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Editorial

Electronic energy transfer
Anthony Harriman, Phys. Chem. Chem. Phys., 2010
DOI: 10.1039/c0cp90032j

Perspectives

Quantum coherence and its interplay with protein environments in photosynthetic electronic energy transfer
DOI: 10.1039/c003389h

Excitation energy transfer in donor–bridge–acceptor systems
Bo Albinsson and Jerker Mårtensson, Phys. Chem. Chem. Phys., 2010
DOI: 10.1039/c003805a

Physical origins and models of energy transfer in photosynthetic light-harvesting
DOI: 10.1039/c003025b

Communication

Formation and energy transfer property of a subphthalocyanine–porphyrin complex held by host–guest interactions
Hu Xu, Eugeny A. Ermilov, Beate Röder and Dennis K. P. Ng, Phys. Chem. Chem. Phys., 2010
DOI: 10.1039/c003479g

Papers

Charge transfer in hybrid organic–inorganic PbS nanocrystal systems
Muhammad N. Nordin, Konstantinos N. Bourdakos and Richard J. Curry, Phys. Chem. Chem. Phys., 2010
DOI: 10.1039/c003179h

Superexchange-mediated electronic energy transfer in a model dyad
Carles Curutchet, Florian A. Feist, Bernard Van Averbeke, Benedetta Mennucci, Josemon Jacob, Klaus Müllen, Thomas Basché and David Beljonne, Chem. Phys., 2010
DOI: 10.1039/c003496g

Switching off FRET by analyte-induced decomposition of squaraine energy acceptor: A concept to transform "turn off" chemodosimeter into ratiometric sensors
Haibo Yu, Meiyan Fu and Yi Xiao, Phys. Chem. Chem. Phys., 2010
DOI: 10.1039/c001504k

Hybrid complexes: Pt(II)-terpyridine linked to various acetylide-bodipy subunits
Francesco Nastasi, Fausto Puntoriero, Sebastiano Campagna, Jean-Hubert Olivier and Raymond Ziessel, Phys. Chem. Chem. Phys., 2010
DOI: 10.1039/c003789c

Conformational dependence of the electronic coupling for singlet excitation energy transfer in DNA. An INDO/S study
DOI: 10.1039/c003131c

On the conveyance of angular momentum in electronic energy transfer
DOI: 10.1039/c002313m

Isotopic effect and temperature dependent intramolecular excitation energy transfer in a model donor–acceptor dyad
DOI: 10.1039/c003113e

Photophysics of conjugated polymers: interplay between Förster energy migration and defect concentration in shaping a photochemical funnel in PPV
Sangeeta Saini and Biman Bagchi, Phys. Chem. Chem. Phys., 2010
DOI: 10.1039/c003217d

Electronic energy harvesting multi BODIPY-zinc porphyrin dyads accommodating fullerene as photosynthetic composite of antenna-reaction center
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Quantum coherence and its interplay with protein environments in photosynthetic electronic energy transfer

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Recent experiments suggest that electronic energy transfer in photosynthetic pigment-protein complexes involves long-lived quantum coherence among electronic excitations of pigments. [Engel et al., Nature, 2007, 446, 782–786.] The observation has led to the suggestion that quantum coherence might play a significant role in achieving the remarkable efficiency of photosynthetic light harvesting. At the same time, the observation has raised questions regarding the role of the surrounding protein in protecting the quantum coherence. In this Perspective, we provide an overview of recent experimental and theoretical investigations of photosynthetic electronic energy transfer paying particular attention to the underlying mechanisms of long-lived quantum coherence and its non-Markovian interplay with the protein environment.

I. Introduction

Photosynthesis provides the energy source for essentially all living things on Earth, and its functionality has been one of the most fascinating mysteries of life. Photosynthetic conversion of the energy of sunlight into its chemical form suitable for cellular processes involves a variety of physicochemical mechanisms.1 The conversion starts with the absorption of a photon of sunlight by one of the light-harvesting pigments, followed by transfer of electronic excitation energy to the reaction center, where charge separation is initiated. At low light intensities, surprisingly, the quantum efficiency of the transfer is near unity, that is, each of the absorbed photons almost certainly reaches the reaction center and drives the charge separation. At high light intensities, the reaction center is protected by regulation mechanisms that lead to quenching of excess excitation energy in light harvesting proteins. The molecular details of these initial stages of photosynthesis are not yet fully elucidated from the standpoint of physical chemistry and chemical physics.

Recently, the technique of two-dimensional (2D) Fourier transform electronic spectroscopy2,3 has been applied to explore photosynthetic light harvesting complexes.4–7 Fleming and coworkers8,9 investigated photosynthetic electronic energy transfer (EET) in the Fenna-Matthews-Olson (FMO) pigment-protein complex1,10 isolated from a green sulfur bacterium, Chlorobaculum tepidum. This complex is tasked with transporting sunlight energy collected in the peripheral light-harvesting antenna to the reaction center. One of their experiments revealed the existence of long-lived quantum coherence among the electronic excited states of the multiple pigments in the FMO complex.9 The observed coherence clearly lasts for

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timescales similar to the EET timescales, implying that electronic excitations travel coherently though the FMO complex rather than by incoherent diffusive motion as has usually been assumed. This spectroscopic observation has led to the suggestion that quantum coherence may be vital in achieving the remarkable efficiency of photosynthetic EET. This speculation is further substantiated by measurements at ambient temperatures. Although quantum coherence in the FMO complex was originally observed at cryogenic temperature, recent experiments detected the presence of quantum coherence lasting up to 300 fs even at physiological temperatures in both a complex isolated from photosynthetic marine algae and the FMO complex. This timescale is consistent with theoretical prediction for the FMO complex. With the general belief that biological organisms have adapted in the course of evolution so as to function most effectively in a given environment, a number of investigations were triggered to unlock the quantum secrets of photosynthetic EET, e.g. the relevance, significance, and universality of quantum coherence in photosynthetic systems. Specifically, recent experiments demonstrated electronic coherence in the light-harvesting complex II (LHCII). LHCII is the most abundant antenna complex in plants containing over 50% of the world’s chlorophyll molecules, and has been extensively studied experimentally and theoretically. While these studies provide new insight into the role of quantum coherence in photosynthetic EET, questions remain regarding the under-lying mechanisms preserving the long-lived quantum coherence and its interplay with the protein environment.

The electronic coupling $hJ$ between pigments and the electron-nuclear coupling characterized by the reorganization energy $h\lambda$ are two fundamental interaction mechanisms determining the nature of EET in photosynthetic complexes. The transfer processes are usually described in one of two perturbative limits. When the electronic coupling $hJ$ is small in comparison with the electron-nuclear coupling $h\lambda$, the original localized electronic state is an appropriate representation and the inter-pigment electronic coupling can be treated perturbatively. This treatment yields Förster theory. In the opposite limit, when the electron-nuclear coupling is small, it is possible to treat the electron-nuclear coupling perturbatively to obtain a quantum master equation. The most commonly used theory from this limit in the literature of photosynthetic EET is Redfield theory.

Ordinarily, photosynthetic EET is discussed only in terms of the mutual relation between magnitudes of the two couplings, as just described. However, we should not overlook that the nature of EET is also dominated by the mutual relation between two timescales, the characteristic timescale of the nuclear reorganization, $t_{\text{rxn}}$, and the inverse of the electronic coupling, $J^{-1}$, that is the time the excitation needs to move from one pigment to another neglecting any additional perturbations. In the case of $t_{\text{rxn}} \ll J^{-1}$, it is impossible to construct a wave function straddling multiple pigments. The nuclear reorganization introduces fast dephasing, and hence EET occurs after the nuclear equilibration associated with the excited pigment. In this situation, EET is described as a diffusive motion similar to classical random walk; it follows classical rate laws where the transition rate is given by Förster theory. In the contrary case of $J^{-1} \ll t_{\text{rxn}}$, the excitation can travel almost freely from one pigment to others according to the Schrödinger equation until the nuclear configurations are quenched by the reorganization. The excitation travels through photosynthetic complexes as a quantum mechanical wave packet keeping its phase coherence. Thus, this process is termed coherent transfer. It is worth noting that the timescale of energy transport does not exceed that of $J^{-1}$ whenever $t_{\text{rxn}} \ll J^{-1}$ or $J^{-1} \ll t_{\text{rxn}}$.

Obviously, there exists regimes of EET where the two coupling magnitudes and/or the two timescales compete against one another, i.e. $\lambda \sim J$ and/or $t_{\text{rxn}} \sim J^{-1}$. These intermediate regimes are typical situations for photosynthetic EET, and therefore they are of considerable interest. From a theoretical point of view, descriptions of these regimes are challenging because no vanishingly small parameters allow us to employ common perturbative and Markovian treatments. That is to say, photosynthetic EET is generally in a cumbersome nonperturbative and non-Markovian regime. Although several...
These states are defined by the electronic Schro¨dinger dynamic effects of the same protein portions, fluctuations in stratifies that the electronic energies of the pigments experience dynamical point of view, on the other hand, eqn (2.3) demon-

The potential energy surface influenced by the surrounding protein, Renger and coworkers55 protein degrees of freedom. To evaluate the electronic energies to interpolate between the conventional Fo¨rster and Redfield theories to treat the intermediate regimes, 28,29,50–53 there exists no explicit evidence that these theories are capable of no explicit evidence that these theories are capable of

The aim of this Perspective is to provide reports on recent theoretical and experimental progress in photosynthetic EET specifically addressing the underlying mechanisms of quantum coherence and its non-Markovian interplay with the protein environment.

II. Modeling a pigment-protein complex: Statistical mechanical point of view

We consider a pigment-protein complex (PPC) consisting of N pigments. To describe EET in the PPC, it is advisable to separate the PPC Hamiltonian, \(H_{\text{PPC}}\), into intra-pigment contributions and inter-pigment Coulomb interactions as follows:49,54

\[
H_{\text{PPC}} = \sum_{m=1}^{N} H_m + \sum_{m,n} U_{mn}. 
\]

The intra-pigment contributions \(H_m\) reads

\[
H_m = T_{m}^{\text{exc}} + H_{m}(R), 
\]

where \(H_{m}^{(j)}(R)\) comprises all electronic contributions of the \(m\)th pigments and the associated intra-nuclear interaction, and depends parametrically on the set of the relevant nuclear coordinates including protein degrees of freedom, \(R\). The nuclear kinetic energy has been denoted by \(T_{m}^{\text{exc}}\). For the following, the electronic states of a pigment are labeled by \(a\).

These states are defined by the electronic Schrödinger equation, \(H_{m}^{(j)}(R)|\varphi_{ma}\rangle = e_{ma}(R)|\varphi_{ma}\rangle\), and hence the nuclear dynamics associated with an electronic state \(|\varphi_{ma}\rangle\) is described by

\[
H_{na}(R) \equiv \langle \varphi_{ma}|H_{m}(R)|\varphi_{ma}\rangle = T_{m}^{\text{exc}} + e_{ma}(R). 
\]

The potential energy surface \(e_{ma}(R)\) is different from that in vacuum because \(\Phi_{m}^{(j)}(R)\) includes the influence of the relevant protein degrees of freedom. To evaluate the electronic energies influenced by the surrounding protein, Renger and coworkers55 developed a method combining quantum chemical calculations based on time-dependent density functional theory on the pigments in vacuum with electrostatic Poisson–Boltzmann type calculations on the whole PPC in atomic detail. This method was successfully tested on the seven bacteriochlorophyll molecules in the FMO complex.56,57 From the dynamical point of view, on the other hand, eqn (2.3) demonstrates that the electronic energies of the pigments experience modulations by the protein motion. Due to a huge number of the protein degrees of freedom, such dynamic modulations can be modeled as random fluctuations and thus one can resort to statistical mechanical approximations. If different pigments share dynamic effects of the same protein portions, fluctuations in their electronic energies would be correlated.15,58–61

In this Perspective, we restrict the electronic spectrum of each pigment to the singlet ground state \(S_0\) (\(a = g\)) and the first singlet excited state \(S_1\) (\(a = e\)). Further, we assume that there exist no nonadiabatic transitions between \(S_0\) and \(S_1\) on a relevant timescale. In order to characterize the possible states of the whole complex of excitable units, product states are introduced as \(|\varphi_{ma}\rangle\). This Hartree-like ansatz is reasonable only if different \(|\varphi_{ma}\rangle\) do not overlap and the exchange interaction is negligible. Thus, the PPC Hamiltonian in eqn (2.1) can be expressed as

\[
H_{\text{PPC}} = \sum_{m=1}^{N} \sum_{k,g} |\varphi_{ma}\rangle H_{mg}(R)|\varphi_{ma}\rangle 
\]

+ \sum_{m \neq n} |\varphi_{ma}\rangle |\varphi_{mg}\rangle \hbar J_{mn} |\varphi_{mg}\rangle \langle \varphi_{ma}|. 
\]

The so-called excitonic coupling \(\hbar J_{mn}\) has to be deduced from the inter-pigment Coulomb interaction, \(U_{mn}\).47,55,62–64 The excitonic coupling may be also modulated by nuclear motions.49,65,66 In the following, however, we assume that nuclear dependence of \(\hbar J_{mn}\) is vanishingly small and employ the Condon-like approximation as usual. For later convenience, we order the product state with respect to the number of elementary excitations. The overall ground state with zero excitations reads \(|0\rangle \equiv |\varphi_{0a}\rangle\), whereas the presence of a single excitation at the \(m\)th pigment is described by \(|m\rangle \equiv |\varphi_{ma}\rangle \Pi_{k \neq m,0} |\varphi_{k0}\rangle\). Description of EET on the basis of \(|\langle m|\rangle\) is termed the site representation. The corresponding expansion of the complete PPC Hamiltonian yields

\[
H_{\text{PPC}} = H_{0}^{(0)} + H_{1}^{(1)} + \cdots, 
\]

where \(H_{\text{PPC}}^{(n)}(n = 0,1,\ldots)\) describes \(n\)-exciton manifold comprising \(n\) elementary excitations. The Hamiltonian of the zero-exciton manifold reads

\[
H_{\text{PPC}}^{(0)} = \sum_{m} H_{mg}(R)|0\rangle \langle 0|, 
\]

whereas the Hamiltonian of the single-exciton manifold takes the form,

\[
H_{\text{PPC}}^{(1)} = \sum_{m} \left[ H_{mg}(R) + \sum_{k \neq m} H_{kg}(R) \right] |m\rangle \langle m| 
\]

+ \sum_{m,n} \hbar J_{mn} |m\rangle \langle n|. 
\]

Since the intensity of sunlight is weak, the single-exciton manifold is of primary importance under physiological conditions. However, nonlinear spectroscopic techniques such as 2D electronic spectroscopy and photon echo measurement can populate some higher exciton manifolds, e.g. the double-exciton manifold comprising \((mn)\) \(\equiv |\varphi_{ma}\rangle |\varphi_{mb}\rangle \Pi_{k \neq m,a} |\varphi_{k0}\rangle\). The Hamiltonians for higher exciton manifolds can be derived straightforwardly from eqn (2.4) in the same fashion.

If the potential energy surfaces, \(e_{ma}(R)\), have a well-defined minimum and if only small deviations of the nuclear coordinates from the stationary point are important, the normal mode analysis is possible for the PPC nuclear dynamics.54,67 Thus, the nuclear Hamiltonian associated to the electronic ground state of the \(m\)th pigment can be expressed as

\[
H_{mg}(R) = e_{mg}(R_{mg}) + \sum_{i} \frac{\hbar \omega_{i}^{2}}{2} (p_{i}^{2} + q_{i}^{2}), 
\]
where \( R_{mg}^0 \) is the equilibrium configuration of the nuclear coordinates associated with the \( m \)th pigment, and \( q_j \) is the dimensionless normal mode coordinate with accompanying frequency \( \omega_j \) and momentum \( p_j \). This normal mode treatment can be justified by the principal component analysis of a molecular dynamics simulation trajectory of a protein.\(^6\)\(^8\)\(^-7\) Gó and coworkers demonstrated that 95% of the total number of modes in human lysozyme are harmonic modes with small amplitudes and fast timescales, whereas anharmonic modes involving conformational changes are just 0.5%. Such anharmonic modes with large amplitudes and slow timescales can be assumed to be irrelevant to photosynthetic EET. Generally, the potential energy surfaces of the electronic excited state can be assumed to be irrelevant to photosynthetic EET. The reorganization dynamics, in principle, can be measured by the three-pulse photon echo peak shift measurement.\(^7\)\(^3\)\(^,\)\(^4\) In addition, environmental reorganization involving the dissipation of reorganization energy can be understood as the response to sudden change of electronic state via the vertical Franck–Condon transition, and thus can be characterized by the symmetrized correlation function defined by

\[
\langle \mathcal{F} \tilde{u}_m(t_2) \tilde{u}_m(t_{2n-1}) \cdots \tilde{u}_m(t_2) \tilde{u}_m(t_1) \rangle_{mg} = \sum_{a, p, \beta} \langle \mathcal{F} \tilde{u}_m(t_2) \tilde{u}_m(t_1) \rangle_{mg},
\]

(2.12)

where \( \tilde{u}_m(t) = e^{iH_{mg} t} u_m e^{-iH_{mg} t} \), and \( \langle \cdots \rangle_{mg} \) denotes averaging over \( \rho_{eq} = e^{-\beta H_{mg}}/\text{tr} e^{-\beta H_{mg}} \) with \( \beta \) being inverse temperature.

The sum is over all possible ways of picking pairs (a,p,p) among \( 2n \) operators, and \( \mathcal{F} \) denotes an ordering operator which orders products by some rule. Therefore, all the phonon-induced relaxation processes can be quantified by two-point correlation functions of \( \tilde{u}_m(t) \). In this perspective we assume the fluctuation-dissipation processes in one pigment are not correlated to those in others. Fluctuations in the electronic energy of the \( m \)th pigment are described by

\[
S_n(t) \equiv \frac{1}{2} \bigl( \tilde{u}_m(t) \tilde{u}_m(0) + \tilde{u}_m(0) \tilde{u}_m(t) \bigr)_{mg}.
\]

(2.13)

Information on this function can be obtained by means of time-dependent fluorescence Stokes shift experiment.\(^7\)\(^3\)\(^,\)\(^4\) In addition, environmental reorganization involving the dissipation of reorganization energy can be understood as the response to sudden change of electronic state via the vertical Franck–Condon transition, and thus can be characterized by the response function

\[
\chi_m(t) \equiv \frac{i}{\hbar} \langle [\tilde{u}_m(t), \tilde{u}_m(0)] \rangle_{mg}.
\]

(2.14)

The reorganization dynamics, in principle, can be measured by the time-dependent fluorescence Stokes shift function,\(^7\)\(^3\)\(^,\)\(^4\) where the direct observable quantity is the relaxation function defined by

\[
\Gamma_m(t) \equiv \int_0^\infty ds \chi_m(s),
\]

(2.15)

where \( \Gamma_m(0) = 2\hbar \lambda_m \) is the Stokes shift magnitude. The quantum fluctuation-dissipation theorem allows us to express the symmetrized correlation function and the response function as

\[
S_m(t) = \frac{\hbar}{\pi} \int_0^\infty d\omega \chi_m''(\omega) \coth \frac{\beta \hbar \omega}{2} \cos \omega t,
\]

(2.16)

\[
\chi_m(t) = \frac{2}{\pi} \int_0^\infty d\omega \chi_m''(\omega) \sin \omega t.
\]

(2.17)
Here, $\gamma'_m[\omega]$ is the imaginary part of the Fourier-Laplace transform of the response function,

$$\gamma'_m[\omega] \equiv \text{Im} \int_0^\infty dt e^{i\omega t} Z_m(t), \quad (2.18)$$

which is termed the spectral density. The term “spectral density” may mislead unless we draw attention to its definition. It gives the spectrum of the phonon modes weighted by the environmental phonons. For this modeling, the timescale of the fluctuation-dissipation processes is simply

$$\frac{d}{dt} S_m(t) = -k_B T Z_m(t), \quad S_m(t) = k_B T \Gamma_m(t), \quad (2.19)$$

where $k_B$ is Boltzmann constant and $T$ is temperature. Generally, fluctuation tends to drive any system to an “alive” state, while dissipation tends to relax the system to a “dead” state. The balance between the fluctuation and dissipation is required to guarantee a thermal equilibrium state at long times. This is the physical significance of the fluctuation-dissipation theorem expressed as eqn (2.16)–(2.19). In reality, stochastic models without any dissipative effects correspond to unphysical pictures where the fluctuation continues to activate the system toward an infinite temperature. The Haken–Strobl model is in this category. Further, owing to the fluctuation-dissipation theorem, the symmetrized correlation function, the response function, the relaxation function, and the spectral density contain the same information on the phonon dynamics, whose characteristic timescale is given by

$$\Gamma_m(t) \equiv \frac{1}{\Gamma_m(0)} \int_0^\infty dt \Gamma_m(t), \quad (2.20)$$

The relaxation function and the associated spectral density may have complicated forms involving various components in this Perspective. We model the relaxation function by an exponential decay form,

$$\Gamma_m(t) = 2h_m e^{-\gamma_m t},$$

where $h_m$ and $\gamma_m$ are the parameters to be determined experimentally. This model does not include discrete high-frequency modes of the environment or vibronic coupling. For this modeling, the timescale of the fluctuation-dissipation processes is simply $\gamma_m = \gamma_m^{-1}$, and the spectral density is expressed as an Ohmic form with a Lorentz-Drude regularization or the so-called overdamped Brownian oscillator model, i.e. $\gamma'_m[\omega] = 2h_m \omega^2 e^{-\gamma_m (\omega^2 + \gamma_m^2)}$. This model does not include discrete high-frequency modes of the environment or vibronic coupling, and thus removes the vibrational coherence contribution, allowing electronic coherence to be distinguished from the vibrational one and examined separately. Inclusion of such vibrational contributions is straightforward. Although this spectral density has been successfully employed for analyses of experimental results, it may produce qualitatively different vibrational sidebands from the experimental results in the zero temperature limit. In order to address this issue, super-Ohmic spectral densities, $\gamma'_m[\omega] \propto \omega^p (p \geq 2)$, are sometimes employed. However, it should be noticed that the symmetrized correlation and relaxation functions associated with super-Ohmic spectral densities may present non-oscillatory negative values even at high temperatures, whose physical origins are obscure. The fuller study of accurate spectral densities lies outside the scope of this Perspective.

### III. Förster theory: prelude to non-Markovian dynamics

Förster theory still has a significant impact on wide areas of physics, chemistry, and biology. The theory is employed to describe incoherent diffusive motion of electronic excitation localized on individual pigments and is not capable of describing quantum coherent EET. Nevertheless, the theory is thought-provoking regarding the interplay between electronic excitation and its associated phonons. In this section, we give a brief review of Förster theory with a specific account of its intrinsic non-Markovian features, i.e. site-dependent reorganization and the nature of optical lineshapes involved in the theory, which play a crucial role in exploring appropriate theories of quantum coherent EET in photosynthetic PPCs.

Förster derived the EET rate expression with the use of the Fermi golden rule approach with a second-order perturbative treatment of the excitonic coupling between the pigments. The resultant rate constant is expressed as the overlap integral between the fluorescence spectrum of a donor and the absorption spectrum of an acceptor as follows:

$$k_{m-n}^F = \frac{4}{\pi \hbar} \int_0^\infty \frac{d\omega}{\omega} \text{Re} A_m[\omega] \text{Re} F_n[\omega].$$

Here, $A_m[\omega]$ and $F_n[\omega]$ are the absorption and fluorescence lineshapes of the $m$th pigment as expressed:

$$A_m[\omega] = \int_0^\infty dt e^{i\omega t} e^{-i\Omega_m t} g_m(t), \quad (3.2)$$

$$F_n[\omega] = \int_0^\infty dt e^{i\omega t} e^{-i\Omega_n t} g_n(t), \quad (3.3)$$

respectively, where $g_m(t)$ is the line-broadening function defined by

$$g_m(t) = \frac{1}{\hbar R^2} \int_0^R ds_1 \int_0^R ds_2 \left[ S_m(s_2) - \frac{1}{2} Z_m(s_2) \right]. \quad (3.4)$$

It should be noticed that the derivations of eqn (3.2)–(3.4) are based on the Gaussian property given in eqn (2.12).

The expression of Förster rate implies the following: First, the reorganization of the initial state, $|n\rangle = |\phi_{m0}\rangle \Pi_{k \neq m} |\phi_{k*}\rangle$, takes place instantaneously. Subsequently, the electronic de-excitation of the $n$th pigment and the excitation of the $m$th pigment occur from the equilibrium phonons of the initial state to the nonequilibrium phonons or hot phonons of the final state, $|m\rangle = |\phi_{m0}\rangle \Pi_{k \neq m} |\phi_{k*}\rangle$, in accordance to the Franck–Condon principle, as depicted in Fig. 2. This sequential process involving the site-dependent reorganization is the key assumption of Förster theory. This transfer process through hot phonons associated with the acceptor state is the physics of the so-called multphonon transition process. Extensions of Förster theory also have been explored to treat finite timescales of the reorganization, i.e. hot transfer mechanism or nonequilibrium effects.
For later discussion of quantum coherent EET influenced by the surrounding environment, it is advisable to consider the mathematical structure of the lineshapes in eqn (3.2)-(3.4) since the lineshapes provide important insights into the dynamic interactions of a system of interest and its environment. For the sake of simplicity, we employ the so-called Kubo-Anderson stochastic model,89,90

\[ S_m(t) = \hbar^2 \Delta_m^2 e^{-\gamma_m t} \text{ and } \chi_m(t) = 0, \quad (3.5) \]

where \( \hbar \Delta_m \) is the root-mean-squared amplitude of the energy gap fluctuations. It should be noticed that eqn (3.5) neglects the inherent dissipative effects described by the response function \( \chi_m(t) \); thus, the Stokes shift does not exist and the absorption and fluorescence lineshapes coincide. For this model, the lineshape can be represented by a continued fraction,

\[ A_m[\alpha] = \frac{1}{-i\alpha + \Delta_m^2 - i\alpha + \gamma_m - i\alpha + \gamma_m + \cdots}, \quad (3.6) \]

where \( \tilde{\omega} = \omega - \Omega_m \). Takagahara, Hanamura and Kubo gave a comprehensible proof of this expression by introducing auxiliary functions.92

\[ A_m^{[n]}[\alpha] \equiv \int_0^\infty \int_0^\infty ds e^{-\gamma_m t} e^{i\omega t - \gamma_m t}, \quad (3.7) \]

for \( n = 0, 1, 2, \ldots \), and \( A_m^{[0]}[\alpha] = A_m[\alpha] \). Integrating eqn (3.7) by parts, one obtains a set of hierarchically coupled equations of \( A_m^{[n]}[\alpha] \),

\[ (-i\omega + \alpha \gamma_m) A_m^{[n]} + A_m^{[n+1]} - n \Delta_m^2 A_m^{[n-1]} = \delta_{n0} \quad (3.8) \]

with \( \delta_{n0} \) being the Kronecker delta. This three-term recurrence formula constructs the continued fraction.75 Along the lines of this treatment, Tanimura and Kubo derived a hierarchical equation of motion93,94 by the use of the path integral influence functional formalism.95,96 However, the equation invokes a high-temperature approximation, and hence cannot be applied to low temperature systems. Thus, low-temperature corrections97,98 were explored and summarized as convenient forms by Ishizaki and Tanimura99 and Shi et al.100 Extensions of the theories to different spectral densities were also studied.101-104

The continued fraction representation in eqn (3.6) is convenient not only for numerical computations but also for understanding properties of the lineshape. In the fast modulation limit characterized by \( \Delta_m/\gamma_m \ll 1 \) (a Markovian regime), the continued fraction converges at first order and thus the lineshape becomes Lorentzian as

\[ A_m[\alpha] = \frac{1}{-i(\omega - \Omega_m) + \frac{\Delta_m^2}{\gamma_m}}. \quad (3.9) \]

This phenomenon is the well-known motional narrowing.72 In the slow modulation limit of \( \Delta_m/\gamma_m \gg 1 \) (a strong non-Markovian regime), on the other hand, the fraction in eqn (3.6) continues to infinity. However, a continued fraction representation of the complementary error function,93,105

\[ \text{erfc} z = (2/\sqrt{\pi}) \int_z^\infty dt e^{-t^2}, \]

allows us to approximate eqn (3.6) by a Gaussian function as follows:

\[ \text{Re} A_m[\alpha] = \sqrt{\frac{\pi}{2 \Delta_m^2}} \exp \left[ -\frac{(\alpha - \Omega_m)^2}{2 \Delta_m^2} \right]. \quad (3.10) \]

This case is known as the limit of inhomogeneous broadening, where the timescale for nuclear motion is such that the nuclei can be considered to be frozen. In the intermediate regime of \( \Delta_m/\gamma_m \sim 1 \) (a typical situation in photosynthetic EET), the continuous fraction converges at a finite depth, and thus the lineshape presents a mixed profile of Lorentzian and Gaussian forms. In this manner, the ratio of \( \Delta_m/\gamma_m \) lineshape, and depth of the continued fraction provide information concerning the extent of the non-Markovian character of the dynamic interaction of a system of interest and its environment. Note that the depth of the continued fraction is essentially unrelated to the order of perturbative expansion with respect to electron-phonon coupling.

IV. Non-Markovian quantum master equations for electronic energy transfer

In contrast to Förster theory, one of the key approaches to explore quantum coherence in photosynthetic EET is a quantum master equation. In this approach, the key quantity is the reduced density operator, i.e. the partial trace of the total density operator, \( \rho_{PPC} \), over the phonon degrees of freedom: \( \rho \equiv \text{tr}_{\text{ph}}\rho_{PPC} \). The most commonly used theory from this approach is the Redfield equation. Although the Redfield equation has been broadly applied, the form is based on the Markov approximation. In photosynthetic EET, each site of a multichromophoric array is coupled to its local environmental phonons. Additionally, electronic de-excitation of a donor and excitation of an acceptor occur via nonequilibrium phonon states in accordance with the vertical Franck-Condon transitions. The phonons coupled to each pigment then relax to their respective equilibrium states on a characteristic timescale. This process becomes more significant when the reorganization energies are not small in comparison to the electronic coupling, e.g. the regime where Förster theory is an appropriate picture as discussed in the preceding section. However, these site-dependent reorganization processes cannot be described by the Redfield equation due to the Markov approximation.10 The Markov approximation requires the phonons to relax to their
equilibrium states instantaneously, that is, the phonons are always in equilibrium with respect to each electronic state. In order to go beyond the Markov approximation, a feasible path is to employ non-Markovian quantum master equations such as the Nakajima-Zwanzig projection operator technique (time-convolution formalism\textsuperscript{7,106,107} or the time-convolutionless projection operator method\textsuperscript{7,7,108}. They are mathematically exact and hold for arbitrary systems and interactions. However, it is impossible to reduce the explicit expressions for the equations beyond the exact formal structures. Hence, the second-order perturbative expansion with respect to the system-environment interaction is usually invoked to make practical calculations possible.

To advance concrete discussions on non-Markovian quantum master equations, we rewrite the PPC Hamiltonian by substituting eqn (2.8)–(2.11) into eqn (2.5)–(2.7) as

$$H_{PPC} = H_{el} + H_{el-ph} + H_{ph}.$$  \hfill (4.1)

The first term on the right-hand side is the electronic excitation Hamiltonian with respect to the equilibrium nuclear configuration of the electronic ground state, \(\{R_{eq}\}\),

$$H_{el} = \sum_{m} \hbar \omega_{m}[m]\langle m | + \sum_{m,n} \hbar J_{mn} | m \rangle \langle n |;$$  \hfill (4.2)

where we have set \(\sum_{m} \epsilon_{mg}(R_{eq}) = 0\). The second part describes the coupling of nuclear motion to the electronic excitations,

$$H_{el-ph} = \sum_{m} V_{m} \mu_{m},$$  \hfill (4.3)

with \(V_{m} \equiv |m\rangle \langle m|\). The last term in eqn (4.1) is the ensemble of the normal mode Hamiltonians, i.e., the phonon Hamiltonian expressed as \(H_{ph} = \sum_{m} \hbar \omega_{m}(\hat{p}_{m}^{2} + \hat{q}_{m}^{2})/2\). It should be noted that the explicit expressions of \(H_{el}\) and \(H_{el-ph}\) depend on the choice of a reference nuclear configuration. The present expression in eqn (4.3) looks as if only the excited states experience modulations by the nuclear motion. However, this is an erroneous interpretation; the ground states are also experience modulations by the nuclear motion. However, this initial condition is of no consequence because it corresponds to the electronic ground state or an electronic excited state generated in accordance to the vertical Franck–Condon transition.

A. Second-order perturbative time-convolutionless equation

The second-order perturbative time-convolutionless (TCL2) quantum master equation is expressed as\textsuperscript{77}

$$\frac{d}{dt} \rho(t) = -\frac{1}{\hbar^{2}} \int_{0}^{t} ds \text{tr}_{ph} \{[H_{el-ph}(t), [H_{el-ph}(s), \rho(t)\rho_{eq}^{ph}(t)]]\},$$  \hfill (4.5)

where the interaction picture has been employed with respect to \(H_{el} + H_{ph}\), and a tilde indicates an operator in the picture. Eqn (4.5) can be rewritten as

$$\frac{d}{dt} \tilde{\rho}(t) = \sum_{m=1}^{N} \int_{0}^{t} ds \tilde{K}_{m}(t,s) \tilde{\rho}(t)$$  \hfill (4.6)

with the relaxation kernel,

$$\tilde{K}_{m}(t,s) = -\frac{1}{\hbar^{2}} \tilde{V}_{m}(t)^{\times} \times$$  \hfill (4.7)

$$\left[ \tilde{S}_{m}(t-s) \tilde{V}_{m}(s)^{\times} - i \frac{\hbar}{2} \tilde{Z}_{m}(t-s) \tilde{V}_{m}(s)^{\times} \right].$$

Here, we denote \(O^{\times}f \equiv Of - fO\) and \(O^{\times^{2}}f \equiv Of + fO\) for any operators \(O\) and \(f\). Eqn (4.6) has a mathematical advantage of time locality without involving any time-convolution between the relaxation kernel and the density operator.

When the excitonic coupling \(hJ_{mn}\) is vanishing, we have \(\tilde{V}_{m}(t) = V_{m} = |m\rangle \langle m|\) in eqn (4.7), and thus eqn (4.6) yields

$$\langle m | \rho(t) | 0 \rangle = e^{-\int_{0}^{t} \tilde{S}_{m}(t-s) \tilde{V}_{m}(s) \tilde{V}_{m}(s)^{\times} dt}.$$  \hfill (4.8)

Fourier–Laplace transform of eqn (4.8) produces an accurate absorptive lineshape of the \(m\)th pigment, eqn (3.2). Therefore, the TCL2 equation is rigorous for describing linear absorption of a monomer, namely coherence between electronic ground and excited states in a monomer, irrespective of the magnitude of the electron–phonon coupling although it invokes second-order perturbative approximation with respect to the coupling. However, it should be noticed that a two-state system describing a pair of donor–acceptor in EET is completely different from a two-level system corresponding to electronic ground and excited states, as illustrated in Fig. 1 and 2. The donor and acceptor in a two-state system are coupled to individual phonon modes, whereas both of the electronic ground and excited states in a two-level system are associated with the same phonon modes.

To examine the validity and limitation of the TCL2 equation, we discuss numerical results for EET in a dimer consisting of two sites, |1\rangle = |\phi_{1e}\rangle |\phi_{2g}\rangle and |2\rangle = |\phi_{1e}\rangle |\phi_{2g}\rangle. Fig. 3 shows the intersite EET rates from |1\rangle to |2\rangle, \(k_{21}\), as a function of reorganization energy, \(\lambda = \lambda_{1} = \lambda_{2}\), predicted by the TCL2 equation (closed circles). The other parameters are fixed to be \(\Omega_{1} = \Omega_{2} = 100 \text{ cm}^{-1}, J_{12} = 100 \text{ cm}^{-1}, \gamma_{1} = \gamma_{2} = 53 \text{ cm}^{-1}, \gamma_{1}^{1} = \gamma_{2}^{1} = 100 \text{ fs}\), which are typical for photosynthetic EET.\textsuperscript{11} The intersite dynamics calculated by using these parameters is dominantly incoherent for the entire region.
Here, $\hbar \omega_{g|}\equiv E_g - E_e$ is an energy gap between eigenstates and $R_{\mu|\nu'}(t)$ is the time-dependent relaxation tensor given by

$$R_{\mu|\nu'}(t) \equiv \Gamma_{\nu',\mu|}(t) + \Gamma_{\nu',\mu|}(t) - \delta_{\nu'} \sum_k \Gamma_{\mu,k|\nu'}(t) - \delta_{\nu'} \sum_k \Gamma_{\mu,k|\nu'}(t)$$

(4.11)

in terms of the damping matrix,

$$\Gamma_{\mu|\nu'}(t) \equiv \sum_{n=1}^{N} \langle \epsilon_n | V_m | \epsilon_{\nu'} \rangle \langle \epsilon_{\mu'} | V_m | \epsilon_{\nu'} \rangle \epsilon_m [\omega_{e|}, t],$$

(4.12)

where the complex quantity $\epsilon_m [\omega, t]$ is given by the definite integration of the symmetrized correlation and response functions as

$$\epsilon_m [\omega, t] = \frac{1}{\pi} \int_{0}^{t} ds \text{e}^{-i\omega s},$$

(4.13)

Dynamics in the site representation $\{|m|\}$ can be obtained via the unitary transformation of density matrices in the eigenenergy representation. Although the time-dependence of the relaxation tensors, $R_{\mu|\nu'}(t)$, are responsible for non-Markovian nature, eqn (4.11)-(4.13) indicate that the time evolution of the relaxation tensors is independent of that of electronic states, that is, the phonons can relax independently of the electronic states of pigments. For this reason, the TCL2 equation cannot capture the above mentioned site-dependent reorganization processes in spite of its non-Markovian nature. \(^3\) In addition, after the phonon relaxation time, the time-dependent relaxation tensors converge to steady values corresponding to the traditional Redfield tensors involving Fourier–Laplace transform of the phonon correlation functions, $C_{\text{ph}}[\omega, \infty]$. In other words EET after the phonon relaxation time is described by the Markovian Redfield equation.

Although the TCL2 equation fails to describe EET appropriately, particularly in the region of large reorganization energy, the above discussions are suggestive concerning treatment of the electron–phonon coupling. As shown in eqn (4.8), the equation can produce the accurate absorptive lineshape of a monomer irrespective of magnitude of reorganization energy, the TCL2 equation fails to describe the transfer rate in a region of large reorganization energy. The rate predicted by the TCL2 equation is virtually the same as that by the Redfield equation.

In order to clarify the issue, we consider the eigenenergy representation, $H_0|\epsilon_{\mu}\rangle = E_{\mu}|\epsilon_{\mu}\rangle$, where $E_{\mu}$ is the $\mu$th eigenenergy of $H_0$ and $|\epsilon_{\mu}\rangle$ is the accompanying eigenstate. The eigenstates $|\epsilon_{\mu}\rangle$ are usually termed excitons. One should not overlook that these eigenstates and eigenenergies are obtained via diagonalization of the Hamiltonian $H_0$ comprised of the Franck–Condon transition energies, $\hbar \omega_{el}$, However, energies of the actual excitons will deviate from the values of $E_{\mu}$ as the environmental reorganization takes place. To address this issue, excitonic potential energy surfaces were explored. \(^{31,79,110,111}\) In the framework of quantum master equations, the imaginary parts of the relaxation operators are responsible for such deviations. \(^30\) In the eigenstate representation, eqn (4.6) can be expressed as the time-dependent Redfield equation\(^ {112}\) as

$$\frac{d}{dt} \rho_{\mu|\nu'}(t) = -i \omega_{\mu|\nu'} \rho_{\mu|\nu'}(t) + \sum_{\mu',\nu'} R_{\mu|\nu'}(t) \rho_{\mu'|\nu'}(t).$$

(4.10)
which can be recast into
\[
\frac{d}{dt} \hat{\rho}(t) = \sum_{m=1}^{N} \int_0^\infty ds \mathbf{\mathcal{K}}(t,s) \hat{\rho}(s). \tag{4.15}
\]
Due to time non-locality with involving an integro-differential form, eqn (4.15) is not generally tractable. However, if the symmetrized correlation and response functions involved in the relaxation kernel \(\mathbf{\mathcal{K}}(t,s)\) can be expressed as exponential functions, practical calculations become possible.\(^{113}\) For the overdamped Brownian oscillator model with the classical fluctuation-dissipation theorem in eqn (2.19), the non-Markovian relaxation kernel, eqn (4.7), leads to
\[
\mathbf{\mathcal{K}}(t,s) = \Phi_m(t)e^{-\gamma_m(t-s)}\mathbf{\Theta}_m(s), \tag{4.16}
\]
where we have defined the relaxation operators as
\[
\Phi_m \equiv iV_m^\times, \tag{4.17a}
\]
\[
\mathbf{\Theta}_m \equiv i\left(\frac{2\lambda_m}{\beta h} V_m^\times - i\lambda_m^\gamma_m V_m^\gamma\right). \tag{4.17b}
\]
Thus, eqn (4.15) can be expressed as the following set of \(m+1\) coupled equations for the reduced density operator \(\hat{\rho}(t)\):
\[
\frac{d}{dt} \hat{\rho}(t) = -i\mathcal{L}_\alpha \hat{\rho}(t) + \sum_{m=1}^{N} \Phi_m \hat{\rho}_m^{(1)}(t), \tag{4.18a}
\]
\[
\frac{d}{dt} \hat{\rho}_m^{(1)}(t) = -(i\mathcal{L}_m + \gamma_m)\hat{\rho}_m^{(1)}(t) + \mathbf{\Theta}_m \hat{\rho}(t), \tag{4.18b}
\]
with \(\hat{\rho}_m^{(1)}(t)\) being an auxiliary operator defined by
\[
\hat{\rho}_m^{(1)}(t) \equiv \int_0^\infty ds e^{-\gamma_m(t-s)}\mathbf{\Theta}_m(s)\hat{\rho}(s). \tag{4.19}
\]
We discuss numerical results for EET in a dimer consisting of two sites, \(|1\rangle = |\phi_{12}\rangle|\phi_{22}\rangle\) and \(|2\rangle = |\phi_{12}\rangle|\phi_{22}\rangle\); In Fig. 4, we show the intersite EET rates, \(k_{2-1}\), as a function of reorganization energy, \(\lambda = \lambda_{12} = \lambda_{21}\), predicted by the TC2 equation (closed circles). The other parameters are the same as in Fig. 3. For the comparison, the rate calculated from the Markovian Redfield equation in the full form (open circles) and Förster theory (solid line) are shown. Unlike the case of the TC2 equation in the preceding subsection, the transition rate predicted by the TC2 equation deviates strongly from that given by the Redfield equation; it does not show a \(\lambda\)-independent plateau caused by the Markov approximation in the region of large reorganization energy.\(^30\) Similar to Förster theory, the TC2 equation predicts a maximum in the rate in the intermediate region. However, we observe a large quantitative difference between the rate predicted by the TC2 equation and that given by Förster theory.

In order to investigate the cause of the difference, we consider the absorptive lineshape of a monomer produced by the TC2 equation. When the excitonic coupling \(\hbar J_{nm}\) vanishes, eqn (4.18) yields the following expression of absorptive lineshape of the \(m\)th pigment:\(^{41}\)
\[
A_m[\gamma] = \frac{1}{-i(\omega - \Omega_m) + \Delta_m^2/\gamma_m^2 + \lambda_m^2}, \tag{4.20}
\]
where we have defined \(\Delta_m^2 = 2\lambda_m/\beta h\) and \(\delta_m^2 = \lambda_m^2/\gamma_m\). This expression corresponds to the so-called two-state jump modulation model,\(^{91}\) which can be obtained when the continued fraction expansion in eqn (3.6) is taken to second order. In this model, the lineshape for the Markovian regime \((\Delta_m/\gamma_m \ll 1)\) becomes a single Lorentzian line around the \(\omega = \Omega_m\). This phenomenon is known as exchange narrowing in the context of chemical exchange. In the strong non-Markovian regime entailing sluggish fluctuation and/or dissipation of large reorganization energy \((\Delta_m/\gamma_m \gg 1)\), on the other hand, the lineshape is peaked around two resonance frequencies corresponding to only two states of the surrounding environment. For the present modeling of PPCs, however, such peak splitting and correspondingly only two states of the protein environment are completely unphysical. Fig. 5 presents absorptive spectra of a monomer calculated with eqn (4.18). It should be noticed that the TC2 equation produces unphysical peak splitting even though the reorganization energy is quite small compared to typical values in photosynthetic complexes. This fatal flaw is not peculiar to the overdamped Brownian oscillator model. In fact, an arbitrary relaxation function can be numerically

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**Fig. 4**  
Inter-site energy transfer rates from \(|1\rangle = |\phi_{12}\rangle|\phi_{22}\rangle\) to \(|2\rangle = |\phi_{12}\rangle|\phi_{22}\rangle\), as a function of reorganization energy, \(\lambda = \lambda_{12} = \lambda_{21}\), predicted by the TC2 equation (closed circles), the Markovian Redfield equation (open circles), and Förster theory (solid line). The other parameters are the same as in Fig. 3.

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**Fig. 5**  
Linear absorption spectrum of a monomer calculated by the TC2 equation, eqn (4.15), for various values of phonon relaxation time \(\gamma_1^{-1}\) and reorganization energy \(\lambda_1\). The temperature is set to be \(T = 300\) K. In the non-Markovian regime entailing sluggish fluctuation and/or dissipation of large reorganization energy, the lineshape shows unphysical peak splitting.
decomposed to the sum of (complex) exponential functions, as was discussed by Meier and Tannor.\textsuperscript{113} The situation is somewhat ironic: The TC2 equation produces less correct results than the Markovian Redfield equation when it is applied to a non-Markovian regime.

The conclusion in this subsection is that the TC2 equation is applicable only for the nearly Markovian regime in spite of its non-Markovian nature. In order to describe the EET dynamics appropriately, one should explore the time-nonlocal quantum master equations which is capable of producing at least an accurate absorptive lineshape influenced by the Gaussian fluctuation-dissipation from the environmental phonons. It is noteworthy that the Gaussian property of environmental phonons, eqn (2.12), has not been taken into account explicitly in the second-order perturbative quantum master equations.

C. Second-order cumulant and hierarchy expansion

As observed in the preceding sections, it is crucial to consider and describe the dynamics of environmental phonons in a more appropriate fashion in order to elucidate quantum coherence and its interplay with the protein environment in EET. In particular, areas to be commented on include: (a) site-dependent reorganization dynamics of environmental phonons and (b) an appropriate description of Gaussian fluctuations in electronic energies of pigments to produce optical lineshapes. To treat both of the issues (a) and (b), two of the present authors\textsuperscript{31} cast a spotlight on the fact that the cumulant expansion up to second order is rigorous for phonon operators owing to the Gaussian property in eqn (2.12), whereas second-order perturbative truncation is just an approximation. Thus, the formally exact expression for the reduced density operator can be derived as

\[
\tilde{\rho}(t) = T_+ \prod_{m=1}^{N} \exp \left[ \int_{0}^{t} ds_1 \int_{s_1}^{t} ds_2 \, \mathcal{F}_m(s_1, s_2) \right] \tilde{\rho}(0),
\]

(4.21)

whose time evolution is described by the following equation of motion:\textsuperscript{31}

\[
\frac{d}{dt} \tilde{\rho}(t) = T_+ \sum_{m=1}^{N} \int_{0}^{t} ds \, \mathcal{F}_m(t, s) \tilde{\rho}(t).
\]

(4.22)

Although eqn (4.22) is derived in a nonperturbative manner, its expression shows close resemblance to those of the second-order perturbative quantum master equations in eqn (4.6) and (4.15). The first point to notice here is that eqn (4.22) is a time-nonlocal equation unlike the TCL2 equation because the chronological time ordering operator $T_+$ resequences and mixes the hyper-operators $\mathcal{V}_m(t) \times \mathcal{V}_m(t)$ comprised in $\mathcal{K}_m(t, s)$ and $\tilde{\rho}(t)$. Secondly, when the excitonic coupling $\hbar J_{mn}$ is vanishingly small, eqn (4.21) also leads to eqn (4.8), whose Fourier–Laplace transform yields the accurate absorptive lineshape unlike the TC2 equation. These two features are significant for the above two features described in (a) and (b) in elucidating the quantum aspects of EET processes in protein environments. To proceed beyond the formally exact structure, we employ the overdamped Brownian oscillator model with the classical fluctuation-dissipation theorem as well as discussion on the TC2 equation. Owing to the exponential functions in eqn (4.16), the hierarchy expansion technique discussed in Sec. III can be employed and eqn (4.22) can be represented as

\[
\frac{d}{dt} \sigma(n, t) = -i \mathcal{L}_d \sigma(n, t) \\
+ \sum_{m=1}^{N} \left[ \Phi_m \sigma(n_{m+1}, t) + n_m \Theta_m \sigma(n_{m-1}, t) \right]
\]

(4.23)

for sets of nonnegative integers, $n \equiv (n_1, n_2, \ldots, n_N)$. $n_{m+1}$ differs from $n$ only by changing the specified $n_m$ to $n_m \pm 1$, i.e. $n_{m+1} \equiv (n_1, n_2, \ldots, n_{m+1}, \ldots, n_N)$. In eqn (4.23), only the element $\sigma(0, t)$ is identical to the reduced density operator $\rho(t)$, while the others $\sigma(n \neq 0, t)$ are auxiliary operators defined as

\[
\tilde{\sigma}(n, t) = T_+ \prod_{m=1}^{N} \left[ \int_{0}^{t} ds \, e^{-\gamma_m(t-s)} \Theta_m(s) \right]^{n_m} \tilde{\rho}(t).
\]

(4.24)

See also eqn (3.7). Eqn (4.23) corresponds to multidimensional extension of eqn (3.8) and the hierarchical equation of motion derived by Tanimura and Kubo from the path integral approach.\textsuperscript{93,94} The hierarchically coupled equations, eqn (4.23), continue to infinity. However, the numerical calculations can converge at a finite depth of hierarchy for a finite timescale of phonon dynamics as well as the continued fraction representation of absorptive lineshape, eqn (3.6). To terminate eqn (4.23) safely, we replace eqn (4.23) by

\[
\frac{d}{dt} \sigma(n, t) = -i \mathcal{L}_d \sigma(n, t)
\]

(4.25)

for the integers $n = (n_1, n_2, \ldots, n_N)$ satisfying $N^+ \equiv \sum_{m=1}^{N} n_m > \omega_{\text{eq}}/\min(\gamma_1, \gamma_2, \ldots, \gamma_N)$, where $\omega_{\text{eq}}$ is a characteristic frequency for $\mathcal{L}_d$.\textsuperscript{31,94} Thus, the required number of the operators $\{\sigma(n, t)\}$ is evaluated as

\[
\sum_{n=0}^{N^+} \frac{\prod_{k=1}^{N} \left( k + N - 1 \right)}{N - 1} = (N + N^+)/!(N! \cdot i!).
\]

Note that quantum correction terms need to be included into eqn (4.23) if the quantum fluctuation-dissipation theorem, eqn (2.16), should be applied.\textsuperscript{99,100}

In order to examine whether eqn (4.22) and correspondingly eqn (4.23) are able to describe the site-dependent reorganization dynamics, we discuss numerical results by employing a dimer consisting of three states: $|0\rangle = |\phi_{1g}\rangle/|\phi_{2g}\rangle$, $|1\rangle = |\phi_{1e}\rangle/|\phi_{2e}\rangle$, and $|2\rangle = |\phi_{1e}\rangle/|\phi_{2e}\rangle$. Fig. 6 presents the dynamics of electronic excitation and the accompanying phonons as the emission spectrum from $|\phi_{1e}\rangle$ and $|\phi_{2e}\rangle$. The timescale of the phonon reorganization process is $\gamma_1 = \gamma_2 = 100$ fs, and the reorganization energy is $\lambda_1 = \lambda_2 = 200$ cm$^{-1}$. The temperature is set to be $T = 150$ K in order to narrow the spectra. Fig. 6a is the emission spectrum from $|\phi_{1e}\rangle$ as a function of a delay time $t$ after the excitation of pigment 1. Just after the excitation, the maximum value of the emission spectrum is located in the vicinity of $\omega = \Omega_1$. The frequency of a maximum peak position decreases with time, and reaches $\omega = \Omega_1 - 2\lambda_1$ with almost constant magnitude. This indicates that the phonon reorganization dynamics takes place prior to the EET.
This is reasonable because the interaction between the sites occurs at a rate of once every $J_{12} = 265$ fs ($J_{12} = 20$ cm$^{-1}$) whereas the timescale of the phonon reorganization process is $\gamma_1^{-1} = \gamma_2^{-1} = 100$ fs. Fig. 6b shows the emission spectrum from $|\varphi_{2e}\rangle$. The contour line of the lowest level clearly shows that the emission spectrum emerges from close to $\omega = \omega_2$ in the short time region. This indicates that the excitation of pigment 2 occurs from the equilibrium phonons of the electronic ground state $|\varphi_{2g}\rangle$ to the nonequilibrium phonons of the electronic excited state $|\varphi_{2e}\rangle$ in accordance with the vertical Franck–Condon principle. Since the reorganization process takes place subsequently, we observe the emission spectrum in the vicinity of $\omega = \Omega_2 - 2\Delta_2$ in the long time region. The observations from Fig. 6 can be summarized as follows: First, the reorganization process of the initial state, $|1\rangle = |\varphi_{1e}\rangle|\varphi_{2g}\rangle$, takes place. Subsequently, the electronic de-excitation of pigment 1 and the excitation of pigment 2 occurs from the equilibrium phonons of the initial state to the nonequilibrium phonons of the final state, $|2\rangle = |\varphi_{1g}\rangle|\varphi_{2e}\rangle$, in accordance with the Franck–Condon principle. Then, the reorganization process in the final state follows. This sequential process is the key assumption of Förster theory, as discussed in Sec. III: It implies that eqn (4.23) is capable of reproducing Förster rate.

In Fig. 7, we show the EET rates from pigment 1 to pigment 2 as a function of reorganization energy, $\lambda = \lambda_1 = \lambda_2$, predicted by eqn (4.23) (closed circles). The other parameters are the same as in Fig. 3 and 4. For the comparison, we show the rate calculated from the Markovian Redfield equation in the full form$^{30}$ (open circles) and Förster theory (solid line). Clearly, we observe that eqn (4.23) is capable of interpolating between the conventional Förster and Redfield theories in their respective limits of validity. In a region of small reorganization energy, the rate predicted by eqn (4.23) coincides with that of the Redfield equation. The Markov approximation in the Redfield framework requires the phonons to relax to their equilibrium state instantaneously, that is, the phonons are always in equilibrium. For the extremely small reorganization energy, the reorganization process does not play a major role; hence the phonons are almost equilibrium. As the result, we see the coincidence between the rates predicted by eqn (4.23) and the Redfield equation. With increasing reorganization energy $\lambda$, the difference between rates predicted by eqn (4.23) and the Redfield equation becomes large. In a region of large reorganization energy, the rate by the Redfield equation shows a $\lambda$-independent plateau due to the Markov approximation.$^{30}$ However, the rate predicted by eqn (4.23) decreases with increasing $\lambda$, and is in accord with the Förster rate. This is because eqn (4.23) is capable of describing the site-dependent reorganization processes of phonons, which is the key assumption of Förster theory.

Next, we consider the quantum dynamics for the case of stronger excitonic coupling. Fig. 8 presents population dynamics of $|1\rangle = |\varphi_{1e}\rangle|\varphi_{2e}\rangle$ calculated by eqn (4.23) and the full-Redfield equation for various values of reorganization energy, $\lambda = \lambda_1 = \lambda_2$. As the initial condition for numerical calculations, we assume only pigment 1 is excited in accord with the Franck–Condon principle. The other parameters are fixed to be $\Omega_1 - \Omega_2 = 100$ cm$^{-1}$, $J_{12} = 100$ cm$^{-1}$, $\gamma_1 = \gamma_2 = 53$ cm$^{-1}$ ($\gamma_1^{-1} = \gamma_2^{-1} = 100$ fs), and $T = 300$ K. Fig. 8a is for $\lambda = J_{12}/50 = 2$ cm$^{-1}$. The dynamics calculated by the two theories are almost coincident with each other. As mentioned above, the Markov approximation is appropriate in this case because of the extremely small reorganization energy. However, increasing the reorganization energy produces a difference between the dynamics calculated by the two theories. Fig. 8b shows the case of $\lambda = J_{12}/5 = 20$ cm$^{-1}$, which is still small compared to the excitonic coupling. The dynamics calculated by the present theory show long-lasting coherent motion up to 1 ps. On the other hand, the dynamics from the Redfield theory dephases on a timescale of less than 400 fs. The cause of the difference is the breakdown of the Markov approximation. The infinitely fast dissipation of reorganization energy then corresponds to infinitely fast fluctuation according to the fluctuation-dissipation relation. The infinitely fast fluctuation with relatively large amplitude collapses the quantum superposition state. As a result, the coherent motion...
The reorganization energy is expressed as \( h\alpha_m = h\alpha_{ph}d^2/2 \).

The Hamiltonian eqn (4.26) can be easily diagonalized, and then adiabatic excitonic potential surfaces in the single-exciton manifold can be obtained as

\[
E^\pm(q) = \frac{e_1(q) + e_2(q)}{2} \pm \frac{1}{2} \sqrt{(e_1(q) - e_2(q))^2 + (\hbar J_{12})^2}.
\]

In Fig. 9, we draw the adiabatic potential surface for the lower energy, \( E^- (q) \), as a function of two phonon coordinates, \( q_1 \) and \( q_2 \). The parameters in this model are chosen to be \( \Omega_1 - \Omega_2 = 100 \text{ cm}^{-1} \), \( J_{12} = 100 \text{ cm}^{-1} \), \( \omega_{ph} = 53.08 \text{ cm}^{-1} \), and \( \lambda_1 = \lambda_2 = 500 \text{ cm}^{-1} \), which correspond to those in Fig. 8d. Since the reorganization energy is large compared with the electronic coupling, we can observe two local minima which represent the two sites, \( |1 \rangle = |\varphi_{11}\rangle|\varphi_{22}\rangle \) and \( |2 \rangle = |\varphi_{21}\rangle|\varphi_{12}\rangle \). Incoherent hopping EET describes the transition between the local minima. Attention will now be given to the point of origin, which corresponds to the Franck–Condon state. The energy of the point is higher than the barrier between the minima; therefore, we find that the electronic excited state is delocalized just after the excitation despite being in the incoherent hopping regime, \( \lambda > J_{12} \). As time increases, the dissipation of reorganization energy proceeds and the excitation will fall off into one of the minima and become localized. This picture is consistent with Fig. 8d. The dynamic behavior of the intermediate regime, Fig. 8c, can be understood as the combined influence of the slow fluctuation effect in the regime of small reorganization energy and the slow dissipation effect in the large reorganization energy.

In summary, eqn (4.22) or (4.23) based on the Gaussian property of environmental phonons reduces to the conventional Redfield and Förster theories in their respective limits of validity. This capability of interpolating between the two is crucial in order for the model to be reliable in the intermediate region, which is typical in photosynthetic EET. Furthermore, in the regime of quantum coherent EET, the equation predicts several times longer lifetime of quantum coherence between electronic excited states of pigments than does the Redfield.
equation. In the region of small reorganization energy, slow fluctuation sustains long-lived coherent oscillation, whereas the Markov approximation in the Redfield framework cause infinitely rapid fluctuation and then collapses the quantum coherence. In the region of large reorganization energy, on the other hand, sluggish dissipation of reorganization energy increases the time an electronic excitation stays above an energy barrier separating pigments and thus prolongs delocalization over the pigments.

V. Quantum coherence and energy transfer in the FMO complex

In this section, we present and discuss numerical results regarding EET dynamics in the FMO complex of *Chlorobaculum tepidum* with the use of the reduced hierarchy equation in eqn (4.23). Discovery of long-lasting quantum coherence in the FMO complex provides valuable insights into the inner workings of photosynthetic complexes. However, the original measurements were performed outside the physiological range of temperatures. Generally, it is believed that quantum coherence at physiological temperatures is fragile compared to that at cryogenic temperatures because amplitudes of environmental fluctuations increase with increasing temperature. For instance, the root-mean-square amplitude of the electronic energy gap fluctuation in eqn (2.11) can be estimated by means of the fluctuation-dissipation theorem in eqn (2.13)–(2.19) as

$$h\zeta_m \simeq \sqrt{2h\zeta_m k_B T}.$$  \hspace{1cm} (5.1)

Hence, the robustness of quantum coherences under physiological conditions is still a matter of ongoing investigation.

Under physiological conditions, the FMO complex is situated between the so-called baseplate protein of the peripheral light harvesting antenna and the reaction center. The complex is a trimer made of identical subunits, each containing seven bacteriochlorophyll *a* (BChl*a*) molecules. Because the strongest electronic coupling between two BChl*a* molecules in different FMO monomeric subunits is about an order of magnitude smaller than the local reorganization energies,\textsuperscript{55} we assume that the inter-subunit coupling is vanishingly small and we consider the EET within one subunit. To simulate the EET dynamics, we use the electronic Hamiltonian for the trimeric structure of the FMO complex given in ref. 55. Recently, Read *et al.* conducted 2D electronic spectroscopic experiments to visualize excitonic structure in the FMO complex,\textsuperscript{82} and they performed numerical fitting of the 2D spectra by employing the overdamped Brownian oscillator model. To obtain good agreement between the experimental data and numerical fitting, they adopted $\lambda_m = 35$ cm$^{-1}$ and $\tau_m = \gamma_m = 50$ fs as the values of reorganization energy and phonon relaxation time, respectively. Therefore, we also employ these values with the assumption that $\lambda_m$ and $\tau_m$ for the individual BChl*a* molecules are equivalent. Recently, Wen *et al.*\textsuperscript{114} verified by chemical labeling and mass spectroscopy that the FMO complex is oriented with BChl*a* 1 and 6 toward the peripheral antenna whereas BChl*a* 3 and 4 define the target region in contact with the reaction center. Here we use the usual numbering of the BChl*a* molecules\textsuperscript{10} as shown in Fig. 14a. Accordingly, we adopt BChl*a* 1 or 6 as the initial excited pigment for the calculations.

Fig. 10 presents the EET dynamics at the cryogenic temperature of 77 K. These results clearly show that the energy flow in the FMO complex occurs primarily through two pathways, as demonstrated by Brixner *et al.* with 2D electronic spectroscopy.\textsuperscript{4,8} (a) BChl*a* 1 $\rightarrow$ 2 $\rightarrow$ 3 and (b) BChl*a* 6 $\rightarrow$ 5, 7, 4 $\rightarrow$ 3. In Fig. 10a, the long lifetime of BChl*a* 1 is due to the relatively high site energy of BChl*a* 2. Hence, populations of BChl*a* 1 and 3 are dominant at time $t = 1$ ps. In Fig. 10b, on the other hand, those of BChl*a* 3 and 4 are dominant at time $t = 1$ ps owing to very rapid EET. These behaviors are consistent with the transient pump–probe experiment by Vulto *et al.*\textsuperscript{115,116} because BChl*a* 1 participates in exciton 3 and BChl*a* 3 and 4 construct exciton 1, where the numbers give the rank starting with the smallest exciton energy. Furthermore, in both Fig. 10a and b, quantum coherent wave-like motions are visible up to 700 fs. This timescale is consistent with the observation by Engel *et al.* with 2D electronic spectroscopy.\textsuperscript{5}

Fig. 11 gives the EET dynamics at physiological temperature, 300 K. The dynamics is also dominated by the two pathways. More noteworthy is that coherent wave-like motions can be clearly observed up to 350 fs even at the physiological temperature. Note that the phonon relaxation time used here, $\tau_m = 50$ fs, was obtained as a numerical fitting parameter.
for the experimental data; it was not measured directly. Therefore, attention should also be paid to possibilities of different phonon relaxation times. For numerical fitting of other 2D spectra of the FMO complex, Brixner et al.\textsuperscript{4,5} employed an Ohmic form with an exponential cutoff, \( \gamma_\text{m}(\omega) \propto \omega \exp(-\omega/\omega_c) \) with \( \omega_c = 50 \text{ cm}^{-1} \), which yields the phonon relaxation time of \( \tau_{\text{m}} = 166 \text{ fs} \). Calculations employing this slower case predict longer-lasting (up to 550 fs) wave-like motions at 300 K\textsuperscript{14} which cannot be reproduced with conventional Redfield theory because the dynamics are now in the strong non-Markovian regime. On the other hand, Renger and coworkers\textsuperscript{55-57} utilized a super-Ohmic spectral density determined from 1.6 K fluorescence line narrowing spectra of the B777 complex, which consists of an \( \alpha \)-helix and a bound BChl-\( \text{a} \) molecule.\textsuperscript{59} This spectral density yields the phonon relaxation time of \( \tau_{\text{m}} = 35 \text{ fs} \). The relaxation function, eqn (2.15), obtained from this spectral density shows nonoscillatory negative values from 80 fs to 1 ps,\textsuperscript{59} and therefore we have estimated the relaxation time only from the initial decay. Numerical results employing this faster relaxation time also show the wave-like behavior lasting for 350 fs at 300 K, virtually the same as in the case of \( \tau_{\text{m}} = 50 \text{ fs} \).

Therefore, it can be expected that long-lived electronic coherence among BChl-\( \text{a} \) molecules is present in the FMO complex even at physiological temperatures, irrespective of the phonon relaxation times. Recent experiments\textsuperscript{13} support these findings providing experimental evidence for coherence lasting up to 300 fs in the FMO complex at 277 K. In addition, Collini and Scholes showed the presence of quantum coherent EET in the conjugated polymer in solution\textsuperscript{117} and a PPC isolated from photosynthetic cryptophyte marine algae\textsuperscript{12} by means of 2D electronic spectroscopy. Their 2D spectra show that long-lived electronic coherences persist for at least 250 fs after photoexcitation at ambient temperatures. Although the conjugated polymer and the marine algae are different systems than the FMO complex, their experimental observation of long-lived coherence at ambient temperatures also corroborates the present theoretical predictions and suggests the breadth of systems to which this theoretical framework is applicable and necessary.

VI. Quantum coherence and energy transfer in light harvesting complex II

The significance of quantum coherence to energy transfer in photosynthesis cannot be argued without it first being established as a universal phenomenon. If coherence is essential for efficient energy transfer, it should be present in the large antennae complexes whose sole responsibility is to absorb solar energy and funnel it to the reaction centers. Despite having energy transfer as its primary function, the FMO complex is not a key photosynthetic complex with its analog largely absent in higher plants. This begs the question as to whether electronic coherence was important enough to survive evolution. Light harvesting complex II (LHCII) contains 50% of all of the world’s chlorophyll (Chl) in the form of two spectral variants, Chlb and Chla. Recent 2D electronic spectroscopy experiments have revealed evidence of electronic coherence in LHCII as shown in Fig. 12a.\textsuperscript{40} We now address the concern that the coherences generated by ultrashort laser pulses are not relevant to photosynthesis in natural sunlight. The sun excites individual complexes in a molecular ensemble at random times, whereas the ultrashort laser pulses synchronize the entire ensemble at the same time. The ensemble excited by a sequence of ultrashort pulses acts for the duration of the coherence like a single complex. In sunlight the initial event is the absorption of one photon by a single complex independently of the ensemble. Since the coherence is an intrinsic property of the system’s Hamiltonian, the coherence observed experimentally indicates that excitation by the sun also induces quantum coherent EET at the single system level.\textsuperscript{5,9,112}

2D electronic spectroscopy is a powerful technique in its ability to resolve the optical response of a system as a function of the excitation frequency (\( \omega_e \)), emission frequency (\( \omega_o \)), and the delay between excitation and emission (waiting time, \( T \)). For a single waiting time, peaks along the diagonal (\( \omega_e = \omega_o \)) correspond to those in linear absorption, while cross peaks (\( \omega_e \neq \omega_o \)) show coupling and energy transfer between excitons. For recent reviews see ref. 5–7.

Coherence manifests itself as oscillations in the peak amplitudes as a function of \( T \) with beat frequencies equal to the energy differences between the contributing excitons. Coherence pathways associated with diagonal peaks can be isolated through analysis of the nonrephasing signal.\textsuperscript{17} The diagonal, nonrephasing signal of LHCII is shown as a function of \( T \) in Fig. 12a. The strong peaks assigned to Chla (\( \omega \sim 14500 – 15000 \text{ cm}^{-1} \)) as well as the weaker peaks from Chlb (\( \omega \sim 15500 \text{ cm}^{-1} \)) demonstrate clear beating throughout the entire 500 fs duration of the experiment. As the excitons responsible for these beating peaks originate from the chlorophyll molecules, the coherent dynamics can be mapped back onto the site basis. In this way, coherence appears as wavelike energy transfer between the individual pigments as illustrated in Fig. 10 and 11 for the FMO complex.

By Fourier-transforming the \( T \) axis, a power spectrum can be constructed allowing the contributing beat frequencies to be isolated and plotted as a function of the exciton energies along
the diagonal. A portion of the power spectrum from the Chl a region is shown in Fig. 12b. Peaks appearing at smaller beat frequencies indicate coherence between excitons that arise from the same chlorophyll variant. In Fig. 12b, these low energy beat frequencies exhibit strong coherence amongst Chl a excitons. Meanwhile coherences between Chl a and b excitons are evident due to the presence of beat frequencies > 500 cm⁻¹. In addition, as each exciton in LHCII produces a beating diagonal peak with unique frequency components, the power spectrum allows the electronic energy levels to be deconvoluted. Beat frequency peaks align vertically at positions corresponding to individual exciton energies. Analysis of the full power spectrum reveals a relatively evenly-spaced energy landscape in LHCII with a high energy Chl a exciton (ω = 15 130 cm⁻¹) located intermediate to Chl a and b bands. The resulting small energy gap between Chl a and b and the coherences observed between these bands facilitate ultrafast relaxation within LHCII. ⁴⁰

2D spectroscopy can also be used as a technique to directly monitor energy transfer dynamics. 2D spectra illustrating sub-100 fs dynamics are shown in Fig. 13. The relaxation spectra, which display the purely absorptive line shape, are the full 2D spectra. They are shown next to their corresponding isolated nonrephasing contributions. In the nonrephasing spectra, the anti-diagonal extension can better separate features. ⁸² Additionally, nonrephasing off-diagonal features do not contain oscillatory terms superimposed onto the energy transfer cross-peaks. ¹⁷ The larger number of pigments in LHCII produces more complex dynamics than in the FMO complex. 2D and other spectroscopic techniques have shown multiple, parallel relaxation pathways with energy transfer steps on femtosecond and picosecond timescales. ⁴³, ⁴⁶, ¹¹⁸–¹²⁰ While rapid multistep relaxation pathways have been observed, ⁴⁶ including through states located in the intermediate region such as the state introduced above, in this discussion we focus on the initial, ultrafast energy transfer processes. On a sub-100 fs timescale, energy transfer features show relaxation into two peaks within the Chl a band (ω₁ = 14 775 cm⁻¹; ω₂ = 14 900 cm⁻¹) from the Chl b band (ω₁ > 15 200 cm⁻¹), the intermediate region, or the range between Chl a and Chl b (15 000 cm⁻¹ < ω₁ < 15 200 cm⁻¹), and the Chl b band (ω₁ < 15 000 cm⁻¹). This gives rise to five cross-peaks (marked with arrows in the nonrephasing spectra) that appear within 30 fs, as seen in Fig. 13a. At 80 fs, Fig. 13b displays increased relative amplitude of the low energy Chl a. After 100 fs, most of the initially transferred population has relaxed into the low energy Chl b band. ⁴⁶ As these spectra reveal, a component of the initially excited population relaxes across the entire chlorophyll Qy (S₀ → S₁ transition) band on a sub-100 fs timescale, the timescale of coherent motion, similar to the dynamics seen in the FMO complex as shown in Fig. 10b and 11b.

The molecular structure of LHCII can provide insight into the EET dynamics. The light-harvesting function of LHCII requires a large number of closely packed pigments. The high density produces strong coupling between chlorophylls ³¹ that gives rise to the quantum coherence discussed above, and ultrafast excitation energy transfer through quantum coherent motion. The wide range of electronic couplings in LHCII includes five calculated to have magnitudes of J ≳ 50 cm⁻¹ or J⁻¹ ≤ 100 fs. ⁴⁴ The strong couplings, therefore, allow for the experimentally determined sub-100 fs energy transfer steps, in which coherent motion gives rise to ultrafast dynamics. Experimental studies indicate that quantum coherent motion plays a role in excitation energy transfer in LHCII. Quantum coherent motion persists across multiple spectral regions beyond 500 fs, or through the timescale of energy transfer, as seen in Fig. 12. Additionally, as illustrated in Fig. 8, the fast component (≤ 100 fs in the model system) of excitation transfer arises from quantum coherence. Rapid relaxation is seen connecting the entire Qy region and quantum coherence has been identified between excitons well-separated energetically as shown in Fig. 12b. Based on these observations, quantum coherence could facilitate the short time dynamics across a range of energy gaps.

While a reasonable theoretical model has been developed for the mechanisms of the EET in the FMO complex as shown in the preceding sections, the same level of quantitative experimental-theoretical agreement has proved to be more difficult for LHCII due to the larger number of pigments and resultant more complicated dynamics. No current theoretical model accurately reproduces the quantum beating and energy transfer dynamics detected experimentally in LHCII. One major issue in simulating the experimental results is the lack of accurate and detailed information on the total electronic Hamiltonian of the complex.

The protein environment has been speculated to be an integral participant in preserving long-lived electronic coherences since their discovery in photosynthetic PPCs. ⁹ Another potential origin of the theoretical-experimental discrepancy is the treatment of the protein environment. Almost all theoretical models assume homogeneous and uncorrelated protein sites.
Experimental evidence for differences in the protein environment of the pigments in the bacterial reaction center, however, has been observed by Groot, et al. This type of heterogeneity of the protein environment within photosynthetic complexes could indicate a need to vary the reorganization energy magnitude and protein relaxation time of the environment surrounding individual chlorophylls in order to achieve agreement between theoretical and experimental results. The relative magnitude of the reorganization energy and excitonic coupling affects both the rate of energy transfer and the oscillatory motion of the excitation, as illustrated in Fig. 7 and 8, respectively. Therefore, understanding of the excitation energy transfer dynamics and the quantum coherence requires an understanding of the protein environment as well.

In addition to being unable to adequately incorporate the heterogeneity of the protein environments surrounding each pigment, theoretical simulations of these systems have also failed to sufficiently explore the correlation between pigment environments due largely to lacking details about the pigment-protein and protein-protein interactions. Lee et al. clearly demonstrated that strongly correlated fluctuations in the pigment energies can enable long-lasting coherence in a bacterial reaction center while subsequent theoretical work has implicated the correlation in enhancing the efficiency of energy transfer in the FMO complex. The crystal structures of the FMO complex, the bacterial reaction center, and LHCII are shown in Fig. 14. Despite their different physiological functions, all three of these photosynthetic PPCs have been experimentally shown to have long-lasting electronic coherence. The ubiquitous presence of the α-helices explains why this secondary structure has been implicated as a significant source of correlation in the pigments’ surroundings.

While the correlated nature of the environment is not surprising as it is composed of a single protein molecule, it is important to note that the correlation between two pigments can be positive or negative based on their position and orientation relative to the α-helix. To explore effects of positive and negative correlations on EET, we consider the minimal model in eqn (4.26)–(4.28) again. If different pigments share dynamic effects of the same phonon modes, fluctuation in their electronic states would be correlated. Thus, we consider the following models instead of eqn (4.27b) and (4.27c):

$$\varepsilon_1(q) = \varepsilon_0(q) + h\Omega_1 - \hbar\omega_{ph}\xi_1 dq_1 - \hbar\omega_{ph}\xi_2 dq_2,$$

$$\varepsilon_2(q) = \varepsilon_0(q) + h\Omega_2 - \hbar\omega_{ph}\xi_2 dq_2 - \hbar\omega_{ph}\xi_1 dq_1,$$

where the reorganization energy is expressed as $\hbar\omega_{ph} = (1 + \xi_0^2)\hbar\omega_{ph}^2/2$, and the collective energy gap coordinates defined in eqn (2.11) can be expressed as

$$u_m = -\hbar\omega_{ph}\xi_m dq_m - \hbar\omega_{ph}\xi_n dq_n$$

with $m \neq n$. As a result, the auto-correlation function of $u_m(t)$ are obtained as

$$\langle u_m(t)u_m(0) \rangle = \langle 1 + \xi_m^2 \rangle C_{qq}(t),$$

while the cross-correlation function ($m \neq n$) is

$$\langle u_m(t)u_n(0) \rangle = \langle \xi_m \xi_n \rangle C_{qq}(t),$$

where we have introduced $C_{qq}(t) \equiv h^2\omega_{ph}^2\xi^2(q_m(t))d(t)$.

The situations of $\xi_1 + \xi_2 > 0$ and $\xi_1 + \xi_2 < 0$ correspond to the positive and negative correlations, respectively. Fig. 15 illustrates how the dimer system from section IV varies for different extremes of environmental correlation. Similar to Fig. 9, the adiabatic exciton potential surfaces are drawn as a function of two phonon coordinates with minima representing two electronic states. In the case of positive correlation, Fig. 15a, the minima move into the same quadrant reducing their spacing and hence the energy barrier between them. A Franck-Condon transition to the origin lies above the energy barrier in a delocalized excited state promoting coherence. However, for the negative correlation case illustrated in Fig. 15b, the minima exist in opposing quadrants. The large energy barrier between them results in the localized state upon excitation to the origin eliminating coherence. Clearly the

**Fig. 14** Crystal structures of photosynthetic PPCs that have exhibited electronic coherence. (a) The FMO complex with BChl molecules 1–7 in cyan. (b) Bacterial reaction center with BChl in cyan and bacteriopheophytin in purple. (c) LHCII with Chla in green and Chlb in blue. All proteins are shown in gold with the α-helices opaque for emphasis.

**Fig. 15** Adiabatic excitonic potential surfaces for the cases of (a) positive and (b) negative correlated fluctuations. In eqn (6.1), we have chosen $\xi_1 = \xi_2 = 0.5$ for (a) and $\xi_1 = \xi_2 = -0.5$ for (b). The other parameters are the same as in Fig. 9.
protein plays a fundamental role in promoting or demoting the electronic coherence in natural photosynthetic energy transfer. As increasingly complex systems are studied, new experimental and theoretical methods are required to fully characterize and simulate the protein environment.

VII. Concluding remarks

Emerging experimental data from 2D electronic spectroscopy have revealed that electronic excitations of pigments travel though photosynthetic proteins as quantum mechanical wave packets keeping their phase coherence, rather than by incoherent diffusive motion as has usually been assumed.

The ultrashort timescales of photosynthetic EET require that all the relevant timescales in the problem be self-consistently included in any physical model which attempts to elucidate the mechanisms underlying the long-lived quantum coherence and its interplay with the surrounding protein. In this Perspective we showed that properly accounting for non-Markovian effects via theories that also produce realistic optical spectra is critical. Ordinarily, photosynthetic EET is discussed in terms of the mutual relation between magnitudes of reorganization energy characterizing pigment-protein coupling and excitonic coupling between pigments. In this Perspective, however, the main stress fell on the fact that the nature of EET is also dominated by the mutual relation between two timescales, the protein reorganization time and the inverse of the excitonic coupling. Considerations about the finite timescale effects of protein-induced fluctuation-dissipation, i.e. non-Markovian interplay between electronic excitation and the surrounding protein, led to the rigorous theoretical framework describing photosynthetic EET. It reduces to the conventional Redfield and Förster theories in their respective limits of validity and enables to describe long-lived quantum coherence.

While the developed theoretical framework is able to reproduce the experimentally observed quantum coherence and EET pathways in the FMO complex, the same level of experimental-theoretical agreement has proved to be difficult for LHCII. We believe that this is because there exists no accurate electronic Hamiltonian characterizing pigments embedded in LHCII in addition to there being no detailed information about the pigment-protein interaction, LHCII in addition to there being no detailed information. We believe that this is because there exists no accurate electronic Hamiltonian characterizing pigments embedded in LHCII.