Corrigendum: Energy transfer, entanglement and decoherence in a molecular dimer interacting with a phonon bath (2010 New J. Phys. 12 065045)

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Abstract
In this corrigendum, we present the analytic corrections to the paper Hossein-Nejad and Scholes 2010 New J. Phys. 12 065045. Due to a mathematical error in the computation of the oscillator traces, the conclusions of that paper with regards to dynamics of an interacting dimer are incorrect. In this corrigendum we provide analytic expressions for the quantity of interest in Hossein-Nejad and Scholes (2010): the reduced density matrix of a weakly coupled dimer that interacts with a high frequency oscillator mode. Our result is valid for system–oscillator coupling that is smaller than the oscillator frequency, and can readily be generalized to multiple oscillator modes.

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1. Introduction

In a previous paper, we considered the dynamics of the reduced density matrix of a system consisting of two interacting molecules coupled to a vibrational bath [1]. We realized that there was a mistake in the computation of the oscillator traces that resulted in incorrect dynamics and the erroneous conclusion that the anti-correlated bath results in different dynamics than an independent bath, as pointed out by Lim et al [2]. We agree with the comments of Lim et al [2] with regards to the equivalence of independent (and identical) baths and an anti-correlated bath, as far as electronic energy transfer is concerned.

The problem originated in [1, equation (22)], where non-commutativity of the density matrix of the oscillator, with the time evolution operator, was not accounted for. The subsequent conclusions are, therefore, no longer valid. In this corrigendum, we take the opportunity to present the correction to the original paper, and discuss the regime of validity of the introduced approximation. We demonstrate that our theory is valid for a weakly coupled dimer that interacts with a high frequency oscillator mode, provided that the energy of the oscillator is larger than the thermal energy of the environment. Moreover, the strength of the system–oscillator coupling $h$, and the energy of the mode $\omega$, must satisfy the relation $h < \omega$. More details of the calculations are provided in the supplementary information (available from stacks.iop.org/NJP/16/019502/mmedia). The results for the dephasing of a single molecule, presented in the first section of the original paper, are correct and will not be discussed.

2. Dephasing in a dimer: analytic solution

2.1. Fulton–Gouterman (FG) versus site basis

The Hamiltonian describing the interaction of the singly excited states of a molecular dimer with a bosonic bath is given by [3]

$$H = -J (a_1^\dagger a_2 + a_2^\dagger a_1) + \sum_{i=1}^2 a_i^\dagger a_i \left[ \epsilon + \frac{1}{2} \sum_k h_{ik}(b_k^\dagger + b_k) \right] + \sum_k \omega_k b_k^\dagger b_k,$$  

where $J$ is the electronic coupling, $\{a_i^\dagger, a_i\}$ are the raising and lowering operators for molecule $i$, and $\epsilon$ is the energy gap between the ground and excited state of each molecule. The molecules are assumed to be diagonally coupled to a harmonic bath described by the creation and annihilation operators $\{b_k^\dagger, b_k\}$. The coupling between molecule $i$ and the oscillator mode $k$ is given by the electron–phonon coupling $h_{ik}$. We consider the case of an anti-correlated bath where exciton–phonon couplings of the two molecules satisfy the relation $h_{1k} = -h_{2k}$. We next write the Hamiltonian in the single excitation subspace as a matrix in the site basis

$$H = \begin{pmatrix} H_b + \epsilon + \frac{1}{2} \Delta & -J \\ -J & H_b + \epsilon - \frac{1}{2} \Delta \end{pmatrix},$$

where $\Delta = \sum_k h_{1k}(b_k^\dagger + b_k)$. At this point we drop the subscript $k$ and focus on a single oscillator mode. Extension to many modes is straightforward and the multimode result is quoted at the end of this section. The dimer Hamiltonian can be diagonalized in the electronic basis by applying
the following Fulton–Gouterman (FG) transformation [4–7]

\[
U = \frac{1}{\sqrt{2}} \begin{bmatrix} 1 & R \\ -R & 1 \end{bmatrix},
\]

(3)

where \( R = (-1)^{b^b} \). The parity operator \( R \), adds a phase factor of +1 (-1) to states with an even (odd) number of phonons, thereby dividing the Hilbert space into subspaces of even and odd parity. The transformed Hamiltonian \( D = U H U^\dagger \), is found to be

\[
D = \begin{bmatrix} A & 0 \\ 0 & B \end{bmatrix},
\]

(4)

\[
A = H_b + \frac{1}{2} \Delta - J (-1)^{b^b} + \epsilon,
\]

(5)

\[
B = H_b - \frac{1}{2} \Delta + J (-1)^{b^b} + \epsilon.
\]

(6)

Note that the basis states are reorganized such that all states of combined spin and oscillator parity +1 \((-1)\) are used to write \( A(B) \). This Hamiltonian is diagonal in the electronic basis, but infinite dimensional in the oscillator basis. Diagonalization via the FG transformation implies the relation

\[
e^{-iDt} = U e^{-iHt} U^\dagger.
\]

(7)

We now focus on computing the reduced density matrix in the FG basis analytically; the corresponding calculation in the site basis is discussed in the supplementary information (available from stacks.iop.org/NJP/16/019502/mmedia) and the results are quoted in this paper.

### 2.2. Density matrix in the FG basis

The evolution of the reduced density matrix in the FG basis is relatively straightforward to compute and is determined by

\[
\tilde{\sigma}(t) = \text{Tr}_b \{ \tilde{\rho}(t) \}
\]

(8)

\[
= \text{Tr}_b \{ U \rho(t) U^\dagger \}
\]

(9)

\[
= \text{Tr}_b \{ U e^{-iHt} \rho(0) e^{iHt} U^\dagger \},
\]

(10)

where we have used bars to denote states in the FG basis. We assume separable initial conditions in the site basis, i.e. \( \rho(0) = \rho_b \otimes \sigma(0) \), where \( \rho_b \) is the density matrix of the oscillator modes. The oscillator is assumed to be at thermal equilibrium initially

\[
\rho_b = \frac{e^{-\beta H_b}}{\text{Tr}_b \{ e^{-\beta H_b} \}}.
\]

(11)

Using equation (7), we next replace exponentials of the Hamiltonian with exponentials of \( D \) and arrive at the following expression:

\[
\tilde{\sigma}(t) = \text{Tr}_b \{ e^{-iDt} U \rho_b \sigma(0) U^\dagger e^{iDt} \},
\]

(12)

\[
= \text{Tr}_b \{ e^{-iDt} \rho_b \tilde{\sigma}(0) e^{iDt} \},
\]

(13)
The last line could have been written from the outset, as it merely states that the evolution of the transformed density matrix is determined by the diagonalized Hamiltonian. Note that \( \rho_b \) does not commute with \( D \); writing \( \rho_b \) to the left of the time evolution operator in [1, equation (22)] was the source of the error in the original paper. By writing equation (13) in the form
\[
\tilde{\sigma}(t) = \text{Tr}_b \left\{ \begin{bmatrix} e^{-iAt} & 0 \\ 0 & e^{-iBt} \end{bmatrix} \begin{bmatrix} \tilde{\sigma}_{11}(0) & \tilde{\sigma}_{12}(0) \\ \tilde{\sigma}_{21}(0) & \tilde{\sigma}_{22}(0) \end{bmatrix} \rho_b \begin{bmatrix} e^{iAt} & 0 \\ 0 & e^{iBt} \end{bmatrix} \right\},
\]
we arrive at the following expressions for the evolution of population and coherence:
\[
\tilde{\sigma}_{11}(t) = \text{Tr}_b \{ \tilde{\sigma}_{11}(0) \rho_b \},
\]
\[
\tilde{\sigma}_{12}(t) = \text{Tr}_b \{ e^{-iAt} \tilde{\sigma}_{12}(0) \rho_b e^{iBt} \}.
\]
Populations thus remain invariant in the FG basis. As the initial conditions in the FG basis may be unknown, we rewrite these expressions in terms of the initial density matrix in the site basis. Recalling that
\[
\tilde{\sigma}(0) = U \sigma(0) U^\dagger,
\]
we write \( U \) in the matrix form and substitute equation (17) into equation (14), thereby expressing the time-evolution in the FG basis in terms of the site basis initial condition. The final solution reads
\[
\tilde{\sigma}_{11}(t) = \frac{1}{2} + \text{Re} \{ \sigma_{12}(0) \} \text{Tr}_b \{ R \rho_b \},
\]
\[
\tilde{\sigma}_{12}(t) = \left[ \frac{1}{2} - \sigma_{11}(0) \right] \text{Tr}_b \{ e^{-iAt} \rho_b R e^{iBt} \} + i \text{Im} \{ \sigma_{12}(0) \} \text{Tr}_b \{ e^{-iAt} \rho_b e^{iBt} \},
\]
where \( \text{Re} \) and \( \text{Im} \) indicate the real and imaginary parts, respectively. The problem is thus reduced to the evaluation of the traces over the oscillator mode. The details of the calculations presented in this section may be found in the supplementary information (available from stacks.iop.org/NJP/16/019502/mmedia).

2.2.1. Approximated solution in the FG basis. All calculations up until this point have been exact. The trace \( \text{Tr}_b \{ R \rho_b \} \) can readily be evaluated analytically. The remaining traces, however, cannot be evaluated unless an approximation is introduced. In order to do this, we expand the parity operator and truncate up to terms linear in the number operator \( \hat{n} \). This approximation renders all oscillator traces linear in exponentials of bosonic operators. The parity operator reads
\[
\tilde{\sigma}(t) = \frac{1}{2} + \text{Re} \{ \sigma_{12}(0) \} \tanh(\frac{1}{2} \beta \omega),
\]
\[
\tilde{\sigma}_{12}(t) = \exp \left\{ i \frac{(h/2)^2}{\omega^2 - 4 J^2} \Phi_1(\omega, J, t) + 2iJt \right\}
\times \left[ \frac{1}{2} - \sigma_{11}(0) \right] \exp \left[ \frac{(h/2)^2 \Theta_1(\omega, J, t)}{\omega^2 - 4 J^2} \tanh \left( \frac{\beta \omega(t)}{2} \right) \right]
+ \frac{i \text{Im} \{ \sigma_{12}(0) \} (1 - e^{-\beta \omega(t)})}{1 - e^{-\beta \omega(t)}} \exp \left[ \frac{(h/2)^2 \Theta_1(\omega, J, t)}{\omega^2 - 4 J^2} \coth \left( \frac{\beta \omega(t)}{2} \right) \right].
\]
\[ \Phi_\ell(\omega, J, t, \ell) = -\Delta \omega t + \sin(\Delta \omega t) - 2\omega \left[ \frac{\sin(\omega_+ t)}{\omega_+} - \frac{\sin(\omega_- t)}{\omega_-} \right], \] (23)

\[ \Theta_\ell(\omega, J, t, \ell) = -\frac{\omega_+^2 + \omega_-^2 + \omega_+ \omega_-}{\omega_+ \omega_-} - \cos(\Delta \omega t) + 2\omega \left[ \frac{\cos(\omega_+ t)}{\omega_+} + \frac{\cos(\omega_- t)}{\omega_-} \right], \] (24)

where

\[ \omega_\pm = \omega \pm 2J, \] (25)

\[ \Delta \omega = \omega_+ - \omega_-, \] (26)

\[ \tilde{\omega}(t) = \omega + i \frac{\Delta \omega}{\beta} t. \] (27)

At \( t = 0 \) these expressions are reduced to

\[ \tilde{\sigma}_{11}(0) = \frac{1}{2} + \text{Re} \left[ \sigma_{12}(0) \right] \tanh \left( \frac{1}{2} \beta \omega \right), \] (28)

\[ \tilde{\sigma}_{12}(0) = \left[ \frac{1}{2} - \sigma_{11}(0) \right] \tanh \left( \frac{1}{2} \beta \omega \right) + i \text{Im} \left[ \sigma_{12}(0) \right], \] (29)

which establishes a relationship between the initial conditions in the two bases, and is equivalent to equation (17). To understand the implications of the truncation, we expand the FG Hamiltonian for the excited state in the combined exciton–oscillator basis. Denoting the exciton states by \(|\pm\rangle\), the basis states of the problem are the tensor products of the electronic and the oscillator parts, that is \(|\pm\rangle \otimes \{|n\rangle\} = \{|\pm; 0\rangle, |\pm; 1\rangle, |\pm; 2\rangle, \ldots\}\). For the \(|+\rangle\) state, the transformed Hamiltonian is given by

\[ A = \begin{pmatrix}
\epsilon - J & \frac{1}{2} \hbar & \cdots \\
\frac{1}{2} \hbar & \omega + J + \epsilon & \sqrt{2} \hbar \\
\sqrt{2} \hbar & 2\omega - J + \epsilon & \sqrt{3} \hbar \\
\sqrt{3} \hbar & 3\omega + J + \epsilon & \sqrt{4} \hbar \\
\vdots & \vdots & \ddots 
\end{pmatrix}. \] (30)

The collective oscillator–exciton states associated to the state \(-\rangle\) can similarly be expressed in the \(|-\rangle \otimes \{|n\rangle\} \) basis. The total Hamiltonian in the FG basis is the direct sum of these two contributions: \( D = A \oplus B \). Upon the approximation of equation (20) we arrive at the following expression for \( A \):

\[ A \approx \begin{pmatrix}
\epsilon - J & \frac{1}{2} \hbar & \cdots \\
\frac{1}{2} \hbar & \omega + J + \epsilon & \sqrt{2} \hbar \\
\sqrt{2} \hbar & 2\omega + 3J + \epsilon & \sqrt{3} \hbar \\
\sqrt{3} \hbar & 3\omega + 5J + \epsilon & \sqrt{4} \hbar \\
\vdots & \vdots & \ddots 
\end{pmatrix}. \] (31)
The diagonal elements thus quickly diverge owing to the truncation of the parity operator. The validity of the theory is therefore limited to scenarios where no more than a few oscillator modes are populated. Given that the initial occupancy of the oscillator states is given by a Boltzmann factor \( n(\omega) = \frac{\exp (\beta \omega) - 1}{\exp (\beta \omega) + 1} \), where \( \beta = 1/k_B T \) is the inverse temperature, the theory is valid at low temperatures with respect to the oscillator energy \( (\omega > k_B T) \). Moreover, the electronic coupling needs to be small in comparison to the oscillator frequency \( (J \ll \omega) \) such that diagonal elements are sufficiently well approximated for the populated oscillator states. If the initial state is chosen such that \( \text{Im} [\sigma_{12}(0)] = 0 \), the FG dynamics are simplified to

\[
\sigma_{11}(t) = \frac{1}{2} + \text{Re} [\sigma_{12}(0)] \tanh \left( \frac{1}{2} \beta \omega \right),
\]

\[
\sigma_{12}(t) = \exp \left\{ \frac{(h/2)^2}{\omega^2 - 4 J^2} \Phi_s(\omega, J, t) + 2i J t \right\} \times \left\{ \frac{1}{2} - \sigma_{11}(0) \right\} \exp \left[ \frac{(h/2)^2 \Theta_s(\omega, J, t)}{\omega^2 - 4 J^2} \tanh \left( \frac{\beta \tilde{\omega}(t)}{2} \right) \right].
\]

A generalization of this result to multiple oscillator modes is as follows:

\[
\sigma_{11}(t) = \frac{1}{2} + \text{Re} [\sigma_{12}(0)] \prod_k \tanh \left( \frac{1}{2} \beta \omega_k \right),
\]

\[
\sigma_{12}(t) = \exp \left\{ \sum_k \frac{(h/2)^2}{\omega_k^2 - 4 J^2} \Phi_s(\omega_k, J, t) + 2i J t \right\} \left[ \frac{1}{2} - \sigma_{11}(0) \right] \times \left\{ \prod_q \left( \frac{1 - e^{-\beta \omega_q}}{1 + e^{-\beta \omega_q}} \right) \exp \left[ \sum_k \frac{\hbar^2}{4 \omega_k^2 - 4 J^2} \tanh \left( \frac{\beta \tilde{\omega}_k(t)}{2} \right) \right] \right\}.
\]

### 2.2.2. Approximated solution in the site basis.

The solutions presented in the previous section can equivalently be expressed in the site basis. The basis transformation needs to be applied before the trace over the oscillator mode is evaluated. The details of this calculation are presented in the supplementary information (available from stacks.iop.org/NJP/16/019502/mmedia). The final solution for a general initial state and a single oscillator mode are as follows. The evolution of the population is determined by

\[
\sigma_{11}(t) = \frac{1}{2} + \left[ \sigma_{11}(0) - \frac{1}{2} \right] \text{Re} \left\{ e^{2i J t} \exp \left[ \frac{\hbar^2}{4 \omega_+ \omega_-} \Phi_a(\omega, J, t) \right] \times \left( \frac{1 - e^{-\beta \omega}}{1 - e^{-\beta \tilde{\omega}(t)}} \right) \exp \left[ \frac{\hbar^2}{4 \omega_+ \omega_-} \Theta_a(\omega, J, t) \coth \left( \frac{1}{2} \beta \tilde{\omega}(t) \right) \right] \right\} \right\}

+ \text{Im} [\sigma_{12}(0)] \left\{ e^{2i J t} \exp \left[ \frac{\hbar^2}{4 \omega_+ \omega_-} \Phi_a(\omega, J, t) \right] \times \left( \frac{1 - e^{-\beta \omega}}{1 + e^{-\beta \tilde{\omega}(t)}} \right) \exp \left[ \frac{\hbar^2}{4 \omega_+ \omega_-} \Theta_a(\omega, J, t) \tanh \left( \frac{1}{2} \beta \tilde{\omega}(t) \right) \right] \right\}. \]
The real part of the coherence is given by

\[ \text{Re} [\sigma_{12}(t)] = \frac{1}{2} \text{Re} [\sigma_{12}(0)] \left\{ \exp \left[ \frac{\hbar^2}{2} \coth \left( \frac{1}{2} \beta \omega \right) \left( \frac{\cos (\omega_s t) - 1}{\omega_s^2} \right) \right] \right. \\
+ \exp \left[ \frac{\hbar^2}{2} \coth \left( \frac{1}{2} \beta \omega \right) \left( \frac{\cos (\omega_c t) - 1}{\omega_c^2} \right) \right] \right\} \\
+ \frac{1}{4} \tanh \left( \frac{1}{2} \beta \omega \right) \left\{ \exp \left[ \frac{\hbar^2}{2} \tanh \left( \frac{1}{2} \beta \omega \right) \left( \frac{\cos (\omega_s t) - 1}{\omega_s^2} \right) \right] \right. \\
- \exp \left[ \frac{\hbar^2}{2} \tanh \left( \frac{1}{2} \beta \omega \right) \left( \frac{\cos (\omega_c t) - 1}{\omega_c^2} \right) \right] \right\}, \] (37)

and the imaginary part is

\[ \text{Im} [\sigma_{12}(t)] = \left[ \frac{1}{2} - \sigma_{11}(0) \right] \text{Im} \left\{ e^{2iJt} \exp \left[ i \frac{\hbar^2}{4\omega_s \omega_0} \Phi_s(\omega, J, t) \right] \right. \\
\times \frac{1 - e^{-\beta \omega}}{1 + e^{-\beta \omega(t)}} \exp \left[ \frac{-\hbar^2}{4\omega_s \omega_0} \Theta_s(\omega, J, t) \coth \left( \frac{1}{2} \beta \tilde{\omega}(t) \right) \right] \} \\
+ \text{Im} [\sigma_{12}(0)] \text{Re} \left\{ e^{2iJt} \exp \left[ i \frac{\hbar^2}{4\omega_e \omega_0} \Phi_e(\omega, J, t) \right] \frac{1 - e^{-\beta \omega}}{1 - e^{-\beta \tilde{\omega}(t)}} \right. \\
\times \exp \left[ \frac{-\hbar^2}{4\omega_e \omega_0} \Theta_e(\omega, J, t) \coth \left( \frac{1}{2} \beta \tilde{\omega}(t) \right) \right] \} \right\}, \] (38)

where we have defined the following functions:

\[ \Phi_s(\omega, J, t) = -\Delta \omega t - \sin (\Delta \omega t) (\omega_s - \omega_0) \left[ \frac{\sin (\omega_s t)}{\omega_s} + \frac{\sin (\omega_c t)}{\omega_c} \right], \] (39)

\[ \Theta_s(\omega, J, t) = -\frac{\omega_s^2 + \omega_c^2}{\omega_s \omega_c} + [1 + \cos (\Delta \omega t)] (\omega_s - \omega_0) \left[ \frac{\cos (\omega_s t)}{\omega_s} - \frac{\cos (\omega_c t)}{\omega_c} \right]. \] (40)

2.3. Numerical results

2.3.1. Single mode oscillator, estimation of the eigenenergies. To gain a better understanding of the range of validity of the approximation introduced, in this section we consider the approximated and the exact eigenenergies of the system as \( \omega, J \) and \( \hbar \) are varied. Figure 1 is a plot of the first four pairs of eigenstates. The solid (dashed) lines represent the diagonalization of the exact (approximated) Hamiltonian. Both Hamiltonians are truncated at a large value of \( n \), such that addition of further states does not alter the depicted eigenstates. The plots illustrate that the approximations are improved as \( \omega/J \) is increased. The temperature and the oscillator frequency must satisfy the relation \( \omega > k_B T \) such that the high energy oscillator states remain unpopulated, rendering the crude estimation of their energy inconsequential. The theory may therefore be applied at room temperature if the energy of the oscillator is larger than 200 cm\(^{-1}\). In the context of electronic energy transfer, to model both the high and the low frequency vibrational modes, our theory can be applied alongside a more standard approach, such as Redfield theory. The low frequency part of the environmental fluctuation spectra can be
modelled via the Redfield tensor, whereas the high frequency contribution can be modelled via the present treatment.

2.4. Single mode oscillator, comparison of the dynamics with the brute force diagonalization

In this section we compare the dynamics of a dimer interacting with a single mode as predicted by the present analytical model with the results of a brute force calculation. The brute force method proceeds by truncating the exact Hamiltonian of the oscillator. The truncation level is increased until the dynamics of the dimer are converged. Provided that sufficient states are included, this method can in principle be applied to any set of \( \{\omega, J, h\} \). However, if over the course of the dynamics, the number of occupied oscillator states is large, this method becomes impractical.

We consider the parameters of figure 1(b), where the first few pairs of eigenenergies are reasonably well approximated, and present the dynamics of the site population as predicted by the two approaches for different values of the system–oscillator coupling. The agreement between the coherences computed via the two methods is similar to that of the populations and are therefore not shown. Figure 2 illustrates the population dynamics for four different values of the system–oscillator coupling \( h \). We observe excellent agreement for \( 2h \leq \omega \) and reasonable agreement for \( h < \omega \). For large values of the oscillator–system coupling \( h \), the dynamics involves large displacements \( [h/(2\omega)] \) of the oscillator from the initial Gibbs state.
This populates the high energy oscillator levels whose energies are crudely approximated. An equivalent explanation is that as $h$ becomes large, pairs of true eigenstates of opposite parity approach each other. Since the approximation involved an expansion of the parity operator in the FG-transformed Hamiltonian, pairs of eigenstates of the approximated Hamiltonian remain separated (as shown in figure 1) and the approximation fails to reproduce the correct behaviour in that region.

Note that although the numerical method becomes inefficient for multiple oscillator modes, our analytic solution can readily be applied to any finite number of modes.

### 2.4.1. Multi-mode oscillator at finite temperature

In this section we compute the evolution of the reduced density matrix in the site basis for a weakly coupled molecular dimer interacting with multiple oscillators. The computation of the dynamics via diagonalization of the exact Hamiltonian becomes quickly intractable as the number of oscillator modes is increased. This is where the usefulness of the present approach becomes apparent.

We consider a system of 70 oscillators where $\omega_n = \omega_0 + (\Delta \omega)n$, $\Delta \omega = 1 \text{ cm}^{-1}$, $\omega_0 = 30 \text{ cm}^{-1}$ and integer $n$. The oscillator couplings are assumed to take the form $h_k = C \omega_k e^{-0.05 \omega_k}$ where $C = 3$. The temperature is set to be 30 K or 20.8 cm$^{-1}$. We compute the dynamics over a narrow range of $J$, and for the reorganization energy of $E_R = 46 \text{ cm}^{-1}$ where reorganization energy is defined to be $E_R = \sum_k (h_k/2)^2/\omega_k$. Figure 3 illustrates the reduced density matrix in the site basis for the initial state $\sqrt{0.8}|e\rangle \otimes |g\rangle + \sqrt{0.2}|g\rangle \otimes |e\rangle$. The decoherence time is significantly shorter than the equilibration time of the site populations and is unaffected by small
Figure 3. Dynamics of the reduced density matrix in the site basis for the initial state $\sqrt{0.8}|e\rangle \otimes |g\rangle + \sqrt{0.2}|g\rangle \otimes |e\rangle$ with multiple oscillator modes. Interaction with multiple modes results in equilibration of the populations and the damping of the coherence.

variations in the electronic coupling. Electronic coupling influences the population equilibration time as expected, with larger coupling resulting in faster transfer.

3. Conclusion

We have presented the corrections to the results of Hossein-Nejad and Scholes [1] and have discussed the regimes of validity of the theory. The assumption of equation (20) has important consequences for the validity of the model that were discussed and explored in this paper. The comment of Lim et al [2] is valid as the incorrect results of Hossein-Nejad and Scholes [1] produced different behaviour for the two bath models. We have produced the correct results for the approximated method of Hossein-Nejad and Scholes [1] and analysed the validity of the approximation. While the parameter regime of the model is limited, it significantly simplifies computational complexity of analysing a multiple mode Hamiltonian in the region of its validity, thus supplying analytical intuition to the study of decoherence in complex open systems.

Molecular dimers coupled to high energy oscillator modes are of interest in a variety of systems; for instance, it has been shown that in certain light harvesting complexes high frequency vibrational modes activate the energy transfer pathways [8]. Since the energy of such modes is significantly larger than thermal energy, the high energy states remain unpopulated and only a few oscillator states participate in the dynamics. Under such circumstances the formalism presented in this paper can be applied to obtain the dynamics of the dimer as influenced by the high energy oscillator mode(s). In the context of electronic energy transfer, the theory can be used alongside more standard approaches, such as the Redfield theory, to incorporate both the low frequency environmental modes via the Redfield tensor, as well as the discrete high energy vibrational modes.

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Abstract. We study the dynamics of energy transfer and dephasing in a molecular dimer with degenerate energies interacting with an anti-correlated, collective vibrational bath. By diagonalizing the total Hamiltonian, we obtain an analytic expression for the dephasing rate as a function of temperature, resonance coupling, system–bath coupling and the spectrum of the bath. Eigenstates of the total Hamiltonian are identified as a natural basis set for studies of decoherence dynamics, and the study is motivated by observations of persistent coherence in two-dimensional (2D) photon echo experiments on photosynthetic light-harvesting proteins (Collini et al 2010 Nature 463 644–7). We find that, under the influence of a collective phonon bath, coherence survives longer in systems with weak electronic couplings, in agreement with observations of long-lasting coherence in weakly coupled multichromophoric systems.
1. Introduction

The energy of light absorbed by a molecule can be efficiently transferred to a nearby molecule by electronic energy transfer (EET), equivalently known as resonance energy transfer (RET) or Forster resonance energy transfer (FRET). Numerous applications and instances of EET are known. For example, EET is used in photosynthetic proteins, known as light-harvesting proteins, to increase the spectral and spatial cross-section for the capture of solar energy by reaction center proteins (photosystems). Most typically, EET is modeled as an incoherent process where excitation energy is first localized on a donor molecule and is subsequently transferred to an acceptor. The EET ‘hop’ is promoted by an electronic coupling matrix element $J$, which results in the characteristic $R^{-6}$ distance dependence of the Forster EET rate, under the assumption of a dipole–dipole electronic interaction.

There are several notable early theoretical studies that examined EET in cases where the weak coupling (electronic coupling) assumption does not apply and the dynamics are influenced by coherence. Chief among them is the generalized master equation (GME) approach of Kenkre and Knox [2] in which the transition rates are expressed in terms of a bath memory function. Application of this formalism to the standard model of linear exciton–phonon coupling captures both the wavelike and the diffusive aspects of exciton transport [3]. The distinct dynamics of transport in the weak and strong coupling regimes were also noted by Soules and Duke [4], who studied the energy transfer between localized electronic states in a crystal. The reduced density formalism of Redfield theory was first applied to molecular dimers by Wertheimer and Silbey [5], who critiqued the assumption of ultrafast (Markovian) correlations of the Haken–Strobel model [6, 7]. Jackson and Silbey subsequently applied Redfield theory with non-Markovian correlations to the molecular dimer and found the non-Markovian fluctuations in the site energies to be manifested in the dynamics and the line shapes [8]. An early theoretical study of the role of coherence in photosynthetic units was reported by Nedbal and Szoecs [9],
who investigated the motion of excitons in a photosynthetic unit using the Haken–Strobel model and estimated the coherence lifetime of the excitons.

In recent years, theoretical interest in this topic has re-emerged owing to the development of experimental tools that have revealed evidence of electronic coherence in EET [1], [10]–[17]. Stimulated by these new discoveries of more prevalent coherent EET than was previously envisaged, a number of new theoretical studies have been reported. The role of the environment in protecting quantum coherence has, in particular, been a subject of numerous studies [18]. Exciton delocalization together with pure dephasing induced by stochastic fluctuations of the environment has been demonstrated to improve the efficiency of quantum transport in multichromophoric systems [19]–[23]. Furthermore, bath-induced correlated fluctuations in the site energies are shown to counterbalance the dephasing processes [24]–[27]. Sharing of the bath modes in particular can generate such correlated fluctuations [28]. The mesoscopic nature of the phonon bath in such systems must also be accounted for, as it can cause qualitatively different dynamics than a macroscopic bath with a continuum of modes [29].

A key question is, what are the limitations of the available theoretical approaches in modeling the EET dynamics in biological systems? The Redfield equation [30]–[32], the GME [33] and the Lindblad equation [24, 34, 35] have been extensively applied in studies of EET. Redfield theory in its original form [36, 37] suffers from the limitation of secular approximation, which disentangles the evolution of the populations from the coherences, thus opening the possibility of erroneous insights regarding the interplay of EET and quantum coherence. Ishizaki and Fleming [31] have demonstrated that, even without the secular approximation, Redfield theory can only be applied when the reorganization energy of each chromophore is small in comparison with the electronic coupling. The second limitation of most master-type equations arises from a perturbation expansion that assumes the system–bath coupling to be small in comparison with electronic coupling. The validity of this assumption is questionable for biological systems, where the fluctuations induced in the site energies are of the same order as the electronic coupling between the pigments [27]. A common approach for non-weakly coupled systems is to reduce the strong coupling regime to the weakly coupled regime by a transformation method. The small-polaron transformation is a widely used example and it can be applied when the system–bath coupling is linear in the bath coordinates [38]. This technique has been employed in rigorous extensions of Forster–Dexter theory [39]–[41] and the GME [25, 29, 42].

In this paper, we specialize in a scenario where a dimer of identical molecules undergoes dephasing due to the coupling of electronic degrees of freedom to its vibrational modes. This case is of current experimental importance as the collective vibrational modes in multichromophoric systems are believed to play the role of a dephasing bath, influencing the dynamics of energy transfer. We strive to obtain an analytic solution for the dynamics of the dimer by reducing the dimer Hamiltonian to that of a single molecule, for which exact analytic solutions are known. The Foulton–Gouterman diagonalization recipe [43, 44] is employed to achieve this goal. The reduced dynamics of the system are subsequently obtained by applying multiple small-polaron transformations in an approach similar to the calculations of Reichman and Silbey [45] for single molecules. No assumptions regarding the relative size of the electronic and bath couplings have been introduced; the theory, therefore, is applicable in all regimes of coupling. To investigate the influence of coherence on EET, the dynamics of the off-diagonal, as well as the diagonal, elements of the reduced density matrix are studied. The analysis is restricted to the single exciton manifold of the dimer, in which the existence of site coherence...
implies the existence of non-local, quantum mechanical correlations (entanglement) between the sites [46]. The dynamical evolution of site entanglement is therefore also computed, and the timescale over which the sites are disentangled is investigated.

The main result of this paper is that the states which the decohering processes drive the system towards, known as the pointer states, are the most suitable basis set for studies of decoherence dynamics. We also demonstrate that an anti-correlated collective vibrational bath predicts longer coherence times for weakly coupled systems as opposed to strongly coupled ones. This result cannot be reproduced with an independent bath model and may be the key to understanding the persistent coherence observed in two-dimensional photon echo (2DPE) experiments among weakly coupled chromophores in light-harvesting antenna proteins.

Physical systems that may be adequately described by our model include dimers of organic molecules in the gas phase, where the ground and excited electronic states are known to exhibit different torsional motion along the symmetry axis of the molecules [47, 48]. The torsional degrees of freedom constitute a shared phonon bath that may be suitably described within the framework of the displaced harmonic oscillator model. The suitability of the present formalism in understanding the vibrationally resolved spectra of these dimers is the subject of our current investigation and will be discussed in a subsequent publication.

2. Dephasing in a two-level system

We begin by reviewing the dephasing process in a two-level system, modeled as two electronic surfaces harmonic in the nuclear coordinates and differing only in their respective equilibrium nuclear positions. The surfaces represent the states of a quantum subsystem, and the nuclear degrees of freedom are modeled as a harmonic oscillator bath. This so-called displaced harmonic oscillator model has been investigated extensively in the literature [49]–[53] and is described by the following Hamiltonian:

\[ H = \left[ \epsilon + \sum_k h_k (b_k + b_k^\dagger) \right] a^\dagger a + \sum_k \omega_k b_k^\dagger b_k, \]  

(1)

where \( \epsilon \) is the energy splitting between the electronic ground and excited states, \( \omega_k \) and \( h_k \) are the frequency and the electron–phonon coupling for mode \( k \) of the bath, respectively, \( \{ a^\dagger, a \} \) are the excitonic raising and lowering operators and \( \{ b_k^\dagger, b_k \} \) are the bosonic operators for mode \( k \) of the bath. Following the approach of Reichman and Silbey [45], we compute the dynamical evolution of the subsystem by solving for the reduced density operator. The state of the subsystem and bath is assumed to be initially separable:

\[ \rho(0) = \sigma(0) \rho_b, \]

(2)

where \( \sigma(t) \) is the density operator of the subsystem and \( \rho_b \) is the density operator of the bath as governed by a thermal distribution,

\[ \rho_b = \frac{e^{-\beta H_b}}{\text{Tr}_b[\rho_b \rho(t)]}. \]

(3)

The evolution of \( \sigma(t) \) is determined by

\[ \sigma(t) = \text{Tr}_b [\rho_b e^{-iHt} \sigma(0) e^{iHt}], \]

(4)

where \( \text{Tr}_b \) indicates an ensemble average over the bath modes, and \( H_b = \sum_k \omega_k b_k^\dagger b_k \). By exponentiating the Hamiltonian of (1), it is straightforward to show that the diagonal elements
of the reduced density operator remain stationary. The evolution of the off-diagonal elements is determined by

$$\sigma_{12}(t) = \sigma_{12}(0)e^{-i\Delta t} \text{Tr}_b[e^{-i(H_b + \Delta t)e^{-iH_b t}}],$$

where $\Delta = \sum_k h_k(b_k + b_k^\dagger)$. The Hamiltonian can be diagonalized by applying a small-polaron transformation [38, 54]. Upon this transformation we obtain

$$\sigma_{12}(t) = \sigma_{12}(0)e^{-i\bar{\epsilon} t} \text{Tr}_b[\rho_b M^\dagger(t)M],$$

where $M$ is the unitary operator that brings the Hamiltonian to the diagonal form and $\bar{\epsilon}$ is the polaron shift,

$$M(t) = \exp \left[ \sum_k \frac{h_k}{\omega_k}(b_k^\dagger e^{i\omega_k t} - b_k e^{-i\omega_k t}) \right];$$

$$\bar{\epsilon} = \epsilon - \sum_k \frac{h_k^2}{\omega_k}.$$

Using the expression for the thermal expectation value of bosonic operators [55], we arrive at the following expression for the time evolution of coherence,

$$\sigma_{12}(t) = \sigma_{12}(0)e^{-\gamma(t)}e^{-i\varphi(t)},$$

where $\gamma(t)$ and $\varphi(t)$ are the time-dependent decay function and phase function, respectively,

$$\gamma(t) = \sum_k (1 - \cos \omega_k t) \coth (\beta \omega_k / 2)(h_k^2 / \omega_k)\epsilon^2;$$

$$\varphi(t) = \bar{\epsilon} t - \sum_k (h_k^2 / \omega_k)\epsilon^2 \sin (\omega_k t).$$

Before discussing the origin of each term and the significance of time-dependent decay, we compare this exact solution with the approximate solution obtained from the Markovian Lindblad equation. The evolution of the reduced density matrix as governed by the Lindblad master equation is given by

$$\frac{\partial \sigma}{\partial t} = -\sum_m c \left( K_m^2 \sigma + \sigma K_m^2 - 2K_m \sigma K_m \right),$$

where $K_m$ are the Lindblad operators and the unitary part of the evolution has been dropped. The system–bath interaction is assumed to be of the form $H_{\text{int}} = \sum_n \Phi_n K_n$, where $\Phi_n$ are the bath operators and $K_n$ are the system operators. The interaction is assumed to be ultrafast (Markovian bath) such that the reservoir correlation function can be approximated as [56]

$$C_{mn}(t) = \langle \Phi_m(t)\Phi_n(0) \rangle_\mathcal{R} \approx \delta(t)\delta_{m,n}c.$$  

For the dephasing vibrational bath under consideration, $\Phi$ and $K$ can be identified as

$$\Phi = \sum_k h_k(b_k^\dagger + b_k),$$

$$K = a^\dagger a.$$ 

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The Lindblad equation (12) can now be solved straightforwardly. As before, the populations remain stationary while the coherences decay with time. That is,
\[ \sigma_{12}(t) = \sigma_{12}(0) e^{-ct}, \]
(16)
\[ c = \sum_k h_{1k}^2/\omega_k \coth(\beta\omega_k/2). \]
(17)

Equation (17) can be compared directly to the exact decay rate of (10). In both cases, the total dephasing rate is a summation of contributions from different bath modes, where the thermal factor \( \coth(\beta\omega_k/2) \) ensures that dephasing is dominated by lower frequency modes. In (10), each bath mode contributes an oscillating term to the dephasing rate. These oscillations are characteristic of non-Markovian dynamics and do not appear in the Lindblad solution. For a macroscopic bath with a continuum of modes, the different oscillating contributions interfere destructively and the dynamics will be dominated by the thermal factor. For a mesoscopic bath with a finite, discrete number of modes, the oscillations lead to reversible coherence dynamics which cannot occur in a macroscopic bath. This is a general result we shall revisit in the next section, where we study the coherence dynamics of a dimer.

The exact solution of (10) reduces to the Lindblad solution in the \( \omega_k \to 0 \) limit. Lindblad theory predicts the correct thermal factor but, rather curiously, the incorrect time dependence. The assumption of ultrafast bath correlations has led to oversimplifications in the dynamics of dephasing; in actuality, coherences do not obey a simple exponential decay, but rather each bath mode contributes a time-dependent term to the overall decay rate. For a mesoscopic bath, the correct dynamics can only be obtained if the interference between these time-dependent contributions is properly accounted for.

3. Dephasing in a dimer

3.1. Exact solution

We now extend the methodology of the previous section to study the dephasing dynamics of a dimer. The displaced harmonic oscillator model of (1) can straightforwardly be extended to the case of coupled two-level systems [54, 57]:
\[ H = -J (a_1^\dagger a_2 + a_2^\dagger a_1) + \sum_{i=1}^2 a_i^\dagger a_i \left[ \epsilon + \frac{1}{2} \sum_k h_{ik}(b_k^\dagger + b_k) \right] + \sum_k \omega_k b_k^\dagger b_k, \]
(18)
where \( J \) is the electronic coupling and \( \{a_i^\dagger, a_i\} \) are the raising and lowering operators for the \( i \)th molecule. The exciton–phonon couplings of the two molecules satisfy the relation \( h_{1k} = -h_{2k} \), because the fluctuations are specified as stretching vibrational modes in the coordinate system of the two interacting molecules. For example, if the dephasing bath is an interchromophore vibrational mode of the dimer, then the second-quantized bath coordinate \( x \propto (b^\dagger + b) \) quantifies the separation between the molecules. We next write the Hamiltonian in the form of a matrix in the site basis:
\[ H = \begin{pmatrix} H_b + \epsilon + \frac{1}{2} \Delta & -J \\ -J & H_b + \epsilon - \frac{1}{2} \Delta \end{pmatrix}, \]
(19)
where $\Delta = \sum_k h_{1k}(b_k^+ + b_k)$. The dimer Hamiltonian can be diagonalized by applying the following Fulton–Gouterman transformation [43, 44, 58]

$$V = \frac{1}{\sqrt{2}} \left( - \frac{1}{\prod_k(-1)^{b_k^+ b_k}} \prod_k(-1)^{b_k^+ b_k} \right).$$  

(20)

The diagonalized Hamiltonian $\tilde{H} = VH\hat{V}^\dagger$ is found to be

$$\tilde{H} = \begin{pmatrix} H_b + \frac{1}{2} \Delta - J \prod_k(-1)^{b_k^+ b_k} + \epsilon & 0 \\ 0 & H_b - \frac{1}{2} \Delta + J \prod_k(-1)^{b_k^+ b_k} + \epsilon \end{pmatrix}. \tag{21}$$

The eigenstates of the diagonalized Hamiltonian are unaffected by the dephasing bath and, in the language of Zurek, constitute the pointer basis of the system [59]. The pointer states are the excitonic eigenstates dressed by the phonon bath, and they are reduced to the unperturbed excitonic eigenstates in the limit of vanishing exciton–phonon coupling. A system in the superposition of the pointer states is dynamically driven to a statistical mixture of the pointer states with no coherence between them. The rate at which superpositions of the pointer states decohere is the rate of reduction of the wave-packet [60], and this can be computed by considering the evolution of the off-diagonal elements of the reduced density matrix in the pointer basis. To investigate this decoherence, we proceed as before and recall (4),

$$\sigma(t) = \text{Tr}_b[\rho_b e^{-i\tilde{H}t} \sigma(0)e^{i\tilde{H}t}]. \tag{22}$$

By substituting (21) into (22) and applying multiple polaron transformations, it is straightforward but tedious to show that the evolution of coherence is determined by the following exact equation:

$$\tilde{\sigma}_{12}(t) = \tilde{\sigma}_{12}(0)e^{-i\epsilon_p t} \text{Tr}_b \left\{ \rho_b \exp \left[ - \sum_k \frac{h_k}{\omega_k} (b_k^+ - b_k) \right] \exp \left[ -i(H_b - J U^\dagger e^{i\pi \sum_k b_k^+ b_k} U)t \right] \right\} \times \exp \left[ \sum_k \frac{h_k}{\omega_k} (b_k^+ - b_k) \right] \exp \left[ i(H_b + J U e^{i\pi \sum_k b_k^+ b_k} U^\dagger)t \right], \tag{23}$$

where $\epsilon_p$ is the polaron energy and $U = \exp \left[ - \sum_k \frac{h_k}{2\omega_k}(b_k^+ - b_k) \right]$. We now simplify (23) by noting that

$$U e^{i\pi \sum_k b_k^+ b_k} U^\dagger = \exp \left[ \sum_k \frac{i\phi_k^2 \pi}{2} \right] \exp \left[ i\pi \sum_k (b_k^+ b_k + \phi_k(b_k^+ + b_k)) \right], \tag{24}$$

where $\phi_k = h_k/2\omega_k$. At this point, we introduce the only approximation in our model by writing the exponential of (24) as a normal ordered expansion. Keeping all terms that are linear in both the phonon operators and the exciton–phonon coupling [61], as well as all terms linear in the boson number operator $b_k^+ b_k$, we arrive at the following approximation:

$$\exp \left[ i\pi \left( b_k^+ b_k + \phi_k(b_k^+ + b_k) \right) \right] \simeq 1 - 2 \left( b_k^+ b_k + \phi_k(b_k^+ + b_k) \right). \tag{25}$$

The approximation demands $h_k^2/(4\omega_k^2) < 1$ and is satisfied if the Huang–Rhys factors associated with the bath modes are sufficiently small. Substituting (25) into (23) and applying multiple...
small-polaron transformations (see appendix A), we arrive at the following expression for the evolution of coherence,

$$\tilde{\sigma}_{12}(t) = \tilde{\sigma}_{12}(0)e^{-ie't} \text{Tr}_b \left\{ \rho_b \exp \left[ -\sum_k \alpha_k (b_k^\dagger - b_k) \right] \exp \left[ -2iJ \sum_k A_kb_k^\dagger b_k t \right] \right\} \times \exp \left[ \sum_k \alpha_k^* \left( b_k^\dagger(t) - b_k(t) \right) \right] \exp \left[ -2iJ \sum_k A_kb_k^\dagger b_k t \right], \quad (26)$$

where $\epsilon'$, $\alpha_k$ and $A_k$ are defined in appendix A. The exponents in (26) only contain terms that are linear or quadratic in the bath operators. Standard expressions involving the thermal expectation value of bosonic operators can therefore be applied to compute the trace over the reservoir [55]. To perform this task, we first demonstrate that for suitable values of $\theta_k$, $\eta_k$ and $\psi_k$, (26) can be recast as (see appendix B)

$$\tilde{\sigma}_{12}(t) = \tilde{\sigma}_{12}(0) \exp \left[ \sum_k \psi_k(t) \right] \text{Tr}_b \left\{ \rho_b \exp \left[ \sum_k (\eta_kb_k + \theta_kb_k^\dagger) \right] \exp \left[ 2\sum_k C_kb_k^\dagger b_k \right] \right\}. \quad (27)$$

The trace over the bath in (27) can be evaluated straightforwardly. We arrive at the following final expressions for the evolution of coherence,

$$\tilde{\sigma}_{12}(t) = \tilde{\sigma}_{12}(0)e^{-\gamma_d(t)}e^{-i\varphi_d(t)}, \quad (28)$$

where the decay function $\gamma_d(t)$ and the phase function $\varphi_d(t)$ are defined as

$$\gamma_d(t) = -\text{Re} \sum_k \left\{ \mu_k(t) + \ln \left[ \frac{1 - e^{-\beta\omega_k}}{1 - e^{-\beta\omega_k} e^{2C_k}} \right] + \coth (\beta\omega_k/2 - C_k) \right\}, \quad (29)$$

$$\varphi_d(t) = -\text{Im} \sum_k \left\{ \mu_k(t) + \ln \left[ \frac{1 - e^{-\beta\omega_k}}{1 - e^{-\beta\omega_k} e^{2C_k}} \right] + \coth (\beta\omega_k/2 - C_k) \right\}. \quad (30)$$

The parameters appearing in (29) and (30) are defined as follows:

$$\mu_k(t) = -i \left[ \frac{\hbar_k^2}{\omega_k} - \frac{\hbar_k'^2}{\omega_k - 2J A_k} + \frac{\hbar_k'^2}{\omega_k + 2J A_k} - 2A_kJ \right] t + \psi_k(t), \quad (31)$$

$$h_k' = -2J A_k \phi_k, \quad (32)$$

$$\phi_k = \frac{h_k}{2\omega_k}, \quad (33)$$

$$A_k = e^{i\pi \phi_k^2/2}, \quad (34)$$

$$\psi_k(t) \simeq \frac{1}{2} \alpha_k^* (s_{1k} e^{-i\omega_k t} - s_{2k} e^{i\omega_k t}), \quad (35)$$

$$\alpha_k = \frac{h_k}{\omega_k} + \left[ \frac{\hbar_k'}{\omega_k + 2J A_k} \right]^* - \frac{\hbar_k'}{\omega_k - 2J A_k}, \quad (36)$$

$$s_{1k} = -\alpha_k - \frac{G_k}{C_k} (e^{-C_k} - 1 + C_k), \quad (37)$$

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The evolution of the density matrix in the pointer basis is therefore of the form

\[
\tilde{\sigma}(t) = \begin{pmatrix}
0 & 0 & 0 & 0 \\
0 & \tilde{\sigma}_{11}(0) & \tilde{\sigma}_{12}(0)e^{-\gamma_d(t)} & \epsilon^{-i\varphi(t)} \\
0 & \bar{\sigma}_{21}(0)e^{-\gamma_d(t)} & \tilde{\sigma}_{22}(0) & 0 \\
0 & 0 & 0 & 0
\end{pmatrix}.
\] (42)

In the limit of vanishingly small resonance coupling, (29) approaches the single-molecule dephasing rate of (10). In this limit the site basis is also the eigenstate basis, and the decay of coherence occurs at a rate independent of the electronic coupling. Figure 1(a) is a plot of \(\gamma_d(t)\) versus time for different electronic couplings for a mesoscopic Ohmic bath. The dephasing rate is substantially increased with increasing resonance coupling. This explains why strongly coupled chromophores dephase faster [14] than weakly coupled systems [10, 12], and it suggests that long-lasting coherences are more likely to be observed in weakly coupled systems than strongly coupled molecules in an assembly. Figures 1(b) and (c) are the corresponding plots for the off-diagonal element. For an electronic coupling of 4 cm\(^{-1}\) and a bath reorganization energy of 13.8 cm\(^{-1}\), the decoherence time is found to be 60 fs at 77 K, decreasing to 20 fs at 300 K. Equation (42) can be re-expressed in the site basis,

\[
\sigma_{11}(t) \simeq \frac{1}{2} - \text{Re}[\tilde{\sigma}_{12}(0)e^{-\gamma_d(t)} \cos \varphi_d(t)],
\] (43)

\[
\sigma_{12}(t) = \frac{1}{2}[\tilde{\sigma}_{11}(0) - \tilde{\sigma}_{22}(0)] + i\text{Im}[\tilde{\sigma}_{12}(0)e^{-\gamma_d(t)} \sin \varphi_d(t)],
\] (44)

where the initial conditions in the two basis are related via the following equations:

\[
\tilde{\sigma}_{11}(0) = \frac{1}{2} + \text{Re}[\sigma_{12}(0)],
\] (45)

\[
\tilde{\sigma}_{12}(0) = \frac{1}{2}[\sigma_{22}(0) - \sigma_{11}(0)] + i\text{Im}[\sigma_{12}(0)].
\] (46)

An initial imbalance of populations in the pointer basis is therefore manifested as a persisting site-coherence. It is furthermore evident that pointer-basis decoherence drives the population towards the acceptor site. For larger values of \(\gamma_d(t)\), steady-state populations are more rapidly established; large electronic coupling results in rapid decoherence and consequently fast transport.

### 3.2. The Lindblad solution

A direct consequence of ultrafast bath correlations is that the electronic part of the Hamiltonian does not influence the relaxation of the system and the loss of coherence occurs at a rate...
Figure 1. (a) Coherence decay function $\gamma_d(t)$ versus time for different values of the resonance coupling $J$ (cm$^{-1}$). In the monomer limit where $J \to 0$, the decoherence rate approaches the single-molecule dephasing rate of equation (10). The ratio of the electronic coupling to the bath reorganization energy is 0.29 ($J = 4$ cm$^{-1}$), 0.22 ($J = 3$ cm$^{-1}$) and 0.14 ($J = 2$ cm$^{-1}$). (b) Real part of the off-diagonal density matrix in the pointer basis as governed by $\text{Re}[\sigma_{12}(t)] = \text{Re}[\sigma_{12}(0)]e^{-\gamma_d(t)}\cos[\varphi_d(t)]$. (c) Magnitude of the off-diagonal density element as a function of time, $|\sigma_{12}(t)| = |\sigma_{12}(0)|e^{-\gamma_d(t)}$.

independent of the electronic coupling. For a shared vibrational bath, the Lindblad equation for a dimer is given by

$$\frac{\partial \sigma}{\partial t} = -\sum_{m=1}^{2} c_{mm} \left( [a_m^+ a_m a_m^+ a_m, \sigma]_+ - 2a_m^+ a_m \sigma a_m^+ a_m \right) $$

$$ - (c_{12} + c_{21}) \left( [a_1^+ a_1 a_2^+ a_2, \sigma]_+ - a_1^+ a_2 \sigma a_2 a_1^+ a_1 - a_1 a_1^+ a_2 a_2^+ \right),$$

(47)
where $c_{nm}$ is the dephasing rate due to bath correlations at sites $m$ and $n$; $c_{mn} = \int_0^\infty \text{d}t C_{mn}(t) \delta(t)$ and $C_{mn}(t) = \langle \Phi_m(t) \Phi_n(0) \rangle_R$. The evolution of the reduced density matrix in the single excitation manifold in the site basis is found to be

$$
\sigma(t) = \begin{pmatrix}
0 & 0 & 0 & 0 \\
0 & \sigma_{11}(0) & \sigma_{12}(0)e^{-\Gamma t} & 0 \\
0 & \sigma_{21}(0)e^{-\Gamma t} & \sigma_{22}(0) & 0 \\
0 & 0 & 0 & 0
\end{pmatrix},
$$

(48)

where $\Gamma = c_{11} + c_{22} - c_{12} - c_{21}$. If the molecules are coupled identically to the bath, $c_{mn} = c$ for all $m$ and $n$, and $\Gamma = 0$. If the couplings are equal in magnitude but opposite in sign, $c_{11} = c_{22} = c$ and $c_{12} = c_{21} = -c$, and we obtain $\Gamma = 4c$, where $c$ is the single-molecule dephasing rate of (17). The general conclusion that coherences in the coupled system decay faster is in agreement with the findings of the previous section. However, unlike the exact solution, the Lindblad equation predicts the site basis to be the pointer basis of the system, a result that can only be true in the weak coupling limit. It therefore appears that the assumption of ultrafast reservoir correlations has led to independence of the dephasing rate on the resonance interaction. The theory fails to take into account the formation of delocalized eigenstates and makes incorrect qualitative predictions regarding population transfer and dephasing dynamics.

### 4. Numerical results and discussion

We now use the analytic solutions obtained in the previous section to compute the reduced dynamics of the density operator in the site basis for two different initial states: a localized and a coherent superposition state. The loss of coherence between the sites is monitored by evaluating the entanglement between the two molecules. Since the Hilbert space of the problem is restricted to the single excitation manifold, entanglement can be thought of as a normalized measure of site coherence [46]. Wootters’ concurrence has been used as a measure of bi-partite entanglement [62]. Concurrence is an entanglement monotone defined by the equation $C(\rho) = \max(0, \sqrt{\lambda_1} - \sqrt{\lambda_2} - \sqrt{\lambda_3} - \sqrt{\lambda_4})$, where $\lambda_i$ are the eigenvalues of $\rho = \rho(\sigma_y \otimes \sigma_y)\rho^*(\sigma_y \otimes \sigma_y)$, $\rho$ is the density matrix of the bipartite system and $\sigma_y$ is the Pauli $y$-matrix. The bath is assumed to contain a mesoscopic number of modes ($\sim 100$) with an Ohmic distribution: that is, $h_k = A\omega_k e^{-B\omega_k}$, where $A$ and $B$ are arbitrary constants (see figure 2). Decoherence dynamics...
are dominated by lower frequency modes of the bath, whose energy is of the order of $k_B T$. It is therefore safe to restrict the bath spectrum to lower frequencies (e.g. by inserting a cut-off frequency), as one obtains the same qualitative picture as long as the bath is quasi-continuous, independent of the details of the spectrum.

### 4.1. Population dynamics

The upper panel in figure 3 is a plot of the donor population versus time. The initial state is localized on a site in figure 3(a) and is a coherent superposition of localized states in figure 3(b). The coherences in the pointer basis decay at a rate determined by (29), which leads to the transfer of excitation in the site basis (the populations in the pointer basis remain unchanged). The rate of population transfer is sensitive to the magnitude of the electronic coupling; in general, larger coupling gives rise to faster transfer (not shown in the figure). The degeneracy of the monomer energies ensures that, after the transfer process is complete, the donor and acceptor states are equally populated. At low temperatures, the excitation can oscillate back and forth between the sites. In figure 3(b), the system begins in the superposition state $\frac{1}{\sqrt{5}}|a\rangle + \frac{2}{\sqrt{5}}|d\rangle$, where $|d\rangle$ and $|a\rangle$ indicate localized donor and acceptor states, respectively. The initial donor population is therefore less than unity, but the transfer dynamics are otherwise identical to figure 3(a). Initial site-coherences do not influence the transfer dynamics when the site energies are degenerate.

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4.2. Dephasing dynamics in the site basis

Dephasing in the site basis can be investigated by computing the evolution of the site entanglement. The lower panel in figure 3 shows plots in entanglement versus time for an initially localized state (figure 3(c)) and a coherent superposition state (figure 3(d)). A localized state is a superposition of the eigenstates of the system and therefore has a large coherence in the pointer basis. Coherences in the pointer basis decay at a rate determined by $\gamma_d(t)$, and this leads to population transfer and damped oscillatory entanglement. Entanglement reaches a maximum once coherent population transfer has completely delocalized the excitation between the two molecules. At low temperatures (or for a few participating bath modes), the transfer dynamics is dominated by non-Markovian oscillations. Coherent shuffling of excitation back and forth between the donor and the acceptor leads to oscillations in entanglement; the entanglement maxima in figure 3(c) correspond to instances when the donor population in figure 3(a) is exactly 0.

At high temperatures (or for a large number of participating bath modes), coherent oscillations are suppressed, and entanglement reaches a maximum following the initial delocalization but decays rapidly afterwards as the system evolves to a maximally mixed state.

Figure 3(d) shows the entanglement dynamics for the superposition state $\frac{1}{\sqrt{5}}(|a\rangle + 2|d\rangle)$. At first glance it might appear surprising that the superposition state can maintain a finite entanglement indefinitely. This can be understood by recalling that decoherence prevents superpositions of the preferred basis states from persisting. The dynamics will therefore take any superposition state to a mixture of the pointer states. The pointer states are robust against further decoherence and are least affected by the environment [59]. Now, if the pointer states of the system are delocalized and have finite entanglement, the system can, in principle, maintain this entanglement. This result is a direct consequence of the purely dephasing nature of the system–bath interaction. In reality, the single exciton state has a finite lifetime due to long-range energy transfer among light-harvesting proteins, trapping at the reaction center or spontaneous emission, which in a more realistic model must be accounted for. The distinct dynamics of localized and delocalized states can be further understood by recalling that, according to (44), an initial imbalance of populations in the pointer basis is manifested as a persisting coherence in the site basis, that is

$$\sigma_{12}(t \to \infty) = \frac{1}{2}[(\bar{\sigma}_{11}(0) - \bar{\sigma}_{22}(0)].$$

(49)

For a localized initial state, the pointer states are equally populated, that is $\bar{\sigma}_{11}(0) = \bar{\sigma}_{22}(0) = 0.5$; a localized state therefore loses all site-coherence in the $t \to \infty$ limit. A delocalized state, on the other hand, is an unequal superposition of pointer states and can maintain a finite site-coherence indefinitely.

In summary, in a molecular dimer with an initial imbalance of pointer state populations, two distinct disentanglement timescales may be identified: (i) $\tau_C$, the time over which oscillations in concurrence die out; (ii) $\tau_1$, the lifetime of the single exciton state. $\tau_C$ is the coherence lifetime in the pointer basis. Given that $\tau_1 \gg \tau_C$, sites can maintain a finite entanglement, due to long-range electronic interactions, long after all pointer basis coherence has vanished. For an assembly of molecules with small electronic couplings, this finite asymptotic entanglement is likely to be very small. It is therefore safe to conclude that $\tau_C$ is a more realistic measure of disentanglement time in weakly coupled multichromophoric systems with long exciton lifetimes. Viewed in this light, pointer basis coherence and entanglement decay on the same timescale, and an observation of one is a necessary and sufficient condition for existence of the other.

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4.3. Comparison with other treatments

In this section, we present a comparison of the present formalism with other treatments of excitation transfer. We shall focus on the following theories: (i) Kenkre–Knox formalism [2, 3], (ii) the theory of Kimura–Kakitani [33], (iii) Grover–Silbey theory [61] and (iv) the treatment of Jang [63].

Kenkre and Knox develop a non-Markovian theory of population transfer where the population dynamics are governed by a convolution integral involving a time-dependent memory function. Population transfer is found to be reversible at a microscopic level, and the ‘onset of irreversibility’ is argued to arise from the equal weight macroscopic summation, carried out over all microscopic modes of the bath. In this work, we have demonstrated that this onset of irreversibility is also the origin of dephasing and that decoherence occurs when a quasi-continuum of modes ensures the destructive interference of phases. Furthermore, Kenkre observes the cross-over between the purely coherent and the purely diffusive aspects of transport, by assuming different forms of the memory function: a vanishing memory time recovers Forster–Dexter theory, infinite memory results in wavelike coherent transfer, and a finite memory gives rise to an intermediate regime of damped oscillatory populations. These limits can also be observed in our theory without making explicit assumptions regarding the bath memory function: the bath memory is entirely determined by the temperature, the spectrum of the bath and the relative size of the exciton–phonon coupling to the electronic coupling. Figure 3(a) therefore demonstrates the Forster–Dexter limit of excitation transfer at 300 K and a combination of diffusive and coherent motion at 77 K.

The theory of Kimura and Kakitani is an extension of the Kenkre and Knox formalism, in which, by assuming a finite bath memory, analytic expressions regarding transfer rates in different coupling regimes are obtained. Our treatment shows that any assumption regarding the nature of the bath correlation is reflected directly in the dynamics of dephasing. The assumption of a time-independent decay rate for the bath memory can, at best, be valid for a quasi-continuum of modes, as the dynamics of bath correlations are inherently oscillatory at a microscopic level. Given the nature of the bath, our treatment effectively allows a calculation of the bath memory function, rendering explicit assumptions regarding the memory time obsolete.

The Grover–Silbey theory of exciton migration obtains approximate expressions for the time-dependent hopping probability with the aid of cumulant expansions. The approximations of this theory are similar to ours: the quadratic terms in the phonon operators have been neglected, analogous to (25), making the theory exact in the limit of vanishing exciton–phonon interactions. For a bath with finite memory, we find the qualitative dynamics of population transfer to be in agreement with our findings.

Unlike the Kenkre–Knox and Grover–Silbey theories, Jang’s formalism allows the computation of population dynamics for coherent initial conditions. One interesting observation of Jang is that, for a super-Ohmic bath, the two states \((|d⟩ + |a⟩)/\sqrt{2}\) and \((|a⟩ − |d⟩)/\sqrt{2}\) have distinct population dynamics, provided that the electronic energies are non-degenerate. Our theory is restricted to degenerate energies and predicts no dependency of the population dynamics on the initial site-coherences. We therefore conclude that, as far as degenerate dimers are concerned, the energy transfer process is not influenced by the initial site-coherences.

The above theories focus solely on the transfer dynamics where the site basis is the natural basis of choice. The issue of selecting the right basis is less trivial in calculations of dephasing,
as the localized states or the bare excitonic eigenstates all undergo decoherence. We have argued in the present paper that the robustness of Zurek’s pointer states to dephasing makes them the most natural choice for studies of decoherence.

5. Conclusion

We have presented an analytic solution to the displaced harmonic oscillator Hamiltonian for a resonantly coupled donor–acceptor pair, valid to second order with respect to fluctuating displacements about the equilibrium vibrational position. We have identified Zurek’s pointer states as the natural basis for the study of decoherence dynamics, and have motivated this study by speculating that the coherences observed in the 2DPE experiments can be explained in terms of the pointer basis dynamics. Several features of our model were designed to capture the properties of multichromophoric biological systems in which persistent coherence has been observed: (i) molecular dimers are the building blocks of light-harvesting antenna proteins, (ii) collective vibrational modes are believed to play the role of a dephasing bath, and mode sharing is suggested to be the origin of persistent coherence in such systems and (iii) no assumptions regarding the relative size of the electronic and system–bath coupling were made, as the fluctuations in the diagonal energies in these systems are of the same order as the off-diagonal couplings.

One of the main results of this work is that, for an anti-correlated shared bath, coherence survives longer in weakly coupled systems than strongly coupled ones. This insight is in agreement with observations of coherence in 2DPE experiments and cannot be reproduced with an independent bath model. If each molecule were assumed to be coupled to its own vibrational bath, the opposite would be observed and coherence would decay faster as the ratio of the electronic to system–bath coupling is decreased.

Specific examples of physical systems that may quantitatively be described by our model are phenyl-substituted amines in the gas phase, where the ground and excited electronic states are known to exhibit different torsional motion along the nitrogen inversion coordinate [47, 48]. The displaced harmonic oscillator model with a shared (torsional) phonon bath might therefore be applicable to studying the coherence dynamics as well as the vibrationally resolved spectra of these dimers. This is the subject of our current investigation.

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Appendix A. Derivation of equation (26)

We recall (24),

\[ U e^{i \pi \sum \Delta \varepsilon_k b_k b_k^\dagger} U^\dagger = \exp \left[ \sum_k \frac{i \phi_k^2 \pi}{2} \right] \exp \left[ i \pi \sum_k \left( b_k^\dagger b_k + \phi (b_k^\dagger + b_k) \right) \right], \]  

(A.1)
and expand the exponential to first order:

\[ e^{i \pi (b^\dagger_k b_k + \phi_k (b^\dagger_k + b_k))} \simeq 1 - 2 \left( b^\dagger_k b_k + \phi_k (b^\dagger_k + b_k) \right). \]  
(A.2)

The off-diagonal term (23) now has a contribution from the exponential,

\[ \exp \left[ i (H_b + JU e^{i \pi \sum_k b^\dagger_k b_k} U^\dagger) t \right] = \exp \left[ i \sum_k A_k J t \right] \exp \left[ i \sum_k \left( \omega_{1k} b^\dagger_k b_k + \frac{1}{2} \epsilon \right) \right] \exp \left[ i \sum_k \left( \omega_{1k} b^\dagger_k b_k + \frac{1}{2} \epsilon \right) \right], \]  

where \( A_k = e^{i \pi \phi_k^2 / 2}, \) \( \omega_{1k} = \omega_k - 2J A_k \) and \( \epsilon_k = -2J A_k \phi_k. \) The linear term in (A.3) can be removed by applying the small-polaron transform,

\[ F \exp \left[ i \left( \omega_{1k} b^\dagger_k b_k + \frac{1}{2} \epsilon \right) \right] F^\dagger = e^{i \epsilon_f t} e^{i \sum_k \omega_{1k} b^\dagger_k b_k t}, \]  
(A.3)

where

\[ F = \exp \left[ \sum_k e^{i \omega_{1k} k / \epsilon} (b^\dagger_k - b_k) \right], \]  
(A.4)

\[ \epsilon_f = \sum_k \frac{\omega_{1k}^2}{\omega_{1k}}. \]  
(A.5)

We therefore obtain

\[ \exp \left[ i (H_b + JU e^{i \pi \sum_k b^\dagger_k b_k} U^\dagger) t \right] = e^{i \sum_k A_k J t} e^{i \epsilon_f t} F^\dagger e^{i \sum_k \omega_{1k} b^\dagger_k b_k t} F. \]  
(A.6)

Similarly, one can play the same game with the first two exponentials of the off-diagonal term. We find

\[ \exp \left[ -i (H_b - JU^\dagger e^{i \pi \sum_k b^\dagger_k b_k} U) t \right] = e^{i \sum_k A_k J t} e^{-i \epsilon_k t} K^\dagger e^{-i \sum_k \omega_{2k} b^\dagger_k b_k t} K, \]  
(A.7)

where

\[ K = \exp \left[ \sum_k e^{i \omega_{2k} k / \epsilon} (b^\dagger_k - b_k) \right] \]  
(A.8)

\[ \epsilon_k = \sum_k \frac{\omega_{2k}^2}{\omega_{2k}}, \]  
(A.9)

\[ \omega_{2k} = \omega + 2J A_k. \]  
(A.10)

Substitution of (A.6) and (A.7) into (23) gives

\[ \bar{\sigma}_{12}(t) = \bar{\sigma}_{12}(0) e^{-i \epsilon t} \text{ Tr}_b \left\{ \rho_b \exp \left[ - \sum_k \alpha_k (b^\dagger_k - b_k) \right] \exp \left[ -2iJ \sum_k A_k b^\dagger_k b_k t \right] \right\} \times \exp \left[ \sum_k \alpha_k^* \left( b^\dagger_k (t) - b_k (t) \right) \right] \exp \left[ -2iJ \sum_k A_k b^\dagger_k b_k t \right], \]  
(A.11)

where \( \epsilon' = 4 \epsilon_h - \epsilon_f + \epsilon_k - 2 \sum_k A_k J, \) \( \alpha_k = \frac{h_k}{\omega_{1k}} + \left( \frac{h_k}{\omega_{2k}} \right)^* - \frac{h_k^*}{\omega_{1k}}. \)
Appendix B. Derivation of equation (27)

We wish to change the order of the two exponentials $e^{-\alpha_k(b_k^\dagger - b_k)}$ and $e^{-2iJ A_k b_k^\dagger b_k t}$ in (A.11). We use the Zassenhaus combinatoric to approximate the interchanged expression:

$$e^{\theta(X-Y)} = e^{\alpha X} e^{\beta Y} e^{-\alpha Y} e^{\beta X} e^{\frac{1}{2} \omega (\theta_1 X Y + \theta_2 Y X)} e^{-\beta Y} e^{\alpha X} e^{-\alpha Y} e^{\beta X} e^{\frac{1}{2} \omega (\theta_1 X Y + \theta_2 Y X)} \ldots$$  \hspace{1cm} (B.1)

Keeping only the first commutator in (B.1), we obtain

$$e^{-\alpha_k(b_k^\dagger - b_k)} e^{C_k b_k^\dagger b_k} e^{-\alpha_k(b_k^\dagger - b_k)} e^{-1/2(-C_k D_k + C_k G_k) b_k^\dagger b_k},$$  \hspace{1cm} (B.2)

where

$$C_k = -2i J A_k t,$$  \hspace{1cm} (B.3)
$$D_k = \alpha_k (1 + C_k/2),$$  \hspace{1cm} (B.4)
$$G_k = -\alpha_k (1 - C_k/2).$$  \hspace{1cm} (B.5)

The trace in (A.11) now becomes

$$\text{Tr}_b \left\{ \rho_b \exp \left[ \sum_k C_k b_k^\dagger b_k \right] \exp \left[ -\sum_k \alpha_k (b_k^\dagger - b_k) \right] \exp \left[ -\frac{1}{2} \sum_k (-C_k D_k + C_k G_k) b_k^\dagger b_k \right] \right\} \times \exp \left[ \sum_k \alpha_k^* (b_k^\dagger(t) - b_k(t)) \right] \exp \left[ \sum_k C_k b_k^\dagger b_k \right] \}
= e^{\sum_k \psi_k(t)} \text{Tr}_b \left\{ \rho_b e^{\sum_k (\eta_k b_k^\dagger b_k + \theta_k b_k^\dagger b_k)} e^{2 \sum_k C_k b_k^\dagger b_k} \right\},$$  \hspace{1cm} (B.6)

where

$$\eta_k = -s_{2k} - \alpha_k^* e^{-i\omega t},$$  \hspace{1cm} (B.7)
$$\theta_k = s_{1k} + \alpha_k^* e^{i\omega t},$$  \hspace{1cm} (B.8)
$$\psi_k(t) = \frac{\alpha_k}{4} C_k (D_k - G_k) + \frac{1}{2} \alpha_k^* (s_{1k} e^{-i\omega t} - s_{2k} e^{i\omega t}),$$  \hspace{1cm} (B.9)

$$s_{1k}^{(1)} = -\alpha_k - \frac{C_k G_k}{2},$$  \hspace{1cm} (B.10)
$$s_{2k}^{(1)} = -\alpha_k - \frac{C_k D_k}{2},$$  \hspace{1cm} (B.11)

where $s_{1k}^{(1)}$ is a first-order approximation to $s_{1k}$. The approximation can be improved by considering successive orders of the commutator in (B.1). By summation of all infinite commutator orders, we arrive at the following exact equations for $s_{1k}$ and $s_{2k}$, which can subsequently be used to evaluate general expressions for $\theta_k$, $\eta_k$ and $\psi_k$:

$$s_{1k} = -\alpha_k - \frac{G_k}{C_k} (e^{-C_k} - 1 + C_k),$$  \hspace{1cm} (B.12)
$$s_{2k} = -\alpha_k - \frac{D_k}{C_k} (e^{C_k} - 1 - C_k).$$  \hspace{1cm} (B.13)
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