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Description of quantum effects in the condensed phase

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Abstract

Recent experiments on light harvesting complexes have shown clear indication of coherent transport of excitations in these aggregates. We review the theoretical models that have been used to study energy transfer in molecular aggregates, beginning with the early models of Förster and Davydov. We cover the Redfield and Haken Strobl models in some detail, in order to set the nomenclature and because they are the most common and easiest models to understand and work with. We briefly discuss more complex models.

Keywords: exciton; exciton-phonon interactions; multichromophoric aggregates; coherence; decoherence

1. Introduction

1.1 Förster and Davydov

In the late 1940s, Förster in Germany, introduced a model for excitation transfer between donor and acceptor molecules, in order to explain the fluorescent lifetime of an emitter in the presence of acceptors [1]. He showed that the rate of energy transfer, k_{ET} , (which we would now classify as incoherent energy transfer) depends on the distance between donor and acceptor, R , as $k_{ET} \sim (R_0/R)^6$, where R_0 can be calculated from the overlap of the donor emission spectrum and the acceptor absorption spectrum. This theory has been immensely useful in the intervening years, and is now used routinely in single molecule biophysical spectroscopy experiments. There have been a number of recent theoretical generalizations of the theory that make it suitable for situations that are more complex than the original one Förster discussed [2].

At about the same time, Davydov, in the USSR, following earlier work by Frenkel [3], introduced the idea of molecular excitons, in order to discuss the low temperature spectroscopy of molecular crystals and aggregates. His work was translated and appeared in English in a book published in 1962 [4]. Davydov's description of the electronic (and vibronic) states of molecular crystals emphasized coherence: the states were linear combinations of excitations localized on different sites. The theory predicted that in pure molecular crystals in which there were two molecular sites connected by a symmetry operator (e.g. in naphthalene or anthracene crystals, there is a glide plane or screw axis connecting the two sites), each spectral line would be split into two, giving

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rise to the Davydov splitting. If the electronic states were not coherent superpositions, but were localized on a site, there would be no splitting. Experiments found the Davydov splittings in a number of crystals at low temperature [5]. The theoretical model of Davydov has been generalized (e.g. to include charge transfer and other two site states) [6], but the basic ideas have continued to be fertile for experimenters and theorists alike.

Förster only considered incoherent energy transfer between localized excitations; Davydov only considered excitations that were coherently coupled among many sites. A more general model allows for both coherence and interactions with phonons and other excitations in the environment of the excitations that lead to decoherence, so that the Davydov and Förster pictures emerge as limiting cases. This has been the focus of much research in the past decades.

1.2. Early Experiments: the mini-exciton

In 1967, Schwoerer and Wolf [7] discovered an interesting model system to study the effects of coherence and decoherence in molecular aggregates. They looked at isotopically mixed naphthalene crystals (small amount of naphthalene-h8 in a crystal of naphthalene-d8). The naphthalene-h8 excited triplet state is approximately 100 cm^{-1} below the same state of the deuterated molecule. At sufficiently high concentrations of the h8, both monomers and dimers of h8 (made up of the nearest neighbor translationally inequivalent molecules) can be seen in optical spectroscopy and in EPR and ENDOR experiments at low temperature. High resolution optical spectra showed two lines symmetrically placed around the 0-0 transition of the monomer with an energy splitting of 2.5 cm^{-1} , that was identified as twice the interaction between the two molecules. That is, the eigenstates of the dimer at $T = 0\text{ K}$ were taken to be

$$\Phi_{\pm} = 2^{-1/2} \{ |A_{\text{ex}} B_{\text{g}}\rangle \pm |A_{\text{g}} B_{\text{ex}}\rangle \}, \quad (1)$$

The first term represents the state in which the molecule A is excited and the molecule B is in the ground state. The matrix element of the Hamiltonian between the two terms is $J = \langle A_{\text{ex}} B_{\text{g}} | H | A_{\text{g}} B_{\text{ex}} \rangle$, and the splitting between the two eigenvalues is $2J$, so that $J = 1.25\text{ cm}^{-1}$ [Φ_{\pm} was assumed to be the lower state ($J > 0$)].

The question arose as to how to describe the experimental observations, in particular whether the energy transfer between the two localized states should be considered to be incoherent hopping (the Förster picture) or coherent (the Davydov picture). The interaction with phonons in the crystal lattice will cause scattering from Φ_{+} to Φ_{-} and vice versa. If the scattering rate from the upper state to the lower is τ^{-1} , then by detailed balance, the scattering from the lower to the upper state is given by $W = \tau^{-1} \exp(-2J/kT)$. If $W > 2J$, then the better description is hopping, and if $W < 2J$, the better description is coherent transfer. Schwoerer [8] analyzed the EPR line shape between 1.5K and 4.2K and concluded that hopping was the correct description. However, Botter, Schmidt and van der Waals [9] later measured the phase memory time of the triplet spins and the zero magnetic field resonance frequencies (using optical detection) between 1.2 K and 4.2 K. From these measurements, they were able to conclude that $W/2J = 10^{-3}$ at 1.2 K and 10^{-2} at 4.2 K, and thus the coherent description of the states and the energy transfer is preferred.

As experimental optical methods improved, it was possible to perform photon echo experiments on isolated molecules and isolated pairs of molecules in a host crystal. For example, the Fayer group studied the singlet excited states of dimers of tetracene and pentacene in p-terphenyl crystals [10] at liquid He temperatures. This showed that the coherent description of the pair states was again correct. There were a number of other groups that contributed to the study of dimers (and one dimensional molecular excitons [11]) in this period.

The bottom line is that at very low temperatures the coherent description of the electronic states of aggregates and crystals was basically correct, so the energy transfer was dominated by coherent interactions; that is, the electronic (or vibronic) states of the system were wavelike but were

scattered weakly by phonons (and defects). At high temperatures, most experiments continued to be described using the Förster mechanism, so the energy transfer was considered to be incoherent; that is, the scattering of the electronic states was large enough to localize the excitation which then hopped from site to site due to the fluctuation of the interactions.

Interest has now shifted to understanding how the description changes as one goes from low temperature to high temperature, and what are the important interactions and mechanisms that govern the change. Recent experiments in the Fleming [12], Engel [13] and Scholes [14] groups on the excitation dynamics in multichromophoric molecular aggregates have been able to watch the electronic excitations as they start at early times in a superposition state and then, over a few hundred femtoseconds, exhibit decoherence. These light harvesting aggregates are part of biological systems that utilize the energy of the light to drive chemical reactions. Does this long-lived coherence play a role in the efficiency of this process? How does the coherence and decoherence depend on the structure of the system? Does the protein in which these chromophoric molecules are arrayed help or hinder the coherence? Does decoherence play a role in optimizing the efficiency of the transport of the excitation to the reaction center? These are some of the questions that many groups are trying to answer.

2. Theoretical description

2.1 General remarks

In order to theoretically describe the dynamics of excitations in aggregates and crystals, one must use a density matrix formalism, because it is impossible to control the other degrees of freedom (i.e. phonons, librations, two-level defects, etc) in the crystal or protein environment of the chromophores; all one can do is set the temperature. The equation of motion for the density matrix for the entire system, ρ , is

$$d\rho/dt = -i [H, \rho] \quad (2)$$

where the bracket represents a commutator. The Hamiltonian is given in general as

$$H = H_s + H_b + V \quad (3)$$

where H_s is the Hamiltonian of the system under study (e.g. the dimer of h8 molecules mentioned above), H_b is the Hamiltonian of the bath, i.e. the other degrees of freedom (phonons, etc.) and V is the interaction between the system and the bath. Since we only measure properties of the system, we take the trace of ρ over the bath degrees of freedom to find the *reduced* density matrix of the system, $\sigma(t) = \text{Tr}_{\text{bath}} [\rho(t)]$. Using a variety of methods, one can derive an exact equation for the dynamics of $\sigma(t)$, called the stochastic Liouville equation (SLE) [15]:

$$d\sigma/dt = -i [H_s, \sigma] - \int_0^t K(\tau) \sigma(t-\tau) d\tau \quad (4)$$

There are very few (almost none!) models for which the exact form of $K(t)$ can be found; therefore one must use sensible approximations in order to proceed. The most common (and perhaps the most important) of these is due to Redfield [16], who studied the relaxation of nuclear spin states in condensed phases.

2.2 The Redfield equation

Redfield made the approximations (quite appropriate for nuclear spins) that (i) the coupling of the system to the bath was weak and (ii) the dynamics of $\sigma(t)$ was slow compared to the time scale of relaxation of the bath, which governs the time scale of relaxation of $K(t)$. Therefore, one can replace $\sigma(t-\tau)$ by $\sigma(t)$ in Eq.. In addition, if one restricts the time of examination of $\sigma(t)$ to times long compared to the relaxation of the bath, one can take the upper limit of the integral to infinity (to be precise, one must go into the interaction representation with respect to H_s+H_b before doing this [...]). The Redfield equation for the reduced density matrix becomes

$$d\sigma/dt = -i [H_s, \sigma] - R \sigma(t), \quad (5)$$

Here R is the relaxation matrix (it is complex in general). In the eigenbasis of H_s $\{|n\rangle\}$, we can write this as

$$d\sigma_{nm}/dt = -i (E_n - E_m) \sigma_{nm} - \sum_{pq} R_{nm,pq} \sigma_{pq}(t) \quad (6)$$

The diagonal elements $\sigma_{nn}(t)$ are the populations of the eigenstates, and the off-diagonal elements, $\sigma_{nm}(t)$, are the coherences. Note that the coherences oscillate with frequencies given by the difference between the eigenenergies. The populations do not oscillate unless they are coupled to the coherences and the coherences are non-zero.

Because of the assumption of weak coupling, the form of $R_{mn,pq}$ is equivalent to second order perturbation theory. Look at the equation for the populations,

$$d\sigma_{nn}/dt = - \sum_{pq} R_{nn,pq} \sigma_{pq}(t) = - \sum_p R_{nn,pp} \sigma_{pp}(t) - \sum_{p \neq q} R_{nn,pq} \sigma_{pq}(t). \quad (7)$$

If one can neglect the coherences, the equation for the populations becomes a simple kinetic (i.e. master) equation, where the rate of relaxation from state p to state n is given by the Fermi Golden rule rate of scattering from p to n by the interaction with the bath variables.

We now apply this model to model the symmetric dimer case (i.e., molecules α and β have the same excitation energy E_0). For ease of notation, label the *site* states as $|1\rangle = |\alpha_{ex} \beta_g\rangle$ and $|2\rangle = |\alpha_g \beta_{ex}\rangle$, then the Hamiltonian in the site basis is

$$H = E_0 \{|1\rangle\langle 1| + |2\rangle\langle 2|\} + J \{|1\rangle\langle 2| + |2\rangle\langle 1|\} + H_b + V \quad (8)$$

where $V = \delta e_1 |1\rangle\langle 1| + \delta e_2 |2\rangle\langle 2| + \delta J \{|1\rangle\langle 2| + |2\rangle\langle 1|\}$, and the terms δe_1 , δe_2 and δJ are operators of the bath degrees of freedom (e.g. phonon coordinates). In the eigenbasis, $|\pm\rangle = 2^{-1/2} \{|1\rangle \pm |2\rangle\}$,

$$H = E_0 \{|+\rangle\langle +| + |-\rangle\langle -|\} + J \{|+\rangle\langle +| - |-\rangle\langle -|\} + H_b + V \quad (9)$$

$$V = (1/2)(\delta e_1 + \delta e_2) \{|+\rangle\langle +| + |-\rangle\langle -|\} + (1/2)(\delta e_1 - \delta e_2) \{|+\rangle\langle -| + |-\rangle\langle +|\} + \delta J \{|+\rangle\langle +| - |-\rangle\langle -|\} \quad (10)$$

And the R matrix in the equation of motion for $\sigma(t)$ becomes

$$R = \begin{array}{cccc} & -- & ++ & - + & + - \\ -- & A\Gamma & -\Gamma & \psi(0) & \psi(0) \\ ++ & -A\Gamma & \Gamma & -\psi(0) & -\psi(0) \end{array} \quad (11)$$

$$\begin{array}{cccc}
 - + & A\psi(2J) & - \psi(2J) & \Gamma_{PD} + (1+A) \Gamma/2 \quad -(1+A) \Gamma/2 \\
 + - & A\psi(2J) & - \psi(2J) & -(1+A) \Gamma/2 \quad \Gamma_{PD} + (1+A) \Gamma/2
 \end{array}$$

Here, Γ is the relaxation rate from $|+\rangle$ to $|-\rangle$ due to (phonon) scattering, Γ_{PD} is the pure dephasing rate, $A = \exp(-2J/kT)$, and $\psi(\omega)$ is the coupling between populations and coherences. For the model above,

$$\Gamma_{PD} = 2 \int_{-\infty}^{\infty} \langle \delta J(t) \delta J(0) \rangle dt \quad (12a)$$

$$\Gamma = (1/4) \int_{-\infty}^{\infty} \exp(i2Jt) \langle (\delta e_1 - \delta e_2)(t) (\delta e_1 - \delta e_2)(0) \rangle dt \quad (12b)$$

$$\psi(\omega) = (1/2) \int_{-\infty}^{\infty} \exp(i \omega t) \langle (\delta e_1 - \delta e_2)(t) \delta J(0) \rangle dt \quad (12c)$$

The correlation functions $\langle C(t)D(0) \rangle$ are averages over the equilibrium density matrix of the bath and the time dependence of the bath operators are due to the interaction representation: $C(t) = \exp(iH_b t) C \exp(-iH_b t)$.

If we assume that there is no coupling between the site energy fluctuations and the fluctuations in J (i.e. $\psi(\omega) = 0$), then the equations can easily be solved. The population difference of the eigenstates (mini-exciton states) decays monotonically to the equilibrium value; where $\Delta(t) = \sigma_{-}(t) - \sigma_{++}(t)$:

$$\Delta(t) = (1-A)/(1+A) \{1 - \exp[-\gamma_0 t]\} + \exp[-\gamma_0 t] \Delta(0), \text{ where } \gamma_0 = (1/2)(1+A)\Gamma \quad (13)$$

If we now assume that the system is in state $|1\rangle$ at $t = 0$ (the state for which the excitation is localized on molecule α), so that $\sigma_{+}(0) = \sigma_{-}(0) = 1/2$, we find for $X(t) = [\sigma_{+}(t) - \sigma_{-}(t)] = [\sigma_{11}(t) - \sigma_{22}(t)]$ (i.e. the population difference between states 1 and 2 or sites α and β):

$$X(t) = (1/2)[(1 + \gamma_0/\lambda) \exp(\lambda t) + (1 - \gamma_0/\lambda) \exp(-\lambda t)] \exp[-(\gamma_0 + 2\gamma_1)t], \quad (14)$$

where $\gamma_1 = \Gamma_{PD}$ and $\lambda = [\gamma_0^2 - 4J^2]^{1/2}$. In the limit that both γ_0 and γ_1 are zero (no scattering), $X(t) = \cos(2Jt)$, purely coherent transfer. When $\gamma_0^2 - 4J^2 < 0$, then there are oscillations in $X(t)$ as it decays to zero, but if $\gamma_0^2 - 4J^2 > 0$, there are no oscillations. When $\gamma_0^2 \gg 4J^2$, $X(t)$ decays as $\exp[-(2J^2/\gamma_0 + \gamma_1)t]$, which has the same general form as the Förster transfer rate. Thus, the Redfield equations lead to a qualitatively correct description of the energy transfer process between two molecules over a large range of parameters.

If one considers the asymmetric dimer ($E_\alpha \neq E_\beta$), the equations are a bit more complex, but the same general conclusions result. The general form for the relaxation parameters Γ , Γ_{PD} , and $\psi(\omega)$ are given by Wertheimer and Silbey [17]. In general, $\psi(\omega)$ is not zero in this case. However, with the assumption that the population dynamics (in the eigenstate basis) and the coherences are uncoupled, the populations decay monotonically to the equilibrium values. Here, the equilibrium values refer to the Boltzmann distribution of the system. In general, with coherence-population coupling, the reduced density matrix approaches a steady-state, which is not the thermal equilibrium of the system but approximately the projection of the entangled system-bath equilibrium state.

There are some immediate consequences of the Redfield model. (i) The scattering rates between the two states satisfy detailed balance. (ii) The decay of the populations is governed by the scattering between the states, but the decay of the coherences has the added term, the pure dephasing rate, so normally, the coherences decay more rapidly than the populations. (iii) Since the pure dephasing rate is a zero frequency Fourier transform, it normally goes to 0 as T goes to zero, because

the spectral density of phonon (and other) modes goes to zero at zero frequency. (iv) Finally, if the phonon coordinates that cause J to fluctuate (i.e. those contained in δJ) are different from those that cause the site energies to fluctuate, then $\psi(\omega) = 0$, and the populations decouple from the coherences. In this case the populations relax without oscillation. However, if the modes that cause J to fluctuate also cause the energies to fluctuate, there will be coupling between populations and coherences. The results given above are for the symmetric dimer; however, when the energies of the two site state differ, the results are more complicated and, in general, the populations and coherences are always coupled [18].

The Redfield model has been applied to many spin resonance and optical experiments with great success. One must be careful however, because it is inherently a weak coupling model. One consequence of this is the failure to reproduce the Förster rate behavior in the strong coupling limit. Another failure of the Redfield equations is that for some values of the parameters, the predicted populations can become negative or larger than 1. This indicates a breakdown of the model. If this happens, we have to go beyond second order or define a different system Hamiltonian, by, for example, making a unitary transformation that puts some of the coupling to bath modes into the system Hamiltonian [19]. Another approach is to use the Lindblad equation, which guarantees positivity of the reduced density matrix [20].

2.3 Haken Strobl Reineker (HSR) model

Haken and Strobl [20] introduced a model, following earlier work by Sewell [21], that has many attractive features, and so has been used by many groups. The model replaces the time dependence of the phonon operators in the Redfield model by classical stochastic Gaussian white noise, i.e. it assumes that all correlation functions $\langle C(t) D(0) \rangle$ have a $\delta(t)$ time dependence and all fluctuations are Gaussian. The ensuing equations are the same as the Redfield equations given above, but with the matrix elements of R calculated with the HSR assumptions. And these equations are exact within these assumptions, because these assumptions cause the higher than second order cumulants to be zero, and so the weak coupling equations (like Redfield) that only consider the second cumulant become exact.

There are a number of concerns about the HSR model. (i) Assuming a $\delta(t)$ time dependence means that the relaxation of the bath modes is instantaneous and that the bath has energies on all scales, or equivalently the temperature is very large compared to any energy differences in the system. Thus, detailed balance is lost and $A = 1$. (ii) the model predicts that the pure dephasing rate is independent of temperature (although one can always put in a T dependence by hand). It is known that the pure dephasing rate should vanish at low temperatures. (iii) the model predicts that $\psi(\omega)$ is independent of frequency, which neglects the differences in the phonon spectral density of real systems. (iv) the original HSR model neglected the correlations between fluctuations on different sites and on the fluctuations between J and site energies. Neighboring molecules in a crystal or protein environment should exhibit correlations among these quantities and putting them into the model can qualitatively change the results [22].

In spite of these concerns, the HSR model, including all correlations, is useful and important, especially at higher temperatures, where (i)-(iii) are less troubling.

2.4 Explicit models for exciton phonon coupling between the system and the bath modes

The phonons are assumed to be harmonic, $H_b = \sum_{\lambda} (1/2) \{P_{\lambda}^2 + \omega_{\lambda}^2 Q_{\lambda}^2\} = \sum_{\lambda} \omega_{\lambda} (b_{\lambda}^{\dagger} b_{\lambda} + 1/2)$ where b_{λ} and b_{λ}^{\dagger} are the usual Boson operators. The most common form of interaction is a site diagonal excitation-phonon interaction, i.e. the energy at site n in the system varies with the λ phonon coordinate Q_{λ} as $\delta e_n = \sum_{\lambda} d_{n\lambda} Q_{\lambda} = \sum_{\lambda} g_{n\lambda} \omega_{\lambda} (b_{\lambda}^{\dagger} + b_{\lambda})$ [where $g_{n\lambda} = d_{n\lambda}/\sqrt{2\omega_{\lambda}^3}$]. This form might be interpreted as the change in site energy due to a quasi-localized oscillator made up by a linear combination of the normal harmonic modes. For the asymmetric dimer, the Hamiltonian then becomes

$$H = E_1 |1\rangle\langle 1| + E_2 |2\rangle\langle 2| + J \{ |1\rangle\langle 2| + |2\rangle\langle 1| \} + \sum_{\lambda} \omega_{\lambda} (b_{\lambda}^{\dagger} b_{\lambda} + 1/2) + \sum_{\lambda} (b_{\lambda}^{\dagger} + b_{\lambda}) \{ g_{1\lambda} |1\rangle\langle 1| + g_{2\lambda} |2\rangle\langle 2| \} \quad (15)$$

Note, that this is the famous spin-boson problem [23].

In the limit that $J = 0$, the eigenstates are easily found by displacing the coordinates an amount depending on which molecule is excited (polaron transformation). The eigenenergies become $E_n - \sum_{\lambda} g_{n\lambda}^2 \omega_{\lambda} / \hbar$ ($\hbar = 1$). The second term is the reorganization energy of the lattice when the excitation is on site n , and $S_{n\lambda} = g_{n\lambda}^2 / \omega_{\lambda}$ is related to the Huang-Rhys factor used in spectroscopy [24]. Also note the resemblance to the theory of electron transfer.

Using this form for the exciton phonon interaction, we can calculate Γ in the Redfield model to lowest order (i.e. second order perturbation theory)

$$\Gamma = (1/4) \int_{-\infty}^{\infty} \exp(i2Jt) \langle (\delta e_1 - \delta e_2)(t) (\delta e_1 - \delta e_2)(0) \rangle dt = (1/2) \text{Re} \int_0^{\infty} dt \exp(i2Jt) \sum_{\lambda} (g_{1\lambda} - g_{2\lambda})^2 [n_{\lambda} \exp(i\omega_{\lambda}t) + (n_{\lambda} + 1) \exp(-i\omega_{\lambda}t)] \quad (16)$$

where $n_{\lambda} = \exp(-\beta\omega_{\lambda}) / [1 - \exp(-\beta\omega_{\lambda})]$ is the boson occupation number and $\beta = 1/(kT)$. At this order in perturbation theory, only one phonon absorption or emission processes are allowed. In order to go further, we need explicit forms for the frequencies and the coupling constants. Or we can make the following crude approximations and assume that (i) the sum over the harmonic modes yields a decaying exponential function, $\exp(-vt)$, where v is proportional to the phonon bandwidth, (ii) $kT \gg \omega_{\lambda}$, and (iii) $(g_{1\lambda} - g_{2\lambda})^2 \approx g^2(\omega_{\lambda}) (1-c)$, where c is the correlation coefficient between the local modes on site 1 and site 2. Then

$$\Gamma \oplus \langle g^2 \rangle (1-c) kT [v/(v^2 + 4J^2)] \quad (17)$$

where $\langle g^2 \rangle (1-c)$ is the average of $(g_{1\lambda} - g_{2\lambda})^2$ over the phonon band(s). This is very crude, but does give us insight into the process of dephasing or decoherence. If $2J \gg v$, then the dephasing is weak (this is the motional narrowing limit, in which the excitation transfer between sites is so rapid that the phonons cannot keep up). In the opposite limit ($2J \ll v$) the phonon bandwidth is so large that there are so few dephasing processes at $2J$ and again the dephasing is weak. Calculations going to higher order confirm this qualitative picture. We note the similarity to the results of the high temperature Brownian oscillator model introduced by Mukamel for non-linear spectroscopy [24].

Almost all theoretical calculations have been made with the assumption of site energy fluctuations only. If we look at the results of the Haken-Strobl model, we note that the fluctuations of the transfer matrix element, J , are important. In particular, the long time diffusion constant at high temperatures is dominated by these fluctuations. It is important for a full understanding of the problem of energy transfer that we take these fluctuations (and the correlation of fluctuations) into account in theoretical models.

Another approach to the Hamiltonian of Eq. (15) is to realize that it is exactly solvable for $J = 0$ by making the polaron transformation to remove the linear displacements of the harmonic phonons for the states $|1\rangle$ and $|2\rangle$. The transformed Hamiltonian is $H' = UH U^{\dagger}$, where $U = \exp[\sum_{\lambda} (b_{\lambda}^{\dagger} - b_{\lambda}) \{ g_{1\lambda} |1\rangle\langle 1| + g_{2\lambda} |2\rangle\langle 2| \}]$, so

$$H' = [E_1 - \sum_{\lambda} g_{1\lambda}^2 \omega_{\lambda}] |1\rangle\langle 1| + [E_2 - \sum_{\lambda} g_{2\lambda}^2 \omega_{\lambda}] |2\rangle\langle 2| + J\theta |1\rangle\langle 2| + J\theta^{\dagger} |2\rangle\langle 1| + \sum_{\lambda} \omega_{\lambda} (b_{\lambda}^{\dagger} b_{\lambda} + 1/2) \quad (18)$$

where $\theta = \exp[\sum_{\lambda} (b_{\lambda}^{\dagger} - b_{\lambda}) (g_{1\lambda} - g_{2\lambda})]$. In order to go further, we average the term in J over the thermal phonon bath and add and subtract that average from H' . This leads a perturbation term which

is proportional to the difference between J_0 and its average $\langle J_0 \rangle$ [18,25]. In addition, the original transfer matrix element J has been replaced by $\langle J_0 \rangle$ (which is less than J). We find

$$H' = [E_1 - \sum_{\lambda} g_{1\lambda}^2 \omega_{\lambda}] |1\rangle\langle 1| + [E_2 - \sum_{\lambda} g_{2\lambda}^2 \omega_{\lambda}] |2\rangle\langle 2| + \langle J_0 \rangle \{ |1\rangle\langle 2| + |2\rangle\langle 1| \} + \sum_{\lambda} \omega_{\lambda} (b_{\lambda}^{\dagger} b_{\lambda} + \frac{1}{2}) + [J_0 - \langle J_0 \rangle] |1\rangle\langle 2| + [J_0 - \langle J_0 \rangle^{\dagger}] |2\rangle\langle 1| \quad (19)$$

Note that the perturbation term can be interpreted as the *fluctuation* of the transformed transfer matrix element from its average value. This perturbation is small in both the weak coupling limit ($g_{n\lambda}^2 \ll 1$) and the strong coupling limit ($g_{n\lambda}^2 \gg 1$), suggesting that this is a particularly good starting point for studying excitation transfer. In the strong coupling limit, second order perturbation theory reproduces the Förster picture exactly. In the weak coupling limit, it reproduces the Davydov picture with weak scattering of the exciton states.

2.5 Beyond Redfield

A number of authors have made progress in going beyond the standard Redfield equations. We will not give the details of these theoretical treatments but will only discuss them qualitatively, without attempting to be at all definitive.

The simplest extension of Redfield is to keep the upper limit of the integral in Eq. (4), and keep the second order form of $K(t)$, to get (after some mathematical manipulations)

$$d\sigma/dt = -i [H_s, \sigma] - \int_0^t K^{(2)}(\tau) d\tau \sigma(t) = -i [H_s, \sigma] - R(t) \sigma(t) \quad (20)$$

Jang et al [26] used this equation (with careful consideration of the initial conditions) to discuss excitation transfer in a two molecule system. They first applied a polaron transformation to the Hamiltonian [18, 25] which leads to a small perturbation in both the weak coupling and strong coupling regimes of exciton phonon coupling. The results show qualitative differences from those of the Redfield approach in the moderate to strong coupling regime. In particular, there are enhanced oscillations in the populations.

Cao [27] introduced a phase space method for going beyond the Redfield picture for the stochastic Liouville equation and Tanimura et al [28] and Ishizaki and Fleming [29] have discussed hierarchical approaches to improving the approximations to the kernel, $K(t)$. All of these approaches have assumed that the fluctuations are of the Gaussian-Markov type with exponential time dependence in the correlation function. Since the harmonic phonon bath is Gaussian, this is a good assumption. Ishizaki and Fleming show that for the two molecule system their approach yields results that are valid in both the weak and strong coupling regimes.

The Reineker group [30] treated the dimer with dichotomic noise, i.e stochastic fluctuations that take only two values with a correlation function in time. With this assumption, the hierarchical equations close [31]; thus, this procedure is exact in principle, but requires much computation.

2.6 Recent theoretical calculations on light harvesting complexes

In the last few years, a number of theoretical groups have examined the effect of decoherence (due to noise or fluctuations) on the *efficiency* of energy transfer, in model systems and in the FMO protein [32-36]. The focus of this work has been on whether noise can increase the efficiency of the transfer process, instead of, as is usually thought, that noise can only decrease the transfer rate (as in the Förster model) and so decrease the efficiency. However, it was found in a number of theoretical studies the efficiency of transport to the reaction center in the FMO protein depends non-monotonically on the amount of noise (i.e dephasing rate), and there is an optimal noise. How does this happen? If we look at the exciton states of the FMO system in the total absence of noise, we find that some of these coherent exciton states have no (or almost no) coupling to the

reaction center. Thus if an excitation begins on these exciton states, the trapping time is very long. However, when noise is introduced, the exciton states mix and this opens these channels, so the average trapping time decreases. Thus, a small amount of noise increases the efficiency in this system. If the noise is increased further, efficiency begins to drop and for strong noise goes to the Förster limit, so there is an optimal amount of noise [37].

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References

- [1] Th. Förster, *Naturwiss.* 33 (1946) 166; Th. Förster, *Ann Phys. (Leipzig)* 2 (1948) 55; Th. Förster, *Radiation Research Supplement* 2 (1960) 326-339.
- [2] For a review, see D. Beljonne, C. Curutchet, G. Scholes, R.J. Silbey, *J. Phys. Chem B* 113 (2009) 6583.
- [3] J. Frenkel, *Phys. Rev.* 37 (1931) 17; *ibid* 37 (1931) 1276.
- [4] A.S. Davydov, *Theory of Molecular Excitons* (translated by M. Kasha and M. Oppenheimer) McGraw-Hill, NY 1962; A.S. Davydov, *Zh. Eksp. i Teor* 18 (1948) 210.
- [5] D.S. McClure, *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic Press NY 1959) volume 8, p. 1.
- [6] for an early review, see S.A. Rice and J. Jortner, in *Physics and Chemistry of the Organic Solid State* (Interscience, NY 1967) p. 199-497.
- [7] M. Schwoerer and H.C. Wolf, *Mol. Cryst* 3 (1967) 177; M. Schwoerer, *Habilitationsarbeit*, Univ. Stuttgart (1972).
- [8] B.J. Botter, C.J. Nonhof, J. Schmidt, and J.H. van der Waals, *Chem. Phys. Lett.* 43 (1976) 210.
- [9] F.G. Patterson, W.L. Wilson, H.W. Lee and M.D. Fayer, *Chem. Phys. Lett.* 110 (1984) 7.
- [10] J. Morsink and D. Wiersma, *Chem. Phys. Lett.* 89 (1982) 291.
- [11] J. Schmidt, in *Organic Molecular Aggregates*, ed P. Reineker, H. Haken and H.C. Wolf (Springer NY 1983); See also D. Burland and A. Zewail in *Advances in Chemical Physics*, vol. 40, eds I. Prigogine and S.A. Rice (Wiley, NY 1979).
- [12] G. Engel, T. Calhoun, E. Read, T.-K. Ahn, T. Mancal, Y.C. Cheng, R. Blankenship and G. Fleming, *Nature (London)* 446 (2007) 782; H. Lee, Y.C. Cheng and G. Fleming *Science* 316 (2007) 1462-1465; T. Calhoun et al, *J. Phys Chem B* 113 (2009) 16291.
- [13] G. Panitchaangkoon, D. Hayes, K. Fransted, J. Caram, E. Harel, J. Wen, R. Blankenship and G. Engel, *PNAS* 107 (2010) 12766.
- [14] E. Collini, C. Wong, K. Wilk, P. Curmi, P. Brumer, and G. Scholes, *Nature* 463 (2010) 644.
- [15] K. Blum, *Density Matrix Theory and Applications* (Plenum Press, NY, 1981); R. Zwanzig in *Lectures in Theoretical Physics*, vol III (Interscience, NY 1961); R. Kubo, in *Advances in Chemical Physics* vol 15 (Interscience, NY 1958).
- [16] A. Redfield, *IBM Journal for Research and Development* 1 (1957) 31.
- [17] R. Wertheimer and R. Silbey, *Chem. Phys. Lett.* 75 (1980) 243.
- [18] M. Grover and R. Silbey, *J. Chem. Phys.* 52 (1970) 2099; M. Grover and R. Silbey, *J. Chem. Phys.* 54 (1971) 4843.
- [19] G. Lindblad, *Comm. Math. Phys.* 48, 119 (1976).
- [20] H. Haken and G. Strobl, in *The Triplet State*, Ed A. Zahlan (Cambridge Univ. Press 1967), p 311-314; H. Haken and G. Strobl, *Z. Phys.* 262 (1973) 135; H. Haken and P. Reineker, *Z. Phys.* 249 (1972) 253; V. M. Kenkre and P. Reineker, *Exciton Dynamics in Molecular Crystals and Aggregates* (Springer, Berlin 1982).
- [21] G. Sewell, *Phys. Rev.* 129 (1963) 597.
- [22] X. Chen and R. Silbey, *J. Chem. Phys.* 132 (2010) 204503.
- [23] A. Caldeira and A. Leggett, *Ann Phys*; A. J. Leggett, S. Chakravarty, A. T. Dorsey, M. Fisher, A. Garg, and W. Zwerger, *Rev. Mod. Phys.* 59 (1987) 1.
- [24] S. Mukamel, *Principles of Nonlinear Optical Spectroscopy* (Oxford Univ. Press, 1995).
- [25] S. Rackovsky and R. Silbey, *Molecular Physics* 25 (1973) 61; I. Abram and R. Silbey, *J. Chem. Phys.* 63 (1975) 2317; R. Silbey and R. Harris, *J. Chem. Phys.* 80 (1984) 2615.
- [26] S. Jang, Y.-C. Cheng, D.R. Reichman and J. D. Eaves, *J. Chem. Phys.* 129 (2008) 101104.
- [27] J. Cao, *J. Chem. Phys.* 107 (1997) 3204.
- [28] Y. Tanimura and R. Kubo, *J. Phys. Soc. Jpn.* 58 (1989) 101; Y. Tanimura, *J. Phys. Soc. Jpn* 75 (2006) 082001.
- [29] A. Ishizaki and G. Fleming, *PNAS* 106 (2009) 7255; A. Ishizaki and G. Fleming *J. Chem. Phys.* 130 (2009) 234110 and 234111.
- [30] V. Kraus and P. Reineker, *Phys. Rev. A* 43 (1991) 4182; I. Barvik, C. Warns, and P. Reineker, *Physica A* 259 (1998) 65.
- [31] V. Shapiro and V. M. Loginov, *Physica A* 91 (1978) 563.
- [32] P. Rebentrost, M. Mohseni, I. Kassal, S. Lloyd and A. Aspuru-Guzik, *New J. Phys.* 11 (2009) 033003; P. Rebentrost, M. Mohseni, A. Aspuru-Guzik, *J. Phys. Chem. B* 113 (2009) 9942; M. Mohseni, P. Rebentrost, S. Lloyd, A. Aspuru-Guzik, *J. Chem. Phys.* 129 (2008) 174106.
- [33] F. Fassioli, A. Olaya-Castro, *New J. Phys.* 12 (2010) 085006; F. Fassioli, A. Nazir, A. Olaya-Castro, *J. Phys Chem. Lett.* 1 (2010) 2139; A. Olaya-Castro, C.F. Lee, F.F. Olsen, and N. Johnson, *Phys. Rev. B* 78 (2008) 085115.

- [34] M.B. Plenio and S. F. Huelga, *New J. Phys.* 10 (2008) 113019; A.W. Chin, A. Datta, F. Caruso, S.F. Huelga, M.B. Plenio, *New J. Phys.* 12 (2010) 065002; F. Caruso, A.W. Chin, A. Datta, S.F. Huelga, M.B. Plenio, *Phys. Rev A* 81 (2010) 062346.
- [35] S. Hoyer, M. Sarovar, K.B. Whaley, *New J. Phys.* 12 (2010) 065041; M. Sarovar, A. Ishizaki, G.R. Fleming, and K.B. Whaley, *Nature Physics* 6 (2010) 462.
- [36] J. Cao and R. Silbey, *J. Phys Chem. A* 113 (2009) 13825; J. Wu, F. Liu, Y. Shen, J. Cao and R. Silbey, *New J. Phys.* 12 (2010) 105012.
- [37] J. Wu, J. Cao, R. J. Silbey (to be published).