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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\textbf{Abstract}

In this corrigendum, we present the analytic corrections to the paper Hossein-Nejad and Scholes 2010 \textit{New J. Phys.} \textbf{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 The subsequent conclusions are, therefore, no longer valid.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]

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

where $J$ is the electronic coupling, $\{a_i^+, a_i\}$ 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 $\{b_k^+, b_k\}$. 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

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

where $\Delta = \sum_k h_{1k} (b_k^+ + b_k)$. 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]

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

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 \( D = UHU^\dagger \), is found to be

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

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

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

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

\[
e^{-itD} = U e^{-itH} U^\dagger.
\]

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

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

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

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

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

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

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

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

\[
= \text{Tr}_b \{ e^{-itD} \rho_b \bar{\sigma}(0) e^{itD} \}.
\]
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

\[
\bar{\sigma}(t) = \text{Tr}_b \left\{ \begin{bmatrix} e^{-iAt} & 0 \\ 0 & e^{-iBt} \end{bmatrix} \begin{bmatrix} \bar{\sigma}_{11}(0) & \bar{\sigma}_{12}(0) \\ \bar{\sigma}_{21}(0) & \bar{\sigma}_{22}(0) \end{bmatrix} \rho_b \begin{bmatrix} e^{iAt} & 0 \\ 0 & e^{iBt} \end{bmatrix} \right\},
\]

we arrive at the following expressions for the evolution of population and coherence:

\[
\bar{\sigma}_{11}(t) = \text{Tr}_b [\bar{\sigma}_{11}(0) \rho_b], \quad \text{and} \quad \bar{\sigma}_{12}(t) = \text{Tr}_b [e^{-iAt} \bar{\sigma}_{12}(0) \rho_b e^{iBt}].
\]

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

\[
\bar{\sigma}(0) = U \sigma(0) U^\dagger,
\]

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

\[
\bar{\sigma}_{11}(t) = \frac{1}{2} + \text{Re} \left\{ \sigma_{12}(0) \right\} \text{Tr}_b \{ R \rho_b \}, \quad \text{and} \quad \bar{\sigma}_{12}(t) = \frac{1}{2} - \sigma_{11}(0) \right\} \text{Tr}_b \{ e^{-iAt} R \rho_b e^{iBt} \} + i \text{Im} \left\{ \sigma_{12}(0) \right\} \text{Tr}_b \{ e^{-iAt} \rho_b e^{iBt} \},
\]

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 \( b^\dagger b \) (see supplementary information), that is

\[
\exp \left\{ i \pi b^\dagger b \right\} \simeq 1 - 2 b^\dagger b.
\]

This approximation renders all oscillator traces linear in exponentials of bosonic operators. The tracing can now be carried out straightforwardly. The final solution takes the form

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

\[
\bar{\sigma}_{12}(t) = \exp \left\{ \frac{(h/2)^2}{\omega^2 - 4 J^2} \Phi_1(\omega, J, t) + 2iJt \right\} \times \left\{ \left[ \frac{1}{2} - \sigma_{11}(0) \right] \left[ 1 - e^{-\beta \omega} \right] \right\} \exp \left[ \frac{(h/2)^2 \Theta_1(\omega, J, t)}{\omega^2 - 4 J^2} \tanh \left( \frac{\beta \tilde{\omega}(t)}{2} \right) \right] + \frac{i \text{Im} \left\{ \sigma_{12}(0) \right\} \left[ 1 - e^{-\beta \omega} \right]}{1 - e^{-\beta \tilde{\omega}(t)}} \exp \left[ \frac{(h/2)^2 \Theta_1(\omega, J, t)}{\omega^2 - 4 J^2} \coth \left( \frac{\beta \tilde{\omega}(t)}{2} \right) \right] \right\},
\]

where \( \Phi_1, \Phi_2, \Theta_1, \Theta_2 \) are defined in [1, equations (29, 30, 31, 32)].
\[\Phi_s(\omega, J, t) = -\Delta \omega t + \sin (\Delta \omega t) - 2\omega \left[ \frac{\sin (\omega_+ t)}{\omega_+} - \frac{\sin (\omega_- t)}{\omega_-} \right]. \tag{23}\]

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

where
\[\omega_\pm = \omega \pm 2J, \tag{25}\]
\[\Delta \omega = \omega_+ - \omega_-, \tag{26}\]
\[\Delta \omega = \omega + i \frac{\Delta \omega}{\beta} t. \tag{27}\]

At \(t = 0\) these expressions are reduced to
\[\tilde{\sigma}_{11}(0) = \frac{1}{2} + \text{Re} \left[ \sigma_{12}(0) \right] \tanh \left( \frac{1}{2} \beta \omega \right), \tag{28}\]
\[\tilde{\sigma}_{12}(0) = \left[ \frac{1}{2} - \sigma_{11}(0) \right] \tanh \left( \frac{1}{2} \beta \omega \right) + i \text{Im} \left[ \sigma_{12}(0) \right], \tag{29}\]
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

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

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 \(A\):

\[
A \approx \begin{pmatrix}
\epsilon - J & \frac{1}{2} \hbar & & & \\
\frac{1}{2} \hbar & \omega + J + \epsilon & \frac{\sqrt{2}}{2} \hbar & & \\
\frac{\sqrt{2}}{2} \hbar & 2\omega + 3J + \epsilon & \frac{\sqrt{3}}{2} \hbar & & \\
\frac{\sqrt{3}}{2} \hbar & 3\omega + 5J + \epsilon & \frac{\sqrt{4}}{2} \hbar & & \\
& & & \ddots & \ddots
\end{pmatrix}. \tag{31}\]
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 $n(\omega) = [\exp(\beta \omega) - 1]^{-1}$, 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 $\text{Im} \left[ \sigma_{12}(0) \right] = 0$, the FG dynamics are simplified to

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

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

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

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

$$\tilde{\sigma}_{12}(t) = \exp \left\{ \sum_k \frac{(h_k/2)^2}{\omega_k^2 - 4 J^2} \Phi_s(\omega_k, J, t) + 2iJt \right\} \left[ \frac{1}{2} - \sigma_{11}(0) \right] \times \left\{ \prod_k \left( \frac{1 - e^{-\beta \omega_k}}{1 + e^{-\beta \omega_k}} \right) \exp \left\{ \sum_k \frac{h_k^2}{\omega_k^2 - 4 J^2} \tanh \left( \frac{\beta \bar{\omega}_k(t)}{2} \right) \right\} \right].$$

### 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

$$\sigma_{11}(t) = \frac{1}{2} + \left[ \sigma_{11}(0) - \frac{1}{2} \right] \text{Re} \left\{ e^{2iJt} \exp \left( \frac{h^2}{4\omega_+ \omega_-} \Phi_a(\omega, J, t) \right) \right.$$

$$\times \frac{1 - e^{-\beta \omega}}{1 - e^{-\beta \bar{\omega}(t)}} \exp \left( \frac{h^2}{4\omega_+ \omega_-} \Theta_a(\omega, J, t) \coth \left( \frac{1}{2} \beta \bar{\omega}(t) \right) \right) \right\}$$

$$+ \text{Im} \left[ \sigma_{12}(0) \right] \text{Im} \left\{ e^{2iJt} \exp \left( \frac{h^2}{4\omega_+ \omega_-} \Phi_a(\omega, J, t) \right) \right.$$

$$\times \frac{1 - e^{-\beta \omega}}{1 + e^{-\beta \bar{\omega}(t)}} \exp \left( \frac{h^2}{4\omega_+ \omega_-} \Theta_a(\omega, J, t) \tanh \left( \frac{1}{2} \beta \bar{\omega}(t) \right) \right) \right\}. $$

(36)
The real part of the coherence is given by

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

and the imaginary part is

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

where we have defined the following functions:

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

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

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.
Figure 2. Population dynamics for the initial state $|e\rangle \otimes |g\rangle$ obtained via a numerical method (solid green lines) and the present analytic approach (dashed blue lines). The parameters $\omega$ and $J$ are fixed at $\omega = 100 \text{ cm}^{-1}$ and $J = 2 \text{ cm}^{-1}$. The system–oscillator coupling is varied in each panel: (a) $h = 30 \text{ cm}^{-1}$; (b) $h = 50 \text{ cm}^{-1}$; (c) $h = 70 \text{ cm}^{-1}$; and (d) $h = 90 \text{ cm}^{-1}$.

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 $h_k = C_0 \omega_k e^{-0.05\omega_k}$ 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
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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