Coherent quantum dynamics in donor–bridge–acceptor systems: beyond the hopping and super-exchange mechanisms

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\textit{New Journal of Physics} 15 (2013) 105020 (14pp)
Received 31 May 2013
Published 21 October 2013
Online at \url{http://www.njp.org/}
doi:10.1088/1367-2630/15/10/105020

Abstract. The population transfer dynamics of model donor–bridge–acceptor systems is studied by comparing a recently developed polaron-transformed quantum master equation (PQME) with the well-known Redfield and Förster theories of quantum transport. We show that the PQME approach reduces to these two theories in their respective limits of validity and naturally interpolates between them as a function of the system–bath coupling strength. By exploring the parameter space of our model problem, we identify novel regimes of transport dynamics in bridged systems like those encountered in biological and organic energy transfer problems. Furthermore, we demonstrate that three-level systems like the ones studied herein represent ideal minimal models for the identification of quantum coherent transport as embodied in super-exchange phenomena that cannot be captured by Förster-like hopping approaches.

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1. Introduction

The dynamics of charge and exciton migration in many biological [1–6] and synthetic molecular systems [1, 7–13] proceed through multiple sites or states embedded in a complex interacting environment. Thus an accurate understanding of such processes has significant implications for elucidating the microscopic mechanism of a variety of processes in chemistry, biology and materials science. Unfortunately, a quantitative description of electron and exciton transfer dynamics in condensed phases is usually beyond the reach of present day analytical and numerical techniques. In particular, powerful exact numerical approaches are generally limited to a small number of discrete quantum states and particular forms of the environment and its interaction with those states [14, 15]. Approximate analytical approaches are often tied to particular regions of parameter space where at least one energy scale can be quantified as ‘small’ compared to all others. Approximate numerical techniques, such as semiclassical ‘surface hopping’ [16, 17] and mean-field [17, 18] approaches, have the ability to model large systems with more general reservoirs in a computationally facile manner, but often fail in particular parameter regimes as well, especially when quantum coherence near non-adiabatic crossing points becomes important. Furthermore, the range of validity of such techniques is in general difficult to assess quantitatively due to the lack of apparent small parameters. Given this state of affairs, the development of approximate methods that can bridge the gap between different parameter regimes accurately and that can be adapted to the description of relatively large scale systems is of prime importance.

In terms of the methods mentioned above, quantum master equation (QME) approaches are attractive because they offer the possibility of controlled approximations (that can be corrected via higher order expansions) and the ability to treat large numbers of quantum states. Additionally, while harmonic baths are frequently employed to allow for analytical treatment of bath correlation functions, QMEs offer the flexibility to be paired with semiclassical approaches in the evaluation of more general bath correlations. Standard expansion schemes make use of an approximation exact up to the second order of either the system–bath coupling (Redfield theory and related approaches [19–21]) or the electronic coupling (the ‘non-interacting blip approximation’ [22] yielding Marcus [23] and Förster [24] theories for electron and energy transfer, respectively). While these approaches are successful when their respective expansion parameters are small, they can be grossly inaccurate when extended beyond their limits of
applicability. An important recent example of the distinction between these two limits comes from studies of energy conversion processes such as singlet fission in organic assemblies [25, 26]. Higher order QMEs or the recently developed polaronic QME (PQME) approaches [27–32] can potentially resolve such issues.

A minimal model for dissipative quantum processes that proceed through multiple states consists of donor–bridge–acceptor (D–B–A) states coupled to a phonon bath. In the limit where all of the electronic couplings are small and the energy of state B is comparable with those of states D and A, the dynamics may be described in terms of hopping between different states, with rate kernels determined from Förster-type theory. However, if the energy of state B is substantially different from the energies of states D and A, such that thermal activation is infeasible, then a quantum mechanical super-exchange mechanism must be invoked. Super-exchange involves rates that are fourth-order in the electronic coupling, and thus can be handled by Redfield-like approaches (which treat the electronic coupling non-perturbatively). This interplay between sequential hopping and super-exchange has a rich history in the mechanistic understanding of the primary electron transfer event in photosynthesis [33–36].

Despite many analyses of experimental data, understanding how and when the crossover from hopping to super-exchange occurs is not well understood. It is often suggested in simple rate theories [1, 9, 12, 37] that the sum of the two rates, $k = k_{\text{hop}} + k_{\text{SE}}$, should serve as a reasonable approximation. This implicitly assumes that the two mechanisms can be viewed as additively independent processes. This assumption has been questioned on the grounds that hopping and super-exchange should be considered as two different limits of the same quantum dynamical process [38]. A Padé-resumed rate expression for multi-site systems, first derived by Mukamel and co-workers [39, 40], presents one example of a unified formalism capable of describing both process. Furthermore, many biological or organic energy conversion systems correspond to an intermediate coupling situation where the electronic, electron–phonon, and thermal energy scales are all comparable [41]. In such cases, even the validity of perturbative rate approaches can be called into question.

In this work, we examine the real-time population dynamics of D–B–A systems in detail by comparing a recently developed PQME approach with approaches that treat to second order either the electron–phonon coupling (Redfield theory) or the electronic coupling (a Marcus or Förster-type theory that will henceforth be called the ‘hopping’ approach). As will be detailed below, the PQME-based theory is not a simple perturbation theory and the expansion parameter contains information about both the electron–phonon coupling and the electronic coupling. In other words, the theory captures non-perturbative effects in both the electronic and system–bath couplings as shown partly by model calculations [27–29] and recent applications to two-level systems [30, 31]. Our goal is to demonstrate that the PQME approach correctly interpolates between the two limits described above for generic three-state systems, making it a promising candidate for a theory that is valid for multiple state systems in all parameter regimes.

An alternative approach is the so-called modified Redfield theory, which also interpolates between the weak-coupling Redfield and strong-coupling Förster theories [42, 43], however there are two important differences. Firstly, the interpolation is tuned by the electronic energy gap and not the strength of the system–bath coupling, such that the limiting behavior is not always the physically correct one (for example, the theory always reduces to Redfield theory in the case of degenerate energy levels, and is accordingly confined to weak system–bath coupling for this case). Secondly, the approach yields a rate description of population dynamics in the basis that diagonalizes the system Hamiltonian (the exciton basis in the context of...
photosynthetic energy transfer), and not in the original basis of the problem (the site basis in the same context). This approach might therefore yield a dynamical observable different than the one of interest.

Previous studies have frequently considered the rate behavior of two-level quantum systems, using for example modified Redfield theory [43] or more recently a Markovian version of the PQME approach employed here [44]. In light of the recent interest in the role of quantum coherence in biological systems, we emphasize that the three-level systems considered here are much more enlightening than two-level systems with regards to the contribution of coherent transport effects. The effective tunneling through energetic bridge states barriers as embodied in super-exchange phenomena is a true coherent effect which is straightforwardly identified and characterized. The contribution of this effect to the overall rate, as compared to an activated hopping process can be quantified. These simple metrics are much more illuminating than the non-rigorous but frequently used ones in two-level systems, such as the timescale over which population oscillations are observed.

While a large number of exact numerical studies have been devoted to models with Ohmic baths [36, 45], relatively little is known for the super-Ohmic case, which is a more appropriate model for phonons in many contexts, such as excitation transport in crystals and quantum dot systems [46, 47]. The PQME approach is particularly useful in this important case and is pertinent to real systems as demonstrated recently [47], and we will consider only super-Ohmic coupling in this work. This fact, however, means that we are unable to provide exact benchmark results for comparison. Regardless, we will show that the PQME approach naturally recovers the correct behavior in the two limits where either the system–bath or electronic couplings may be treated up to second order. In this sense, we will demonstrate that the PQME approach serves as a viable approach for the intermediate regime where neither a hopping nor a super-exchange description is appropriate.

This paper is organized as follows. In section 2 we describe the model and introduce parameters relevant to organic and biological charge and energy transfer systems. Section 3 provides a brief description of the PQME approach as well as the perturbative hopping and Redfield theories to which we compare. Section 4 provides results and analysis of our model calculations and we conclude in section 5.

2. Model

Consider a D–B–A system linearly coupled to a bosonic bath. Let us denote D, B and A as 1, 2 and 3, respectively. The total Hamiltonian is given by $H = H_s + H_b + H_{sb}$, where the system Hamiltonian is

$$H_s = E_1|1\rangle\langle 1| + E_2|2\rangle\langle 2| + E_3|3\rangle\langle 3| + J_{12}(|1\rangle\langle 2| + |2\rangle\langle 1|) + J_{23}(|2\rangle\langle 3| + |3\rangle\langle 2|).$$

In the above expression, $E_i$ is the site (or excitation) energy of state $|i\rangle$. $J_{ll'}$ is the electronic coupling between states $|l\rangle$ and $|l'\rangle$. We emphasize that donor and acceptor states 1 and 3 are not directly coupled. Therefore any population transfer from donor to acceptor must be mediated, either physically or virtually, by the bridge state 2. The bath Hamiltonian is given by $H_b = \sum_n \hbar\omega_n (b_n^\dagger b_n + \frac{1}{2})$ and the system–bath interaction has the form $H_{sb} = \sum_{l=1}^3 \sum_n \hbar\omega_n (b_n + b_n^\dagger) g_{n,l} |l\rangle\langle l|$. Each site is assumed to be coupled to an independent super-Ohmic bath, although consideration of common modes or more general and correlated spectral densities is...
possible [27–29]. The spectral density for each state \( l \) is given by the super-Ohmic form

\[
J_l(\omega) \equiv \sum_n \delta(\omega - \omega_n)\omega_n^2 \delta_{n,l} = \frac{\eta_l}{3} \frac{\omega^3}{\omega_{e,l}^2} e^{-\omega/\omega_{e,l}}.
\]

We define the corresponding bath correlation function as

\[
C_l(t) = \int_0^\infty d\omega \frac{J_l(\omega)}{\omega^2} \left[ \coth(\hbar \omega/2k_B T) \cos(\omega t) - i \sin(\omega t) \right],
\]

which fully characterizes the linear response of the bath. The second derivative of the above time correlation function is needed in Redfield theory

\[
C_l^{(2)}(t) = \int_0^\infty d\omega J_l(\omega) \left[ \coth(\hbar \omega/2k_B T) \cos(\omega t) - i \sin(\omega t) \right].
\]

It is interesting to note that \( C_l(t) \) with a super-Ohmic spectral density is equivalent to \( C_l^{(2)}(t) \) with an Ohmic spectral density up to a constant factor. This may explain why the use of Ohmic spectral densities in Redfield-like QMEs often appears to reproduce experimental data even when the actual spectral density might be closer to the super-Ohmic case.

3. Methods

3.1. Polaronic quantum master equation

The main theoretical tool used for exploring D–B–A dynamics in this work is a recently developed PQME approach that combines the conventional QME approach with a polaron transformation [27–29]. A short review of this method is provided first.

Given the total density operator \( \rho(t) \), one can introduce a polaron-transformed density operator, \( \tilde{\rho}(t) = e^{iG} \rho(t) e^{-iG} \), where

\[
G = \sum_l \sum_n g_{n,l} \left( b_n^\dagger b_n \right) |l\rangle \langle l|.
\]

Since \( e^G \) is unitary in the total space of system and bath states, any physical observable can be calculated by taking the trace of \( \tilde{\rho}(t) \) with the corresponding transformation of the physical observable, regardless of whether an actual polaron is formed or not. The time evolution of \( \tilde{\rho}(t) \) is governed by the quantum Liouville equation corresponding to the polaron-transformed Hamiltonian

\[
\frac{d}{dt} \tilde{\rho}(t) = [\tilde{H}, \tilde{\rho}(t)],
\]

where \( \tilde{H} = e^{iG} H e^{-iG} = \sum_{l,l'} \tilde{E}_l |l\rangle \langle l'| + \sum_{l,l'} J_{l'l'} |l\rangle \langle l'| + H_0 \),

and

\[
\tilde{E}_l = E_l - \hbar \omega_n g_{n,l}^2 \quad \text{and} \quad \theta_l = e^{-\sum_n \coth(\hbar \omega_n/2k_B T) g_{n,l}^2/2}.
\]

The state energies are thus shifted by the reorganization energy \( \lambda_l = \sum_n \hbar \omega_n g_{n,l}^2 \) and the off-diagonal couplings have acquired a dynamical modulation due to the bath degrees of freedom. Taking the thermal average of these dynamical couplings, we define the zeroth-order Hamiltonian as

\[
\tilde{H}_0 = \sum_l \tilde{E}_l |l\rangle \langle l| + \sum_{l,l'} J_{l'l'} w_{l'l'} |l\rangle \langle l'| + H_0 = \tilde{H}_0 + H_b.
\]

where \( w_{l'l'} = \text{Tr}_b \{ \theta_l \theta_{l'} \rho_b \} = e^{-\sum_n \coth(\hbar \omega_n/2k_B T) g_{n,l}^2/2} \) with \( \delta g_{n,l} = g_{n,l} - g_{n,l'} \), such that the perturbation Hamiltonian, defined as the difference between \( \tilde{H} \) and \( \tilde{H}_0 \), is given by

\[
\tilde{H}_1 = \sum_{l,l'} J_{l'l'} \left( \theta_l^\dagger \theta_{l'} - w_{l'l'} \right) |l\rangle \langle l'|.
\]
In the interaction picture with respect to $\tilde{H}_0$, the corresponding density operator, $\tilde{\rho}_I(t) = e^{i\tilde{H}_0 t/\hbar} \tilde{\rho}(t) e^{-i\tilde{H}_0 t/\hbar}$, evolves according to the time-dependent Liouville equation

$$\frac{d}{dt} \tilde{\rho}_I(t) = -\frac{i}{\hbar} \left[ \tilde{H}_I(t), \tilde{\rho}_I(t) \right],$$

(8)

where

$$\tilde{H}_I(t) = \sum_{l \neq l'} \mathcal{J}_{ll'} \left\{ \tilde{\theta}(t) \tilde{\theta}(t) - w_{ll'} \right\} \mathcal{T}_{ll'}(t)$$

(9)

with $\tilde{\theta}(t) = e^{-\sum \sigma_{\nu,\nu'}(t) e^{i \omega_{\nu,\nu'} t}}$ and $\mathcal{T}_{ll'}(t) = e^{i\tilde{H}_{0,s} t/\hbar} |l\rangle \langle l'| e^{-i\tilde{H}_{0,s} t/\hbar}$.

Therefore, the parameter to be treated perturbatively in the PQME approach is the instantaneous fluctuation of the bath-modulated hopping from its average value. It is important to note that the renormalized system–bath coupling $\tilde{H}_I(t)$ vanishes in the limit of weak system–bath coupling, $\eta_l \to 0$, and remains bounded by $J_{ll'}$ in the strong coupling limit, $\eta_l \to \infty$. If $J_{ll'} \sqrt{1 - w_{ll'}}$ is sufficiently small, truncating the formally exact QME at the second-order of $\tilde{H}_I(t)$ is valid for all values of $\eta_l$, and the resulting second order PQME can serve as a good approximation covering the entire regime of system–bath coupling.

Using projection operator techniques [48, 49], one can derive a time-local equation of motion for the reduced density operator, $\tilde{\sigma}_I(t) = \text{Tr}_s(\tilde{\rho}_I(t))$, yielding

$$\frac{d}{dt} \tilde{\sigma}_I(t) = -\mathcal{R}(t) \tilde{\sigma}_I(t) + \mathcal{I}(t),$$

(10)

where

$$\mathcal{R}(t) \tilde{\sigma}_I(t) = \frac{1}{\hbar} \sum_{l \neq l'} \sum_{m \neq m'} \mathcal{J}_{ll'} \mathcal{J}_{mm'} w_{ll'} w_{mm'} \int_0^t d\tau \left( e^{-\mathcal{K}_{ll',mm'}(t-\tau) - 1} \mathcal{T}_{ll'}(t), \mathcal{T}_{mm'}(\tau) \tilde{\sigma}_I(t) \right) + \text{h.c.},$$

(11)

with $\mathcal{K}_{ll',mm'} = (\delta_{lm} - \delta_{lm'}) \mathcal{C}_l(t) + (\delta_{lm'} - \delta_{lm}) \mathcal{C}_{l'}(t)$. The source term $\mathcal{I}(t)$ arises for generically non-equilibrium initial conditions. Explicit expressions for this term can be found for the general case where the initial excitation is an arbitrary superposition of the system states [29]. The reduced equation of motion can be solved numerically in the eigenbasis of $\tilde{H}_{0,s}$ as detailed previously [28]. Unlike $\tilde{\rho}_I(t)$, not all the system observables can be calculated from $\tilde{\sigma}_I(t)$, but because $e^{i\tilde{H}_0 s} |l\rangle \langle l| e^{-i\tilde{H}_0 s} = |l\rangle \langle l|$, determination of the site populations is still possible via

$$P_l(t) = \text{Tr}_s \left\{ e^{i\tilde{H}_{0,s} t/\hbar} |l\rangle \langle l| e^{-i\tilde{H}_{0,s} t/\hbar} \tilde{\sigma}_I(t) \right\},$$

(12)

where $\text{Tr}_s$ denotes trace over the system degrees of freedom.

3.2. Hopping dynamics

The master equation that we henceforth refer to as embodying hopping dynamics can also be derived via projection operator techniques, expanding directly in the bare electronic coupling elements $J_{lm}$. The resulting equation of motion for the populations terms is closed and given by the Pauli master equation

$$\frac{dP_l(t)}{dt} = \sum_{m \neq l} \left\{ k_{m \to l}^E(t) P_m(t) - k_{l \to m}^E(t) P_l(t) \right\}.$$
For the time-dependent rates in the above expression, we employ the non-Markovian version of Fermi’s Golden rule [50]:

$$k_{l\rightarrow m}^F(t) = \frac{2(J_{lm}w_{lm})^2}{h^2} \Re \int_0^t d\tau \ e^{i(\tilde{E}_l - \tilde{E}_m)\tau/\hbar} \left( e^{K_{lm}(\tau)} - 1 \right).$$  \hspace{1cm} (14)

Note that a contribution proportional to $\delta(\tilde{E}_l - \tilde{E}_m)$ is subtracted from the above integration. This regularization makes the resulting integration convergent for the super-Ohmic spectral density considered here, which amounts to subtracting the contribution of the zero phonon line to the rate. Note that, aside from the initial condition term $\mathcal{Z}(t)$, the main difference between the PQME and this master equation that describes hopping dynamics is that the latter treats the bare electronic coupling as a perturbation, while the PQME treats the fluctuations of the electronic coupling terms in the polaronic basis as a perturbation. The hopping dynamics can thus only predict quantum effects that are second-order in the couplings $J_{lm}$.

3.3. Redfield theory

At the opposite extreme, we consider Redfield theory [20, 21], which is a QME approach that uses the system–bath coupling as a perturbation and treats the entire system Hamiltonian exactly. As such, this approach encompasses the conventional fourth-order super-exchange result in the high barrier limit and furthermore includes all higher-order electronic interactions for moderate or small barrier heights.

In the interaction picture with respect to $H_0 = H_s + H_b$, the Redfield theory QME takes the form

$$\frac{d\sigma_I(t)}{dt} = -R\sigma_I(t),$$  \hspace{1cm} (15)

where

$$R\sigma_I(t) = \frac{1}{\hbar^2} \sum_{kl} \int_0^\infty d\tau \ C_l^2(t - \tau) \left[ T_{ll}(t), T_{ll}(\tau)\sigma_I(t) \right] + \text{h.c.}$$  \hspace{1cm} (16)

In the above, $T_{ll}(t) = e^{iH_s t/\hbar} |l\rangle \langle l| e^{-iH_s t/\hbar}$. We furthermore employ the secular approximation, where all elements $R_{ij}^{kk'}$ in the basis of system eigenstates for which $|\delta E_{kk}^{ij} - \delta E_{kk'}^{ij}| \neq 0$ are neglected ($\delta E_{kk}^{ij}$ is the difference between the eigenenergies of system eigenstates $k$ and $k'$). The secular approximation prevents unphysical negative or diverging populations in the limit of strong system–bath coupling, where the second-order approximation inherent in the Redfield approach breaks down. More specifically, the secular approximation enforces the equilibrium population $\sigma_{eq} \propto e^{-H_s/k_B T}$ and kinetic rates $k \propto \eta$ for all values of the system–bath coupling, whereas these results are clearly only correct for weak coupling.

4. Results

To probe generic effects of bridge energetics on the mechanistic and quantitative details of population transfer from donor to acceptor, we investigate a small set of model parameters close to those encountered in light harvesting complexes or singlet fission problems. In particular, we are interested in the situation where the electronic couplings, width of spectral densities and the energy difference between donor and acceptor are all comparable. Thus, we use fixed values.
of $J_{12} = J_{23} = 100 \text{ cm}^{-1}$ and $E_1 - E_3 = 100 \text{ cm}^{-1}$ for all the calculations (the latter providing an energetic driving force), and scan a range of physically relevant values for other parameters. Furthermore, we fix the bath of all three sites to have identical spectral densities, such that $\eta_l = \eta$ and $\hbar \omega_c, l = \hbar \omega_c$.

First, we consider the case of $\hbar \omega_c = 200 \text{ cm}^{-1}$ at temperature $T = 300 \text{ K}$, where the spectral range of the bath is comparable to the thermal energy. Both quantum and multiphonon effects of the bath are important in this case. Nine different parameter sets, with $\eta = 0.2, 1, 5$ and $E_2 - E_1 = 0, 200, 800 \text{ cm}^{-1}$ are investigated.

Figure 1 shows the calculated time-dependent populations of the acceptor state, $P_3(t)$. The population based on the PQME exhibits strongly coherent behavior during early times and becomes increasingly incoherent with increasing system–bath coupling or bridge state energy. In the weak system–bath coupling limit ($\eta = 0.2$), the results of the PQME agree with those of Redfield theory, but those of the hopping dynamics differ substantially. In the strong system–bath-coupling limit ($\eta = 5$), the opposite situation occurs. The PQME results agree with those of the hopping dynamics, whereas the Redfield theory results are substantially different. For moderate system–bath coupling ($\eta = 1$), the degree of agreement is sensitive to the value of $E_2 - E_1$, with the agreement worsening for increasing bridge energy. Specifically, the hopping dynamics agree with the PQME results only when $E_2 - E_1 \lesssim k_B T$, consistent with thermal activation. For the largest value of bridge energy considered, $E_2 - E_1 = 800 \text{ cm}^{-1}$, the PQME dynamics are much faster than those of the hopping approach, but slightly slower than those of Redfield theory.
In order to understand the effects of temperature, similar calculations are performed at a lower temperature $T = 100$ K and the results are shown in figure 2. While similar trends as in figure 1 can be seen, the discrepancy between the results of PQME and hopping dynamics are much more pronounced for weak and moderate coupling, and there are still significant differences between the two even for strong coupling. In this low temperature limit, quantum effects dominate not only the dynamics but also the steady state limit. This suggests that delocalized exciton states have more physical meaning in this low temperature limit, for which the localized states (including the system–bath coupling) are not Boltzmann distributed.

Figure 3 shows analogous results when the spectral density is much broader than other energy scales, $\hbar \omega_c = 1000$ cm$^{-1}$. For each column, the reorganization energy of the bath, which is another measure of the strength of system–bath coupling ($\lambda \propto \eta \hbar \omega_c$), is five times the corresponding column of figure 1 or 2. For example, the case of $\eta = 0.2$ in figure 3 has the same reorganization energy as the case of $\eta = 1$ in figure 1. For this situation, the majority of bath modes are no longer resonant with electronic transitions amongst the system energy levels and thus they do not effectively induce dephasing. The resulting dynamics are therefore much more coherent despite the fact that the reorganization energy is five times larger than in the previous examples. Clearly the ability of the PQME approach to accurately capture this short-time quantum coherence is especially encouraging, given the recent interest in such phenomena.

Although many of the results based on the PQME and Redfield theory exhibit such coherent population dynamics, their long-time trends obey nearly exponential decay. For the parameters corresponding to the middle column of figure 1 (i.e. moderate system–bath coupling, $\eta = 1$), calculations were conducted for values of $E_2 - E_1$ in the range of 100–1 000 cm$^{-1}$. The resulting time dependent populations were then fit to the kinetic form

$$P_3(t) = P_3^{eq}(1 - e^{-kt})$$  (17)
Figure 3. The same as in figure 1 except for $\hbar \omega_c = 1000 \text{ cm}^{-1}$.

Figure 4. Population transfer rates versus $E_2 - E_1$ in logarithmic scale (base e) for $\eta = 1$, $\hbar \omega_c = 200 \text{ cm}^{-1}$, $J_{12} = J_{23} = 100 \text{ cm}^{-1}$ and $T = 300 \text{ K}$. The blue solid line is the extrapolation of the Redfield results with slope $-2$, demonstrating super-exchange behavior, $k \sim |E_2 - E_1|^{-2}$. The inset shows the same results with a linear scale for $E_2 - E_1$, demonstrating the exponential dependence of the hopping rate, $k \sim \exp(-|E_2 - E_1|/k_B T)$.

and the extracted values of $k$ are shown in figure 4. The main panel plots the data in logarithmic scale (base e), and the inset shows the same data with the energy difference $E_2 - E_1$ in linear scale. As shown by the extrapolation expected from super-exchange theory (SE-limit), the results of the Redfield calculation clearly demonstrate super-exchange behavior, $k \sim |E_2 - E_1|^{-2}$, for large values of $E_2 - E_1$. This does not necessarily mean that the rates
Figure 5. Logarithmic dependence (base e) of population transfer rates on the strength of the system–bath coupling $\eta$ for $\hbar \omega_c = 200$ cm$^{-1}$, $J_{12} = J_{23} = 100$ cm$^{-1}$ and $T = 300$ K. The upper panel is for $E_2 - E_1 = 200$ cm$^{-1}$ and the lower panel is for $E_2 - E_1 = 800$ cm$^{-1}$.

are the same as those calculated by perturbative (fourth-order) super-exchange theory because there might be non-negligible contributions from the subleading terms. On the other hand, the inset clearly demonstrates that the hopping dynamics exhibit exponential behavior, $k \sim \exp(-|E_2 - E_1|/k_B T)$ indicative of barrier crossing via thermal activation. The results of the PQME calculation instead behave like activated process for small values of the bridge energy and like super-exchange behavior for large values, where the crossover is dependent on other factors including the strength of the system–bath coupling. For all the values of bridge energy considered, the rate predicted by the PQME theory are in-between those of Redfield theory and hopping dynamics, suggesting that the simple approximation of $k = k_{\text{hop}} + k_{\text{SE}}$ is unreliable.

However, the above analysis is based on the assumption that the Redfield rate constant is a reasonable proxy for the super-exchange rate constant, which is not entirely accurate. It remains to be determined whether the Redfield rate is correctly larger than the others because it exactly includes all orders of electronic transport effects or whether the Redfield rate is incorrectly large because it does not properly include the renormalized hopping (or band narrowing) effect associated with a finite system–bath coupling. Without numerically exact data, we cannot answer this question conclusively, however it is instructive to conclude by considering the dependence of the rate on the strength of the system–bath coupling.

Interestingly, we can infer from figure 1 that the population transfer to the acceptor reaches a maximum for appropriate values of the system–bath coupling, $\eta$. In order to explore this aspect in more detail, we have carried out an analogous study of the rate constant for values of the system–bath coupling $\eta$ in the range 0.5–10. The results are shown in figure 5 for two different choices of $E_2 - E_1 = 200$ and 800 cm$^{-1}$. It is clear that the Redfield rate constant is indeed becoming unphysically large with increasing system–bath coupling, due to the aforementioned
weak-coupling prediction, \( k \sim \eta \). On the other hand, the purely hopping behavior grossly underestimates the rate at small values of the coupling, where quantum coherent transfer process dominate because the bath cannot effectively activate classical barrier crossing. Ultimately, we again see encouraging evidence that the PQME approach interpolates between the two limiting cases where each theory is most accurate, and generically exhibits a characteristic turnover behavior, where the turnover can be ascribed to a self-trapping effect (i.e. polaron formation in the case of charged quantum states). The case of \( E_2 - E_1 = 800 \text{ cm}^{-1} \) is especially interesting, because while Redfield theory and the hopping process predict a rate that varies by four orders of magnitude over the range studied, the interpolating behavior of the PQME approach instead predicts a rate which is largely insensitive to the strength of the coupling, varying by less than one order of magnitude.

5. Conclusion

In this paper we have investigated the dynamics of a D–B–A system in detail. The main goal of the work was to show that the PQME approach can capture the limiting behaviors of the Redfield and hopping approaches in the regimes where each is expected to be valid. These regimes include both super-exchange kinetics (when the bridge state energy lies energetically well above the donor and acceptor), as well as incoherent hopping kinetics (when the bridge state energy is sufficiently low that thermal activation is possible). The PQME approach captures these limiting forms by combining a polaron transformation with a novel definition of the perturbation as a fluctuation of the transformed hopping term. This protocol yields a perturbative parameter which is a complex mixture of both system and bath degrees of freedom. When the system–bath coupling is weak, the renormalized hopping parameter is close to the bare one and a linearized coupling due to the fluctuating hopping perturbation is similar to the bare system–bath coupling. Thus, the theory approaches the Redfield limit. When the system–bath coupling is strong, the renormalized hopping term is vanishingly small and the difference between the fluctuating and bare hopping parameters is negligible. Hence, the PQME approach reduces to a hopping-type Förster theory. While it will be important to compare the PQME approach to exact calculations in the future, the fact that it captures the crossover between these two important and distinct regimes supports the possibility that it also captures the essential features of the difficult ‘intermediate coupling’ regime where most perturbative approaches fail. This observation, as well as the efficiency and scalability of the PQME approach, make it promising for studies of the charge and energy transport in large systems within parameter regimes that are problematic for standard approaches.

In addition to the comparison between the PQME and other approaches, our study has also revealed several other interesting facets of the behavior of D–B–A systems. In particular, even in cases where the population exhibits a simple rate behavior, the PQME dynamics, which include quantum coherence effects, are significantly faster than those of the second-order hopping process. Thus, population transfer through a partially coherent mechanism is clearly significant and becomes more dominant as the bridge energy increases into the super-exchange regime. In addition to electronic effects, we have also highlighted novel, non-perturbative system–bath coupling effects beyond the reach of other treatments, such as the robust prediction of a non-monotonic dependence of the rate on the system–bath coupling strength. All of these subtle aspects of D–B–A dynamics are worthy of future study.
Acknowledgments

This research was conducted during a sabbatical stay of SJ at Columbia University. The research contributions of SI, TCB and DRR were supported primarily by the Center for Re-Defining Photovoltaic Efficiency Through Molecule Scale Control, an Energy Frontier Research Center funded by the US Department of Energy, Office of Science, Basic Energy Sciences under Award no. DE-SC0001085. SJ also acknowledges the partial support of the National Science Foundation CAREER award (grant no. CHE-0846899), the Office of Basic Energy Sciences, Department of Energy (grant no. DE-SC0001393) for preliminary development and calculation conducted at Queens College. SJ was partially supported through a Camille Dreyfus Teacher Scholar Award. TCB was partially supported by the Department of Energy Office of Science Graduate Fellowship Program (DOE SCGF), administered by ORISE-ORAU under contract no. DE-AC05-06OR23100.

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