probe field and \( \rho_{pu}^{(2)}(T) \) is the second order contribution to the density matrix in terms of the pump pulse, restricted to the 0-1 excitation manifold. For a Markovian bath and weak excitation, this density matrix \( \rho_{pu}^{(2)}(T) \) can be written as a linear function of the excited state density matrix \( \rho_e(T) \) [69]. Accordingly, we can write Eq. (5.12) in the form

\[ S(\omega, T) \propto \text{Re} \{ \text{Tr}[\mathcal{P}(\omega)\rho_e(T)] \} \]  

(5.13)

where \( \mathcal{P}(\omega) \) is a (linear) superoperator in Liouville space. This equation still holds even for a randomly oriented ensemble for a pump-probe experiment performed in the magic-angle configuration [65], provided that \( \mathcal{P}(\omega) \) and \( \rho_e \) are replaced by their isotropic averages (see Appendix 5.7.1). We then efficiently perform each of these independent isotropic averages by averaging over the x, y and z pump (or probe) polarizations [38].

The ideal authentication procedure for any quantum control experiment is quantum state tomography, in which each element in the density matrix is determined by repeated measurements on an ensemble of identically prepared systems [103]. It is possible to construct protocols for state tomography of excitonic systems that are based on pump-probe spectroscopy [157, 69], but the uncertainty concerning Hamiltonian parameters, together with the averaging over energetic disorder and orientations associated with ensemble measurements, make this an unrealistic target for systems with as many pigments as FMO [69]. Accordingly, here we consider two options for authenticating control that may be realized with current experimental technology. The first is to extend the duration of coherent electronic beating and the second is to generate a novel signature in the pump-probe signal. We note that with a frequency resolved signal as given by Eq (5.12), there are no gains from
optimizing the probe pulse, as long as it is faster than the dynamics of interest and has non-zero amplitude at the frequencies of interest.

Although the evidence for electronic coherence today is more clearly evident in 2D photon-echo spectroscopy [44, 37], the first evidence for quantum beats in excitonic dynamics of the FMO complex were actually found with pump-probe spectroscopy [126]. Under secular Redfield dynamics, the excitonic coherence terms are decoupled from all other dynamics and decay exponentially. Hence to maximize the duration of quantum beating within this description of the dynamics, we merely need to maximize the absolute value of the coherence terms in the excitonic basis. However, predicting the visibility of electronic quantum beats is complicated by the relative orientations of the relevant transition dipole moments, as well as by the need to observe any oscillations before they decay. Accordingly, we demonstrate here the result of numerically maximizing the excitonic coherence $|\rho_{12}|$ between the lowest two exciton energies, since observations of quantum beats in pump-probe spectra have previously been ascribed to this coherence [126]. (We do not optimize for the ensemble value of this coherence, because the ensemble average of excitonic coherences in the eigenbasis of the Hamiltonian without static disorder do not necessarily decay to zero at long delay times.) For this optimization we use the unrestricted parametrization of Eq. (5.7), in order to determine the limits of maximizing this signal. We note that the aforementioned experimental pump-probe study did use a form of incoherent control to maximize the this signal, by scanning the central frequency of the pump pulse [126]. Our results show that we can increase the magnitude of the excitonic coherence $|\rho_{12}|$ by a factor of up to 8.6x compared to an unshaped Gaussian pump. Figure 5.6 illustrates the optimal pulse and its signature on the pump-probe spectra including ensemble disorder. As shown in panel (a), the increased coherence results in increased oscillatory features that will be visible in a magic angle pump-probe experiment, particularly after subtracting away the non-oscillating contribution to the signal [panel (b)]. This subtraction of the non-oscillating signal is similar to the technique used in [108] to estimate the timescale of quantum beats in a 2D photon-echo experiment. Even after including static disorder, the beating signal following the optimized pump shows oscillations with a magnitude about 3x larger than those following the original, unshaped pump pulse. The optimal pulse (c) uses the unsurprising strategy of sending a very short pulse peaked at the relevant exciton transition energies, $\omega_1 = 12170 \text{ cm}^{-1}$, $\omega_2 = 12282 \text{ cm}^{-1}$. Although our optimal pulse uses a total duration of $T = 350\text{ fs}$, all of its meaningful features are in the last 100 fs; indeed, our optimizations for different total times between 100 fs and 500 fs showed only a small variation in the factor of enhancement of the 1-2 coherence, ranging from 8.4 to 8.6.

To further demonstrate the feasibility and authentication of coherent control of energy transfer in FMO, we now consider using phase-only control to create new states that are not accessible from unshaped (Gaussian) pulses. This optimization for new states with phase-only control proved to be quite difficult. In most cases, phase-only control only enhances site or exciton populations by at most a few percent in comparison to the unshaped pulse (see Figure 5.2). Verifying such small differences in the population of a specific site or exciton is almost certainly beyond the current experimental state of the art for these open quantum
Figure 5.6: Enhanced coherent beating in the pump-probe signal. (a) Differential absorption [the pump-probe signal given by \(E\)q. (5.12)] at a probe frequency of 12 200 cm\(^{-1}\) following unshaped (solid blue line) or optimized pump (dashed red line) pulses, normalized by the total excited state population following the pump pulse. The probe frequency was chosen as an arbitrary value, in the range of the exciton 1 and 2 transition energies where the oscillatory signal from the optimized pump is clear. Dots show a double exponential fit for each signal of the form \(Ae^{-at} + Be^{-bt} + C\), where \(A\), \(B\), \(C\), \(a\) and \(b\) are constants chosen to minimize the least squares distance between the fit and the differential absorption signal. (b) Beating portion of the signal shown in panel (a) after subtracting the double exponential fits, \(A = 3.13\) cm\(^{-1}\), \(B = 1.79\) cm\(^{-1}\), \(C = -6.89\) cm\(^{-1}\), \(a = 3.11\) ps\(^{-1}\), \(b = 1.29\) ps\(^{-1}\) for the unshaped pulse and \(A = 44.8\) cm\(^{-1}\), \(B = -45.4\) cm\(^{-1}\), \(C = -6.76\) cm\(^{-1}\), \(a = 5.57\) ps\(^{-1}\), \(b = 5.52\) ps\(^{-1}\) for the optimized pulse. (c) Wigner spectrogram showing the time-frequency distribution of the optimized control pulse, depicted in the same style as the pulses in Fig. 5.4.
Achieving phase-only control is especially difficult for natural light harvesting systems because they feature rapid dephasing and energetic relaxation, with each of these operating at a similar time scale to the natural time scale of the energy transfer (see above). Applying phase-shaping by necessity increases the temporal duration of the pulse, and thus in most cases simply drives the system closer to the equilibrium excited state, rather than to a selected state.

The exact dependence of the pump-probe signal on the density matrix $\rho^{(2)}_{pu}(T)$ given by Eq. (5.12) is difficult to determine with high accuracy, even with the assistance of experimental input. Nevertheless, the formal dependence of the signal on the density matrix [Eq. (5.13)] means that this can be used as a witness for coherently controlled formation of new target states. Consider the reference set of states through which the system passes following the end of an unshaped Gaussian pump pulse. Our goal is now to create a state with a spectrum [Eq. (5.13) with any fixed value of $T$] that falls outside this reference set. We achieve this by directly optimizing the difference in a simulated pump-probe spectrum from all possible spectra obtained from the reference set of states. With this procedure we found that it is possible to create a 12.0% relative difference in the signal outside the range of spectra resulting from an unshaped pulse with a time delay. The resulting spectra and visualizations of the optimal pulse constructed from Eq. (5.8) with $N = 10$ terms are shown in Figure 5.7. We chose $N = 10$ because our optimizations seemed to reach a point of diminishing returns; in fact, we were able to achieve a maximum difference of 4.2% with first-order chirp alone ($N = 1$) and 9.8% by adding only one higher order chirp term ($N = 2$). Inspection of the optimal pulse [panels (b-d)] reveals that this is acting to maximize the population in low energy states (excitons 2 and 3) by sending in the higher energy light first, so that the excitons absorbed at these frequencies have time to relax to lower energy states. The population in these states is then further amplified by absorption of a final burst of low energy light just before the pulse ends.

5.6 Discussion and outlook

In this paper we have considered the simplest experimental setup for coherent control of excited state dynamics in light harvesting systems, namely a pump-probe configuration. Most importantly, we showed that in a realistic experimental scenario it should be possible to do two types of coherent control and verification experiments: to create of provably new states with phase-only control, and, if both phase and amplitude shaping are available, to enhance quantum beatings.

We also analyzed in detail the effect of various restrictions to understand what limits control in light harvesting systems. The reference closed quantum system given by just the seven chromophores of a single FMO complex is completely controllable, but when this system is treated correctly as an ensemble of open quantum systems, the extent of control of the excitonic subsystem is significantly reduced. Our systematic investigation of the limits of coherent control under the constraints of decoherence at finite temperatures, orientational
Figure 5.7: Signature of a novel state in the isotropic pump-probe spectra achieved by phase-only coherent control. The gray area in panel (a) indicates the range of pump-probe spectra (black lines) at various time delays (0, 75, 150, 300, 600 and 1200 fs, and in the limit \( T \to \infty \)) after the end of the unshaped pump pulse, and the red dashed line shows the spectrum immediately following the optimal pulse. The time-domain, frequency-domain and Wigner spectrogram of the control pulse are shown in panels (b), (c) and (d), respectively. The dashed line in panels (b) and (d) indicates the temporal end of the control pulse. The scale on each plot is in arbitrary units, except for panel (c) which plots the phase in multiples of \( 2\pi \).
disorder and static (energetic) disorder, revealed that together these three factors restrict the fidelity of achieving both excitonic (energy eigenstates of the electronic Hamiltonian) and site localized target states. Interestingly, our results show that significant improvements in extent of controllability should be possible with experiments on well-characterized single molecules. Such single-molecule experiments based on non-linear fluorescence may indeed be possible in the near future [89, 64].

We expect that optimal control will be an even more powerful technique when applied to more complicated non-linear spectroscopy experiments. For example, simultaneous optimization of the first two pulses in a third order photon-echo experiment would allow for preparing particular targeted phase-matched components of the second order density matrix $\rho^{(2)}$. Although they ultimately reflect the same third order response function, coherent control of the photon echo could be an attractive alternative to full two-dimensional spectroscopy. A novel maximally efficient computational scheme for simulating such signals is presented in Appendix 5.7.2. For higher order spectroscopies the advantages of open loop control for optimal experiment design should be even larger, given that the exponential growth of the state space of possible experimental configurations makes scanning all possible configurations (as in many 2D experiments) increasingly infeasible.

### 5.7 Appendices

#### 5.7.1 Orientational average

For an ensemble of identical, randomly oriented molecules, it is possible to analytically integrate over all possible molecular orientations with a fixed number of system-field interactions. For two interactions (the case for linear spectroscopies), all signals can be written in the form $\langle S \rangle = \sum_{pq} T_{pq} S_{pq}$, where each sum is over all orthogonal orientations $x$, $y$ and $z$ and $T_{pq}$ is the second order tensor invariant $\delta_{pq}$. For four interactions (the case for all 3rd order spectroscopies, including pump-probe), all signals can be written in the form $\langle S \rangle = \sum_{pqrs} T_{pqrs} S_{pqrs}$, where each sum is over all orthogonal orientations $x$, $y$ and $z$ and $T_{pqrs}$ is a linear combination of the fourth order tensor invariants, $\delta_{pq}\delta_{rs}$, $\delta_{ps}\delta_{qr}$ and $\delta_{pr}\delta_{qs}$. The polarization of the pump and probe pulses determines which of these tensor invariants contribute to the observed signal [65]. In the Magic Angle configuration, for which the polarization of the first two interactions is at an angle of $54.7^\circ$ relative to the polarization of the last two interactions, only the invariant $\delta_{pq}\delta_{rs}$ contributes to the observed signal. Since this invariant is the product of the 2nd order tensor invariant for the first and last two interactions separately, the isotropic averages can be performed separately for the first two (pump) and last two (probe) interactions.
5.7.2 Optimal equation-of-motion phase-matching approach for third-order ultrafast spectroscopy

The formalism for pump-probe spectroscopy that we developed in Sec. 4.2 can be extended into an efficient numerical method for simulating arbitrary third-order spectroscopy experiments. In the case of the non-rephasing or rephasing geometries for a third-order experiment under the rotating wave approximation (RWA), this new formalism allows for the most efficient possible calculation of the nonlinear signal field. The technique is a variation of the equation-of-motion phase-matched approach \[51, 43, 50\] and thus provides a solution that is exact to third order in the strength of the applied fields, unlike some approaches built on the solution of equations of motion which do not require any such perturbative approximations \[91\]. We expect this technique could be especially useful for the design of future coherent control experiments using non-linear spectroscopy outside of the pump-probe configuration, as discussed in Sec. 5.6, which is why we include it as an appendix to this chapter. Another appealing use would be simulating transient-grating experiments with selective excitation frequencies, as proposed for a quantum process tomography scheme \[157\].

To set the context, there are two main types of simulation methods for ultrafast non-linear spectroscopy. In the response function approach \[98, 1\], the non-linear polarization results from integrating a non-linear response function over the envelopes of each control pulse. The response function dictates how the system would react to instantaneous (delta-function) control fields. In contrast, equation of motion based approaches determine the non-linear polarization by performing a number of simulations explicitly including Hamiltonian terms from the system-field interaction \[51, 50, 91\]. Which of these approaches is most suitable depends on the particular circumstances. For example, the response function approach is particularly well suited to simulations to simulating 2D spectroscopy, because in its ideal case, 2D spectroscopy is performed with broadband pulses so the third-order response function should closely approximate the 2D signal. Equation of motion based approaches are more suitable when the expense of simulating the full response function is unnecessary, such as in the context of simulating a specific experimental setup with non-impulsive control fields. The formulation of the equation-of-motion phase-matching approach is especially convenient because it does not require any assumptions about the time-ordering of the system-field interactions. However, it turns out that knowledge of the time-ordering in some cases may reduce the computational effort required by a factor of 3.

Our new method involves calculating a density matrix like operator including the first two system-field interactions using a phase-matched equation of motion and then accounting for the last interaction with either another equation of motion or a linear response function. From Eqs. \[1.12, 1.13\], it follows that in general we can write the experimental signal for a third order experiment under the RWA as

\[
P^{(3)}_{k_s}(t) = \int_0^\infty dt_3 R(t_3, \rho^{(2)}_{k_s}(t-t_3)) E_{3s}^u(t-t_3),
\]

(5.14)
in terms of a probe response function

$$R(t, \rho_{k_s}^{(2)}) = \frac{i}{\hbar} \text{Tr} \left[ \mu^{(-)} E(t) V^{(u_2)} \rho_{k_s}^{(2)} \right],$$

(5.15)

where $\rho_{k_s}^{(2)}$ is given by

$$\rho_{k_s}^{(2)}(t) = \left( \frac{i}{\hbar} \right)^2 \int_0^{\infty} dt_2 dt_1 G(t_2) V^{(u_2)} G(t_1) V^{(u_1)} \rho_0 E_{a_2}^{u_2}(t-t_2) E_{a_1}^{u_1}(t-t_2-t_1),$$

(5.16)

in terms of the quantities defined in Sec. 1.2. We note that these equations holds in general even without the RWA if $\mu^{(\pm)}$ and $V^{(\pm)}$ are each replaced by $\mu$ and $V$, respectively.

To calculate the phase-matched contribution to the second order density matrix $\rho_{k_s}^{(2)}$, we use equation of motion phase-matching approach of Domcke and co-workers [50]. Closely following their argument [50], we note that the phase-matched signal depends only on the portion $\sigma_2(t)$ of the system density matrix whose evolution depends on the first two correctly phase-matched components. The evolution of $\sigma_2(t)$, initially set to the ground state $\rho_0$, follows the usual equation of motion for the density matrix (any of those described in Sec. 1.2) under the time-dependent non-Hermitian Hamiltonian

$$H_{1,2}(t) = H + v_1^{(u_1)}(t) + v_2^{(u_2)}(t)$$

(5.17)

where $H$ is the system Hamiltonian (including any bath or vibrational modes) and

$$v_a^{\pm} = V^{(\pm)} \lambda_a E_a^{\pm}(t)$$

(5.18)

is an operator for the system-field interaction, where $V^{(\pm)}$ ($V$ without the RWA) is the relevant transition dipole moment operator, $\lambda_a$ is the intensity of pulse $a$ and $E_a(t) = E_a^{(0)}(t)$ is its complex valued electric field $[E_a^{(0)}(t) \equiv E_a(t)]$. Note that $H_{1,2}(t)$ is non-Hermitian except in the case of pump-probe spectroscopy where $E_1(t) = E_2(t)$ and thus $\sigma_2(t)$ is in general not a valid density matrix. Next, we expand $\sigma_2$ in a formal power series in terms of the strength of the first two electric fields $\lambda_1$ and $\lambda_2$,

$$\sigma_2(\lambda_1, \lambda_2) = \sum_{i,j} \lambda_i^1 \lambda_j^2 \sigma_{ij}$$

(5.19)

$$= \sigma_2^{00} + \lambda_1 \sigma_2^{01} + \lambda_2 \sigma_2^{01} + \lambda_1^2 \sigma_2^{02} + \lambda_2^2 \sigma_2^{02} + \lambda_1 \lambda_2 \sigma_2^{11} + O(\lambda^3),$$

(5.20)

where for conciseness the time-dependence of each density matrix was removed. Noting that $\rho_{k_s}^{(2)} = \lambda_1 \lambda_2 \sigma_2^{11}$, because that is the second order contribution which depends on both $\lambda_1$ and $\lambda_2$ to lowest order, from Eq. (5.20) we have

$$\rho_{k_s}^{(2)} = \sigma_2(\lambda_1, \lambda_2) - \sigma_2(\lambda_1, 0) - \sigma_2(0, \lambda_2) + \sigma_2(0, 0).$$

(5.21)

At this point, we see that the second order density matrix can be calculated from at most three evaluations of equations of motion under time-dependent Hamiltonians like Eq. (5.17).
Note that we need not perform any integrations to determine $\sigma_2(0, 0) = \rho_0$, since the state of the system without any applied fields is stationary.

An additional simplification is possible under the RWA, for experiments utilizing the photon echo or non-rephasing pathways (i.e., excluding the double quantum coherence pathway). For photon echo and non-rephasing pathways, we have $u_1 = \mp$, $u_2 = \pm$ and $u_3 = +$. Under the RWA, only contributions to $\rho_{k_s}^{(2)}$ that include equal numbers of raising and lowering operators can result in diagonal terms that contribute to the trace in Eq. (5.15) after applying an additional lowering and raising operator. Accordingly, we have $R(t, \sigma_2(\lambda_1, 0)) = R(t, \sigma_2(0, \lambda_2)) = R(t, \rho_0)$, so Eq. (5.21) may be replaced by

$$\rho_{k_s}^{(2)} = \sigma_2(\lambda_1, \lambda_2) - \rho_0. \quad (5.22)$$

Thus to calculate $\rho_{k_s}^{(2)}$ under the RWA, we need only integrate the equation of motion given by Eq. (5.17) directly. This fact still holds even in a pump-probe experiments where $k_1 = -k_2$, since we need only multiply the right hand side of Eq. (5.22) by an additional factor of 2 to account for both possible time-orderings of the first two pulses [69].

Once $\rho_{k_s}^{(2)}$ is obtained, the full nonlinear polarization $P_{k_s}^{(3)}$ may be obtained in either of two ways. For an impulsive probe pulse, it is convenient to obtain the nonlinear polarization plugging $\rho_{k_s}^{(2)}$ from Eq. (5.21) or Eq. (5.22) directly into the response function given by Eq. (5.15). The signal under an impulsive probe may be directly useful, because, as noted in Chapters 4 and 5, there appears to be no theoretical advantage to using a non-broadband probe pulse. This is the same technique for which we provided an alternative proof for the restricted case of pump-probe experiments in Chapter 4, although that proof required that the first two pulses be entirely identical, including their polarization, which restricted the technique to the magic angle setup.

Alternatively, for a non-impulsive probe, we construct another time-dependent non-Hermitian Hamiltonian to account for the phase-matched contribution from the last interaction,

$$H_3(t) = H + v_3^{(u_3)}(t). \quad (5.23)$$

Because we have a definite time-ordering between the second and third interaction, we can pick an intermediate time $t_0$ when there are no applied fields (i.e., $H_{1,2}(t_0) = H_3(t_0) = H$) at which to begin applying Eq. (5.23). We then solve for the dynamics $\sigma_3(t)$ under this Hamiltonian with the initial condition $\sigma_3(t_0) = \rho_{k_s}^{(2)}(t_0)$. Analogously to the reasoning above for $\sigma_2$, we see that by expanding the state $\sigma_3$ as a formal power series in terms of the strength of the last interaction $\lambda_3$, to lowest order we obtain

$$\rho_{k_s}^{(3)} = \sigma_3(\lambda_3) - \sigma_3(0). \quad (5.24)$$

Finally, the third-order non-linear polarization is given by inserting $\rho_{k_s}^{(3)}$ into

$$P_{k_s}^{(3)}(t) = \frac{i}{\hbar} \text{Tr} \left[ \mu^{(-)} \rho_{k_s}^{3}(t) \right], \quad (5.25)$$
which is the original equation for the non-linear polarization from which one may derive 
Eq. (5.14–5.16). Under the RWA, $\text{Tr}[\mu^{(-)}\sigma_3(0)] = 0$, so we may safely neglect the contribution of $\sigma_3(0)$ to Eq. (5.24) and only integrate under Eq. (5.23) once.

In total, this new approach requires only 1 full numerical integration of an equation of motion (or 3 without the RWA), unlike the 3 (or 7) integrations required when using the full equation of motion phase-matched approach [50]. In addition, as noted in Sec. 1.4, restricting dynamics to a particular subset of Liouville space can also be an important for maximum computational efficiency. Under the RWA, we obtain all contributions to the signal by simulating $\sigma_2$ restricted to the electronic subspaces $|g\rangle\langle g|$, $|g\rangle\langle e|$, $|e\rangle\langle g|$ and $|e\rangle\langle e|$, and $\sigma_3$ restricted to $|g\rangle\langle g|$, $|e\rangle\langle g|$, $|e\rangle\langle e|$ and $|f\rangle\langle e|$. Since it impossible to numerically simulate dynamics without at least one complete time propagation, our new approach provides for the most efficient possible calculation of individual pump-probe, photon-echo, non-rephasing or transient grating signals under the RWA, with or without an impulsive probe.
References


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