Effectiveness of Perturbation Theory Approaches for Computing Non-Condon Electron Transfer Dynamics in Condensed Phases[†]

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A description of electron transfer in condensed-phase media requires models that adequately describe the coupling of the electronic degrees of freedom to the surrounding nuclear coordinates. The spin-boson model has been the canonical model used to understand quantum dynamic processes in condensed-phase media over the last 25 years. Inherent in the standard model of a two-state quantum system coupled to a bosonic bath is the assumption that the Condon approximation is valid. In this context, the Condon approximation assumes that the bath configurations (coordinates) have no effect on the nonadiabatic coupling matrix element. While this is a useful model for electron transfer in small molecular systems, the validity of this approximation is less likely when large-scale motions of solvent molecules are strongly coupled to the electron transfer event, e.g., in molecular clamps and long-range electron transfer in biopolymers. In the present paper a general model for two-state electron transfer which allows for system−bath coupling in both the diagonal and off-diagonal (nonadiabatic) terms is studied. Time-dependent perturbation theory for this Hamiltonian is developed using a small polaron transformation. As noted in several recent studies, in a certain regime of parameter space, the relevant Hamiltonian admits an exact solution, termed the exactly solvable non-Condon Hamiltonian (or NCE). This limit, for which exact solutions are available, is used to benchmark the short- and long-time accuracy of various perturbative approaches. The validated perturbation equations are subsequently used to explore the role of non-Condon effects on electron transfer by systematically increasing the strength of the non-Condon coupling term from zero (i.e., the canonical spin-boson model) to the value that pertains to the exactly solvable non-Condon model (where non-Condon effects are significant).

1. Introduction

Complete characterization of electron transfer processes in condensed-phase media requires consideration of the effect of the environment on the electron transfer system states. Electron transfer (ET) in the nonadiabatic limit (characterized by small electron tunneling matrix element) is generally well-represented with a Marcus-like model[1−12] and is described by projecting the electron transfer dynamics onto two diabatic states. A donor state is coupled to an acceptor state via the small nonadiabatic coupling matrix element. The effects of the dissipative bath are taken into account in terms of the reorganization energy of the solvent that accompanies electron transfer. In the most commonly studied model, the Condon approximation is typically applied; i.e., solvent fluctuation effects on the nonadiabatic coupling element are assumed to be insignificant.[1,2] While this is a reasonable assumption for small rigid molecular systems, there are many systems where the Condon approximation is known to break down,[13−15,20,21] including electron transfer through thin films,[16,17] protein electron transfer,[18,19] molecular clamps,[22] and electron tunneling through water.[16] The number of important systems that do not fit with a simple electron transfer picture and the availability of modern experimental probes have raised new theoretical issues in electron transfer.

Numerous efforts have indicated that consideration of non-Condon effects may be important for a thorough explanation of the behavior of a number of electron transfer systems. Potential non-Condon effects include unusual temperature dependence of the ET rate observed in conjugated polymers and spectroscopic and kinetic data.[23−27] This accumulation of evidence accentuates the need for theoretical models of condensed-phase electron transfer that incorporate non-Condon effects explicitly into the Hamiltonian.[28−31]

A model Hamiltonian for electron transfer (ET) with non-Condon effects can be developed most simply by assuming that the off-diagonal system−bath coupling terms can be expanded in powers of the bath coordinates about an appropriate reference configuration of the bath. Truncation of this expansion to first-order provides a coupling that is linear in the bath coordinates. This approximation takes into account terms that are usually omitted from the study of electron transfer in dissipative environments.

In a number of recent studies by the authors, a model Hamiltonian has been developed within the context of electron transfer.[32−35] This Hamiltonian is of the type encountered in nonadiabatically coupled electronic state dynamics and is also quite similar to the canonical spin-boson (SB) form.[36−41] The SB model is recovered when the linear coupling to the bath in the off-diagonal terms is neglected. This particular non-Condon electron transfer Hamiltonian[32,33] is a special case of a more general class of nontrivial *N*-level Hamiltonians coupled to a dissipative environment (or bath) for which the time evolution of the composite quantum many-body system can be calculated

exactly. In fact, we[32-35] and others[42-44] have shown that for this general class of Hamiltonians, the exact time dependence of the reduced system dynamics of the *N*-level system can be determined. It should be noted that this general class of Hamiltonians includes a very specific form for the system−bath coupling term, which means that these exactly solvable Hamiltonians are limited to a special region of parameter space. In particular then, for any two-level non-Condon Hamiltonian that fits into this class, exact quantum dynamics can be obtained; we will refer to these as non-Condon exact (NCE) systems.

The advantages of an exactly solvable model Hamiltonian for a condensed-phase problem are obvious; for example, it can be used to study systems beyond the regime of weak system−bath interactions or small nonadiabatic coupling. An exactly solvable model then provides a testing ground for various perturbation theory inspired approximations. This is especially important within the context of electron transfer, where perturbative approximations have been used extensively to model electron transfer processes in complex environments that go far beyond the spin-boson model. Time-dependent perturbation theory[45,46] has been used in the electron transfer literature and applied in many cases where the nonadiabatic coupling term is small.[47-53] Under these circumstances, the electron transfer dynamics can be obtained via kinetic master equations that are truncated to second-order in an expansion where the nonadiabatic coupling terms are treated as a perturbation.

Over the last 25 years, the regime of validity of second-order perturbation theory approximations, including, e.g., various Redfield[46,47] and modified Redfield[48] approaches, has been well established for the spin-boson (SB) Hamiltonian.[47-60] The accuracy of local and nonlocal treatments of the bath correlation functions have been examined in all areas of parameter space. A simple Golden Rule formula for electron transfer rates has been developed in the limit of weak nonadiabatic coupling matrix elements for Markovian bath dynamics, and a generalized Golden Rule formula has also been developed for more complex dynamics of the spin-boson model, such as nonequilibrium initial state preparation.[59-61] In the context of the spin-boson model, a shift of the bath coordinates, termed the small polaron transformation, has also been shown to be quite accurate as a second-order perturbative approach. Using this transformation, second-order perturbation theory can, in some cases, be pushed to larger values of the nonadiabatic coupling term.[62-68] More recently, other transfer matrix and generalized master equation formalisms have been developed as effective approximations to electron transfer Hamiltonians[69,70] and allow for a description of electron transfer in the localized tight-binding regime and the delocalized regime of strong electronic coupling. In the regime of stronger nonadiabatic coupling, the pure dephasing reference system (PDRS) master equation method[70] has been shown to be more accurate than the standard noninteracting blip approximation (NIBA)[36] approach for the spin-boson model in numerical tests. Using this general formalism,[70] approximate equations of motion have been developed to take into account generalizations of the spin-boson model including nonequilibrium initial state preparation, backflow and non-Condon terms.

In this paper, we take advantage of the fact that we have an exactly solvable model for non-Condon electron transfer (NCE) to benchmark the accuracy of time dependent second-order perturbation solutions of the Hamiltonian. In section 2, we review the general structure of the NCEs and derive a set of second-order perturbation equations for the reduced system dynamics. In particular, we use the small polaron approach to develop a set of equations to second-order in the nonadiabetic

coupling strength using time-dependent perturbation theory. The second-order perturbation solutions are generated in terms of the nonadiabatic coupling strength of the two-level system and the coupling to a bosonic bath. In section 3 we examine the accuracy of the perturbation solutions by direct comparison with the exact results. These benchmarks are made using both local (PL) or Markovian, and nonlocal (PN) solutions. In section 4, we use the successfully benchmarked perturbation solutions to study the behavior of more general non-Condon electron transfer models. Our perturbation theory models developed in section 2 can be used to study the long-time reduced system dynamics of more general non-Condon electron transfer systems (i.e., ones that do not fall into the category of NCEs), and the long-time dynamics of these generalized non-Condon models are explored in section 5. Implications for electron transfer and the overall accuracy of the perturbation theory approaches are discussed in section 6.

2. General Perturbation Approach in the Nonadiabatic Coupling Terms

The Hamiltonian of a two-level system coupled to a bosonic bath with both Condon and non-Condon coupling terms can be written most generally as

$$\hat{H} = \underbrace{\begin{bmatrix} \varepsilon & \Delta \\ \Delta & -\varepsilon \end{bmatrix}}_{\hat{H}_S} + \underbrace{\begin{bmatrix} c & d \\ d & -c \end{bmatrix}}_{\hat{R}_S} \underbrace{\sum_j G_j \left(\hat{a}_j^\dagger + \hat{a}_j \right)}_{\hat{R}_B} +$$

$$\underbrace{\hbar \sum_j \omega_j \hat{a}_j^\dagger \hat{a}_j + \frac{\hbar}{2} \sum_j \omega_j}_{\hat{H}_B} \quad [1a]$$

where the sums are over all bath modes. Furthermore, the raising and lowering operators of the bosonic bath are defined in the usual way in terms of the momentum and position operators, i.e., $\hat{p}_j = i[\hbar\omega_j/2]^{1/2}(\hat{a}_j^\dagger - \hat{a}_j)$ and $\hat{x}_j = [\hbar/2\omega_j]^{1/2}(\hat{a}_j^\dagger + \hat{a}_j)$ and G_j is the coupling strength of bath mode *j* to the two-level system (i.e., the electronic degrees of freedom). Note that the electron−phonon (or system−bath) coupling term can be written equivalently as $\sum_j G_j(\hat{a}_j^\dagger + \hat{a}_j) \equiv \sum_j \lambda_j \hat{x}_j$, with $G_j = \lambda_j[\hbar/2\omega_j]^{1/2}$. It is useful to write the system part of the system−bath coupling term as

$$\hat{R}_S = \begin{bmatrix} c & d \\ d & -c \end{bmatrix} \equiv \begin{bmatrix} 1 & \kappa\left(\dfrac{\Delta}{\varepsilon}\right) \\ \kappa\left(\dfrac{\Delta}{\varepsilon}\right) & -1 \end{bmatrix} \quad (1b)$$

for the purposes of this paper. In this form, $\hat{R}_S$ is expressed in terms of a parameter κ, which scales proportionally to the strength of the off-diagonal non-Condon coupling terms. For the exactly solvable NCE Hamiltonian, $\kappa = 1.0$,[32,33] and in the canonical spin-boson model, $\kappa = 0$.[39]

Note that the case where $\varepsilon = 0$, i.e., the limit of a symmetric two-level system, is best excluded from analysis here, as it corresponds to an infinite off-diagonal matrix element in the form of $\hat{R}_S$ given in eq 1b. Because of restrictions in the structure of NCE Hamiltonians, the $\varepsilon = 0$ case describes a situation where there is no diagonal system−bath coupling, i.e., in the context of ET, no direct electron−phonon coupling: all dissipative

effects are contained in the bath coordinate dependence of the nonadiabatic coupling matrix elements. Here we are interested in condensed-phase ET systems characterized by nonzero and often large solvent reorganization energies (i.e, electron–phonon coupling). Thus, we will focus on systems for which $\varepsilon \neq 0$ in the present work.

A small polaron transformation[63–67] of the system Hamiltonian in eq 1a can be made by defining the polaron operator as $\hat{P}_B = \Sigma_j (cG_j/\hbar\omega_j)(\hat{a}_j^\dagger - \hat{a}_j)$. The results of this transformation are most easily stated in terms of the standard 2×2 Pauli σ matrices. In particular, defining the unitary operator $\hat{U} = e^{\hat{\sigma}_z \hat{P}_B}$ then yields the transformed Hamiltonian in the form:

$$\hat{\bar{H}} = \hat{U}\hat{H}\hat{U}^\dagger = \underbrace{\begin{bmatrix} \varepsilon & 0 \\ 0 & -\varepsilon \end{bmatrix} + \left(\hat{H}_B - \sum_j \frac{c^2 G_j^2}{\hbar\omega_j} \right) I}_{\hat{H}_0} + \underbrace{\begin{bmatrix} 0 & e^{\hat{P}_B}\left(\Delta + d\hat{R}_B\right)e^{\hat{P}_B} \\ e^{-\hat{P}_B}\left(\Delta + d\hat{R}_B\right)e^{-\hat{P}_B} & 0 \end{bmatrix}}_{\hat{V}} \quad [2]$$

where I is the 2×2 unit matrix. Defining further, for notational compactness, $\hat{V} = e^{\sigma_z \hat{P}_B}\hat{\sigma}_x(\Delta + d\hat{R}_B)e^{-\sigma_z \hat{P}_B}$, and noting that the term $\Sigma_j(c^2 G_j^2/\hbar\omega_j)$ is a constant (and therefore has no influence on any observable properties associated with the quantum dynamics), we can write $\hat{\bar{H}}\varepsilon\hat{\sigma}_z + \hat{H}_B I + \hat{V} \equiv \hat{H}_0 + \hat{V}$.

If standard time-dependent perturbation theory[71,72] is applied to this Hamiltonian, the perturbation theory solution truncated to second-order at a given time can be obtained by solving the integro-differential equation:

$$\frac{\partial}{\partial t}\hat{\bar{\rho}}_S^I(t) = -\frac{i}{\hbar}\mathrm{tr}_B[\hat{V}^I(t), \hat{\bar{\rho}}^I(0)] - \frac{1}{\hbar^2}\int_0^t \mathrm{tr}_B[\hat{V}^I(t),[\hat{V}^I(t'),\hat{\bar{\rho}}^I(t')]] \, dt' \quad (3)$$

where $\hat{\bar{\rho}}^I(t) = e^{i\hat{H}_0 t/\hbar}\hat{\bar{\rho}}(t)e^{-i\hat{H}_0 t/\hbar}$ is the density matrix in the interaction picture, and $\hat{\bar{\rho}}_S^I(t)$ is the reduced density matrix of the system in the interaction picture, with the bath coordinates traced out, i.e., $\hat{\bar{\rho}}_S^I(t) = tr_B[\hat{\bar{\rho}}^I(t)]$. Equation 3 is derived using an initial density matrix that is separable into system and bath coordinates, so that $\hat{\bar{\rho}}(0) = \hat{\bar{\rho}}_S(0)\hat{\rho}_\beta$, where $\hat{\rho}_\beta$ is the thermal density operator of the bath corresponding to $\hat{H}_B$.

In eq 3 above, the perturbation commutators involving $\hat{V}^I(t)$ are the important quantities. $\hat{V}^I(t)$ is obtained by transforming to the interaction picture with respect to $\hat{H}_0$, to give

$$\hat{V}^I(t) = e^{i\hat{H}_0 t/\hbar}Ve^{-i\hat{H}_0 t/\hbar} = \begin{bmatrix} 0 & e^{(it/\hbar)(\varepsilon+\hat{H}_B)}e^{\hat{P}_B}(\Delta + d\hat{R}_B)e^{\hat{P}_B}e^{-(it/\hbar)(-\varepsilon+\hat{H}_B)} \\ e^{(it/\hbar)(-\varepsilon+\hat{H}_B)}e^{-\hat{P}_B}(\Delta + d\hat{R}_B)e^{-\hat{P}_B}e^{-(it/\hbar)(\varepsilon+\hat{H}_B)} & 0 \end{bmatrix} \quad (4)$$

We can simplify this expression by introducing the operators

$$\hat{\bar{\Delta}}_u(t) = e^{(it/\hbar)(u\varepsilon+\hat{H}_B)}e^{u\hat{P}_B}(\Delta + d\hat{R}_B)e^{u\hat{P}_B}e^{-(it/\hbar)(-u\varepsilon+\hat{H}_B)} = e^{(it/\hbar)(2u\varepsilon)}e^{(it/\hbar)\hat{H}_B}e^{u\hat{P}_B}(\Delta + d\hat{R}_B)e^{u\hat{P}_B}e^{-(it/\hbar)\hat{H}_B} \quad (5)$$

where u is defined here and throughout the paper by $u \equiv \pm = \pm 1$. This yields a compact expression for the nonzero terms in $\hat{V}^I(t)$, namely

$$\hat{V}^I(t) = \begin{bmatrix} 0 & \hat{\bar{\Delta}}_+(t) \\ \hat{\bar{\Delta}}_-(t) & 0 \end{bmatrix}$$

By substituting this expression into eq 3, one can write a general small-polaron transformation-based perturbation solution for the reduced system density matrix in terms of bath correlation functions, e.g., for the reduced system matrix element, $\bar{\rho}_{S11}^I$ (which, for notational simplicity, we will subsequently designate as $\bar{\rho}_{11}(t) \equiv \bar{\rho}_{S11}^I(t)$):

$$\frac{\partial}{\partial t}\bar{\rho}_{11}(t) = \frac{2}{\hbar}\mathrm{Im}\{\bar{\rho}_{12}^*(0)\langle\hat{\bar{\Delta}}_+(t)\rangle\} - \frac{2}{\hbar^2}\int_0^t \bar{\rho}_{11}(t')[\mathrm{Re}\langle\hat{\bar{\Delta}}_+(t)\,\hat{\bar{\Delta}}_-(t')\rangle + \mathrm{Re}\langle\hat{\bar{\Delta}}_-(t)\,\hat{\bar{\Delta}}_+(t')\rangle] \, dt' + \frac{2}{\hbar^2}\int_0^t \mathrm{Re}\langle\hat{\bar{\Delta}}_-(t)\,\hat{\bar{\Delta}}_+(t')\rangle \, dt' \quad (6)$$

In obtaining eq 6, a Redfield-type approximation[71] has been made, namely that the density matrix can be factorized into a product of the system and bath variables: $\hat{\bar{\rho}}(t) = \hat{\bar{\rho}}_S(t)\hat{\rho}_\beta$. The notation $\langle\cdots\rangle \equiv \mathrm{tr}_B(\cdots)$ indicates a trace over the bath variables. The first- and second-order perturbation terms have been simplified by using a number of symmetry properties of these time-dependent correlation functions, e.g., that $\hat{\bar{\Delta}}_{-u}(t) = [\hat{\bar{\Delta}}_u(t)]^\dagger$ and $\mathrm{tr}_B\{\hat{\bar{\Delta}}_{-u}(t)\hat{\rho}_\beta\} = \mathrm{tr}_B\{\hat{\bar{\Delta}}_u(t)\hat{\rho}_\beta\}^*$, etc.

For the case considered here (and throughout this paper) the initial density matrix of the system is diagonal and the system is initially taken to be localized on diabatic surface |1⟩. In this case, the initial reduced system density matrix element in the Schrodinger representation, $\rho_{11}(0)$, is taken to be 1 (all other reduced system density matrix elements being 0), and in addition, $\hat{\rho}_\beta$ is taken to be the bath thermal equilibrium density matrix corresponding to $\hat{H}_B$. Equation 6 then simplifies to give

$$\frac{\partial}{\partial t}\bar{\rho}_{11}(t) = -\frac{2}{\hbar^2}\int_0^t \bar{\rho}_{11}(t')[\text{Re}\langle\hat{\tilde{\Delta}}_+(t)\,\hat{\tilde{\Delta}}_-(t')\rangle +$$

$$\text{Re}\langle\hat{\tilde{\Delta}}_-(t)\,\hat{\tilde{\Delta}}_+(t')\rangle]\,dt' + \frac{2}{\hbar^2}\int_0^t \text{Re}\langle\hat{\tilde{\Delta}}_-(t)\,\hat{\tilde{\Delta}}_+(t')\rangle\,dt' \quad (7)$$

This equation is solved numerically in the next section for the case of a two-level system coupled to a dense bath with an Ohmic spectral density:[39] $J(\omega) = (\pi/2)\eta\omega\exp(-\omega/\omega_C) = \Sigma_j(\lambda_j^2/\omega_j)\delta(\omega - \omega_j)$, where η prescribes the strength of the system—bath coupling and ω_C is a cutoff bath oscillator frequency. Solution of the integro-differential equation (eq 7) will be referred to as the nonlocal second-order perturbation solution and denoted henceforth as "PN". In the case where the system dynamics is much slower than the bath dynamics, a time-local solution to eq 7 becomes valid, namely

$$\frac{\partial}{\partial t}\bar{\rho}_{11}(t) = -\frac{2}{\hbar^2}\bar{\rho}_{11}(t)\int_0^t [\text{Re}\langle\hat{\tilde{\Delta}}_+(t)\,\hat{\tilde{\Delta}}_-(t')\rangle +$$

$$\text{Re}\langle\hat{\tilde{\Delta}}_-(t)\,\hat{\tilde{\Delta}}_+(t')\rangle]\,dt' + \frac{2}{\hbar^2}\int_0^t \text{Re}\langle\hat{\tilde{\Delta}}_-(t)\,\hat{\tilde{\Delta}}_+(t')\rangle\,dt' \quad (8)$$

This solution is subsequently referred to as the local, or "PL" solution. Explicit expressions for the relevant correlation functions $\langle\hat{\tilde{\Delta}}_+(t)\,\hat{\tilde{\Delta}}_-(t')\rangle$ and $\langle\hat{\tilde{\Delta}}_-(t)\,\hat{\tilde{\Delta}}_+(t')\rangle$ are given in the Appendix.

3. Numerical Evaluation of the PN and PL Solutions

The ability of theoretical methods to accurately describe non-Condon effects on electron transfer requires that explicit off-diagonal system—bath coupling terms be included in the Hamiltonian. However, an exact solution of the Hamiltonian prescribed in eq 1 is in general not possible. In this section, we study approximate second-order perturbative solutions of eq 1 using the formulas derived in eqs 7 and 8. As has been previously noted,[32−35] an exact solution of eq 1 can be obtained in the special case where the parameters $\{c, d\}$ have the particular ratio (cf. eq 1) $d/c = \Delta/\varepsilon$ or, equivalently, when the scaling constant takes the value $\kappa = 1.0$. A comparison of the approximations in eqs 7 and 8 for this special value of κ allows us to benchmark the perturbation equations in this region of parameter space. Furthermore, in the limit in eq 1 that $\kappa = 0$, the canonical spin-boson Hamiltonian is recovered, and a study of our perturbative solutions in eqs 7 and 8 enable us to benchmark their accuracy in this limit, too.[73,74]

In this section a comparison of the second-order perturbation theory solutions with the corresponding exact solutions is made for a range of parameters and system—bath coupling schemes. It should be noted that in all of our numerical calculations to generate all figures, $\hbar$ is set to 1. In addition, the reduced system density matrix elements obtained from eqs 7 and 8 pertain to the original Schrodinger representation (after back-transforming from the small-polaron Hamiltonian in eq 2) in all figures. The naming conventions used in this section to label the graphs are given in Table 1.

We first consider Hamiltonians in the NCE class ($\kappa = 1$ in eq 1b) and examine the accuracy of the PN and PL methods in comparison to the exact NCE dynamics. In all such cases, the correct non-Boltzmann limit is predicted by the PN approach, while the PL method in general predicts a different long-time limit, which can be significantly incorrect, as illustrated below. The nonlocal perturbation theory methods provide a reasonable approximation to the exact solution of the NCE system in all cases studied here. In particular, the approximate PN solutions preserve the correct non-Boltzmann "trapped" asymptote of the populations attained in the NCE dynamics.

The accuracy of the PN and PL perturbation theory approaches for a specific bath at different temperatures is shown in Figure 1. At early times, both the PN and PL are quite accurate. In general, in the case of a moderate to weakly coupled bath, or at low temperature, the nonlocal PN method can slightly overestimate the amplitude of the oscillations in the reduced system dynamics, e.g., in Figure 1a. As the time is extended out, both the local PL and nonlocal PN approximations asymptote to a long-time limit. As can be seen in Figure 1, the nonlocal PN always converges to the exact NCE long-time limit, which is temperature independent. As shown in previous work,[32−35] the exact long-time limit of the initial site population is $\rho_{11} \rightarrow (\varepsilon^2 + \frac{1}{2}\Delta^2)/(\varepsilon^2 + \Delta^2)$, and for all nondegenerate two-level systems (characterized by $\varepsilon \neq 0$, and hence asymmetric) examined, we find that to within the limits of accuracy of our numerical calculations the PN approximation converges to this exact NCE long-time limit value. The PL approximation in general converges to a different limit for nondegenerate systems. As shown in Figure 1, the long-time limit predicted by the PL method can be significantly different from the exact NCE limit. The long-time PL limit for ρ_{11} when $\kappa = 1$ depends on the temperature of the bath, but it does not in general coincide with the Golden Rule limit value of $[1 - \tanh(\beta\varepsilon)]/2$, which would be predicted for the system in the absence of non-Condon effects (i.e., for the spin-boson model in the nonadiabatic limit).[36]

The general perturbative solutions are obtained by neglecting higher-order terms in the nonadiabatic coupling strength, Δ, which are present in the exact master equation memory kernels.[75] As such, we would expect the accuracy of the associated reduced density matrix to decrease as Δ increases. Figure 2 shows the densities predicted by PN and PL using the system parameters $\varepsilon = 1$, $\kappa = 1$, and $\Delta = 0.4$ and 0.9 (cf. eq 1b), for bath parameters $\beta = 1$, $\eta = 0.16$, and $\omega_c = 7.5$. We can see that for the system with $\Delta = 0.4$ (relatively small Δ) in Figure 2a, both local and nonlocal perturbation methods capture the dynamics of the NCE very well. In particular, they track well in the short time and tend toward similar long-time limits. For larger Δ, e.g., $\Delta = 0.9$ as in Figure 2b, we see much more divergent behavior from the exact dynamics at intermediate to long times, especially for the PL solution. In the long-time limit, the PL asymptotes to a different population from the exact NCE, while the PN limit coincides (as always) with the exact NCE limit. Thus the error in the PL long-time limit is significantly increased as the nonadiabatic coupling element Δ is increased.

In the case of zero non-Condon coupling terms to the bath ($\kappa = 0$) in eq 1, the canonical spin-boson model is recovered.

TABLE 1: Exact and Approximate Solutions of the Generalized Hamiltonian in Eq 1

label	method	description
NCE	non-Condon exact	exact numerical solution of eq 1 where $c/d = \varepsilon/\Delta$
PN	second-order nonlocal perturbation theory	second-order perturbation theory using eq 7
PL	second-order local perturbation theory	second-order perturbation theory using eq 8

Electron Transfer Dynamics in Condensed Phases
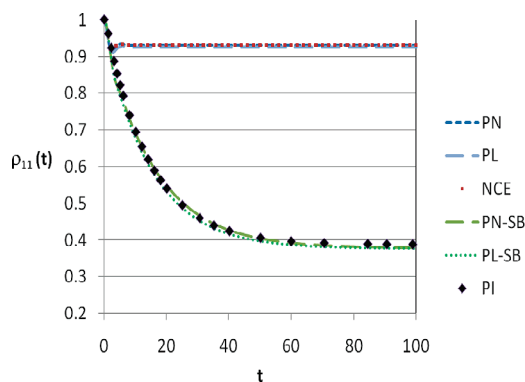
J. Phys. Chem. B, Vol. 113, No. 33, 2009 **11441**
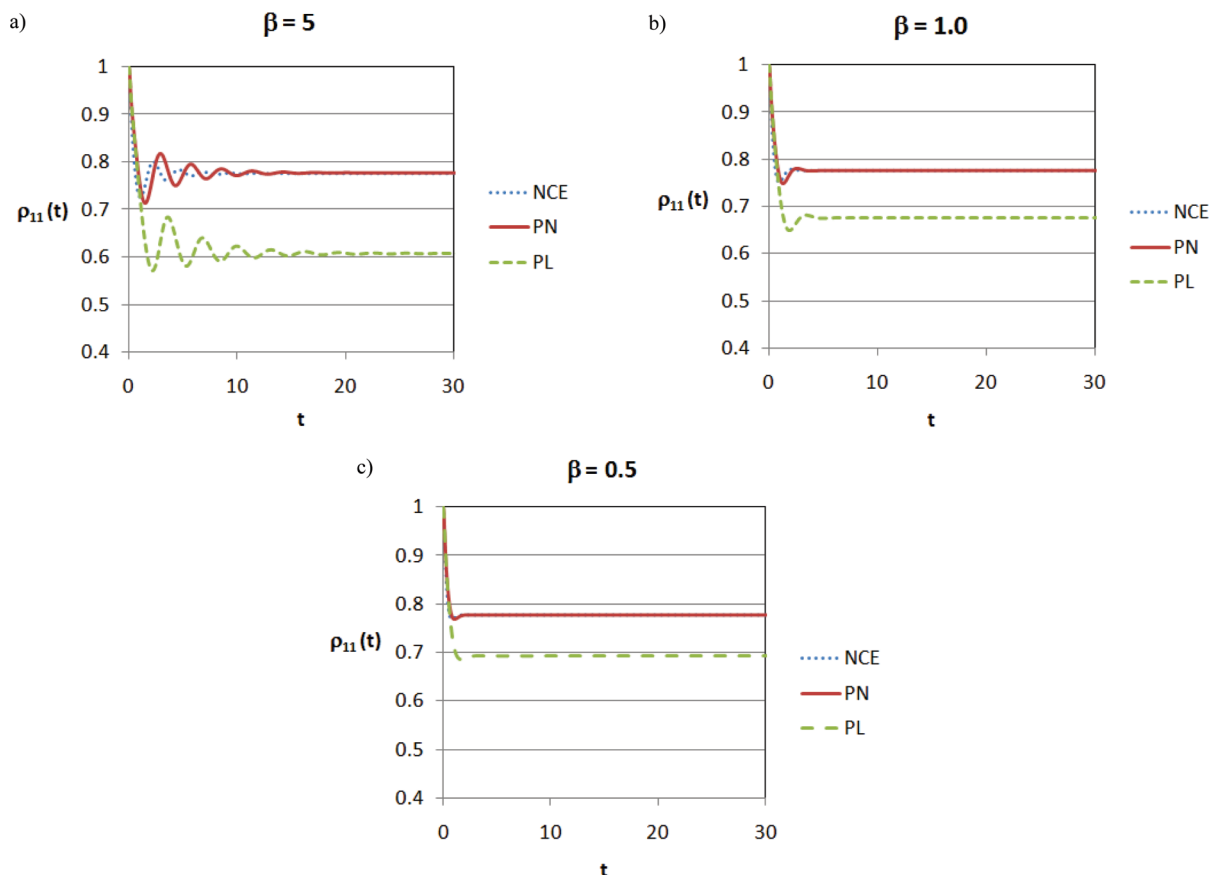
Figure 1. Plot of $\rho_{11}(t)$ vs t for $\hat{H}_S = \begin{bmatrix} 1 & 0.9 \\ 0.9 & -1 \end{bmatrix}$ with $\kappa = 1$. in eq 1 and bath parameters $\eta = 0.16$, $\omega_c = 7.5$ for (a) $\beta = 5$, (b) $\beta = 1$ and (c) $\beta = 0.5$, showing the exact NCE (blue dots), PN nonlocal perturbation solution (red solid), and PL local perturbation solution (green dash).
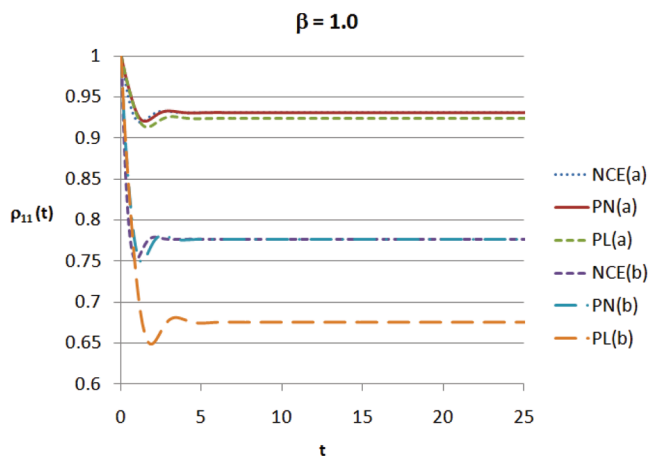
Figure 2. Plot of $\rho_{11}(t)$ vs t with bath parameters $\eta = 0.16$, $\omega_c = 7.5$, and $\beta = 1$, and taking the parameters in eq 1b as $\varepsilon = 1$, $\kappa = 1$ and (a) $\Delta = 0.4$, showing exact NCE (blue dots), PN nonlocal perturbation solution (red solid line), and PL local perturbation solution (green dashed line); and (b) $\Delta = 0.9$, showing exact NCE (purple short dashed line), PN nonlocal perturbation solution (turquoise dot-dashed line), and PL local perturbation solution (orange long dashed line).

Figure 3. Plot of $\rho_{11}(t)$ vs t for $\hat{H}_S = \begin{bmatrix} 0.5 & 0.2 \\ 0.2 & -0.5 \end{bmatrix}$ with bath parameters $\eta = 0.04$, $\omega_c = 7.5$, and $\beta = 0.5$ for two values of κ in eq 1. For the case $\kappa = 1$: exact NCE (red squares), PN (blue dash), and PL (gray long dash). For the case $\kappa = 0$ (spin-boson model limit): path integral (PI) solution (black diamonds), PN-SB (dark green dots), and PL-SB (light green dash-dot).

In this limit, it is also possible to test the performance of the PN and PL in direct comparison with numerically exact solutions.

These numerically exact solutions may be obtained using the transfer matrix path-integral techniques developed by Makri and Makarov[76,77] for the spin-boson model. While the utility of the second-order perturbation theory has been demonstrated in a large number of papers for the spin-boson model,[62−70] for

completeness it is worth showing here, in Figure 3, that both PN and PL approximations work well in the $\kappa = 0$ limit (again, cf. eq 1). In addition, in the case where the value of Δ is relatively small, both PN and PL approximations are relatively accurate in the NCE limit (where $\kappa = 1$). As shown clearly in Figure 3, the PN approximation captures both the NCE long-time limit and the long-time asymptotic behavior of the spin-boson model, which in this range of nonadiabatic coupling predicts the typical Boltzmann asymptotic electronic state populations (reflecting the system asymmetry parameter ε). For

a)

b)
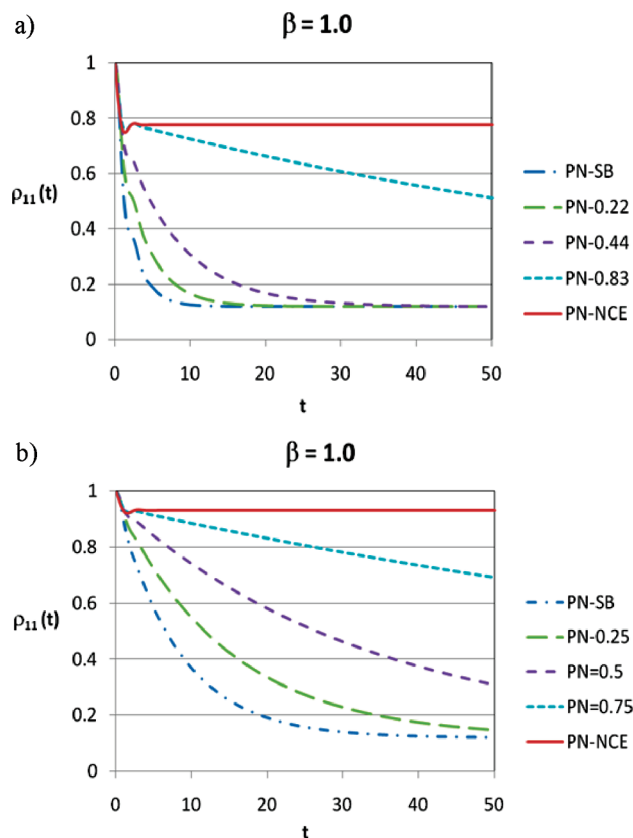
Figure 4. Plot of $\rho_{11}(t)$ vs t with bath parameters $\eta = 0.16$, $\omega_c = 7.5$, and $\beta = 1$ using the PN perturbation solution for (a) $\hat{H}_S = \begin{bmatrix} 1 & 0.9 \\ 0.9 & -1 \end{bmatrix}$ and κ in eq 1 is varied from 0 (spin-boson limit) to 1 (NCE limit, same as in Figure 1b) and (b) $\hat{H}_S = \begin{bmatrix} 1 & 0.4 \\ 0.4 & -1 \end{bmatrix}$ and κ in eq 1 is varied from 0 (spin-boson limit) to 1 (NCE limit).

this particular system Hamiltonian, the NCE long-time limit and the Boltzmann limit are quite distinct.

4. Reduced Dynamics of Generalized Non-Condon Hamiltonians

As demonstrated in Figure 3, in many regions of parameter space the nonlocal second-order perturbation approximation (PN) works well for both the exactly solvable non-Condon Hamiltonian (NCE with $\kappa = 1$ in eq 1) and for the standard spin-boson model (eq 1 with $\kappa = 0$). This suggests that for the particular range of bath parameters studied here, the PN approach should provide an accurate approximation to the reduced system dynamics in the intermediate range as well, e.g., when the scaling parameter of the non-Condon effects is varied from $0 < \kappa < 1$.

In Figure 4, two different system Hamiltonians are chosen (thus defining the basic NCE system in each case). The value of the coupling parameter κ is decreased from the NCE limit where $\kappa = 1$ to the spin-boson limit where $\kappa = 0$ and the PN population dynamics is shown for these two cases as well as for several intermediate values of κ. As can be seen from Figure 4, the population dynamics of these two-level dissipative systems in the intermediate range of the non-Condon parameter κ tend to the Boltzmann long-time limit (which in this case corresponds with the long-time limit of the standard second-order approximations for the reduced system dynamics of the spin-boson Hamiltonian). The approach to this asymptotic limit occurs at a slower rate as the non-Condon terms increase in magnitude

toward the limiting value of $\kappa = 1$. In the limit of the NCE Hamiltonian, the exact NCE long-time limit, which certainly does not correspond to a Boltzmann population distribution, is correctly predicted by the PN approximation. For the PN-predicted population to asymptotically approach this non-Boltzmann limit, we find numerically that the strength of the non-Condon terms must be *exactly* that of the NCE model, i.e., $\kappa = 1$.

5. Analysis of the Long-Time Behavior of Generalized Non-Condon Systems

The numerical studies of the previous section show interesting long-time behavior of the PN and PL approximations. In particular, the PN approximation captures the correct NCE long-time limit, while the PL approximation yields long-time limits that depend on the temperature and that can deviate significantly from the exact solution.

In this section, we examine the properties of the long-time PN and PL solutions of generalized non-Condon Hamiltonians as we adjust the non-Condon scaling term κ to vary from $\kappa = 1$, i.e, the exact NCE model, to $\kappa = 0$, i.e., the standard spin-boson model. This is most conveniently accomplished by examining the Laplace transform (LT) of the relevant integro-differential equations specifying the reduced density dynamics as given in eqs 7 and 8. As a preliminary remark, recall that the limit value of a generic function $f(t)$ at $t = \infty$ (if it exists) is related to its Laplace transform (LT) $\tilde{f}(s) \equiv \int_0^\infty dt\, f(t)e^{-st}$ via the relation $f(\infty) = [s\tilde{f}(s)]_{s\to 0}$.

(a) Long-time limits of PL and PN are identical if the time integrals of the correlation functions converge to a finite nonzero constant. The PN integro-differential equation describing the reduced system dynamics is given by eq 7 above, with $\bar{\rho}_{11}(t)$ designated here as $\rho_{11}(t)$ for notational simplicity:

$$\frac{d}{dt}\rho_{11}(t) = -\int_0^t \rho_{11}(t')[k_{+-}(t-t') + k_{-+}(t-t')]\,dt' +$$
$$\int_0^t k_{-+}(t-t')\,dt' \quad (9a)$$

where the following definitions have been made for notational convenience:

$$k_{+-}(t-t') \equiv \frac{2}{\hbar^2}\text{Re}\langle \hat{\tilde{\Delta}}_+(t)\,\hat{\tilde{\Delta}}_-(t')\rangle$$
$$k_{-+}(t-t') \equiv \frac{2}{\hbar^2}\text{Re}\langle \hat{\tilde{\Delta}}_-(t)\,\hat{\tilde{\Delta}}_+(t')\rangle \quad (9b)$$

From the Appendix, it is easy to see that the two correlations functions above are indeed functions of the time difference $(t - t')$ and that they are analogous to the Golden Rule correlation functions describing the kinetics of the standard spin-boson model.[40] In the Markovian limit, eq 9a reduces to the corresponding PL ordinary differential equation (cf. eq 8):

$$\frac{d}{dt}\rho_{11}(t) = -\rho_{11}(t)\int_0^t [k_{+-}(t-t') + k_{-+}(t-t')]\,dt' +$$
$$\int_0^t k_{-+}(t-t')\,dt' \quad (10)$$

We can establish the long-time limit of eq 9 using Laplace transforms (LTs). Choosing $\rho_{11}(0) = 1$, the LT of eq 9 reads

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$$s\tilde{\rho}_{11}(s) - 1 = -[\tilde{k}_{+-}(s) + \tilde{k}_{-+}(s)]\tilde{\rho}_{11}(s) + \frac{\tilde{k}_{-+}(s)}{s}$$

Rearranging this yields

$$\tilde{\rho}_{11}(s) = \frac{1}{(s + [\tilde{k}_{+-}(s) + \tilde{k}_{-+}(s)])}\left(1 + \frac{\tilde{k}_{-+}(s)}{s}\right) \qquad (11)$$

Defining $\tilde{k}_{+-}(0) = \int_0^\infty k_{+-}(t)\,dt \equiv k_{+-}$ and $\tilde{k}_{-+}(0) = \int_0^\infty k_{-+}(t)\,dt \equiv k_{-+}$, we can draw the following general conclusions:

(1) If k_{+-}, k_{-+} are finite, and k_{-+} is nonzero, then the formula noted above yields for the long-time value of $\rho_{11}(t)$ evolved according to the PN integro-differential equation: $\rho_{11}(\infty) = k_{-+}/(k_{+-} + k_{-+})$. Note that this is exactly the same limiting value obtained from the PL differential eq 10 under the same conditions. Moreover, from the basic structure of Golden Rule rate constants, the Boltzmann distribution limit value of $\rho_{11}(\infty)$ noted in section 3 above is predicted, for any value of κ. Indeed, our numerical results are consistent with this prediction. (Since $k_{-+} = 0$, when $\kappa = 1$, the PN approximation is *not* guaranteed to generate long-time Boltzmann electronic state populations in this special case, as discussed below.)

(2) If both $k_{+-} = k_{-+} = 0$, then the limit $s \to 0$ has to be taken more carefully. In this situation we expand the LT of the correlation functions as

$$\tilde{k}_{-+}(s) = \tilde{k}_{-+}(0) + \tilde{k}_{-+}'(0)s + \dots$$

where

$$\tilde{k}_{-+}'(0) = \left[\frac{\partial}{\partial s}\int_0^\infty dt\, e^{-st}k_{-+}(t)\right]_{s\to 0} = -\int_0^\infty dt\, k_{-+}(t)t$$

and analogously for $\tilde{k}_{+-}(s)$. Then, since $\tilde{k}_{-+}(0) = \tilde{k}_{+-}(0) = 0$:

$$\rho_{11}(\infty) = [s\tilde{\rho}_{11}(s)]_{s\to 0} = \frac{1 + \tilde{k}_{-+}'(0)}{1 + \tilde{k}_{+-}'(0) + \tilde{k}_{-+}'(0)} =$$

$$\frac{1 - \int_0^\infty dt\, k_{-+}(t)t}{1 - \int_0^\infty dt\, k_{+-}(t)t - \int_0^\infty dt\, k_{-+}(t)t} \qquad (12)$$

These integrals can be checked numerically for the specific Hamiltonians studied in section 3. Numerical tests show that the integrals associated with the rate constants $\tilde{k}_{+-}(0)$ and $\tilde{k}_{-+}(0)$ are indeed zero for the NCE limit (where $\kappa = 1$). The numerical data also confirms the assertion that in the NCE limit the PN long-time limit is given by eq 12 and, furthermore, that this limit is in general numerically distinct from the PL asymptote.

(b) The Laplace transforms $\tilde{k}_{+-}(0)$ and $\tilde{k}_{-+}(0)$ are exactly zero in the Quasi-classical (Lax) limit when $\kappa = 1$. Consider the generic electron transfer Hamiltonian:

$$\hat{H} = \hat{h}_1|1\rangle\langle 1| + \hat{h}_2|2\rangle\langle 2| + \mu(\rightarrow\cdot)[|1\rangle\langle 2| + |2\rangle\langle 1|] \qquad (13)$$

Here $\hat{h}_{1,2}$ are diabatic nuclear coordinate Hamiltonians with the structure $\hat{h}_{1,2} = \vec{p}^2/2 + V_{1,2}(\vec{x})$, where $\vec{x} = (x_1, \dots, x_n)$ is the vector of nuclear coordinates (n Cartesian coordinates in all),

and $\vec{p}$ is the corresponding vector of Cartesian momenta. (The masses associated with all coordinates can be taken as unity with no loss of generality.) Note that the two diabatic Hamiltonians are in general characterized by different potential energy surfaces (PESs), with $V_1(\vec{x})$ corresponding to electronic state $|1\rangle$ and $V_2(\vec{x})$ to electronic state $|2\rangle$. Moreover, $\mu(\vec{x})$ is the appropriate nonadiabatic coupling function, which in general depends on the nuclear coordinates.

Assume that the system is prepared in thermal equilibrium on the ground electronic state PES, i.e., the initial electro-nuclear density matrix is given by $\bar{\rho}(0) = |1\rangle\langle 1|\hat{\rho}_{\beta,1}$, where the nuclear coordinate density matrix operator is the Boltzmann operator corresponding to $\hat{h}_1$: $\hat{\rho}_{\beta,1} = \exp[-\beta\hat{h}_1]/\mathrm{tr}\{\exp[-\beta\hat{h}_1]\}$ with the trace being taken over nuclear coordinates. Then the Fermi Golden Rule rate constant for transition of electronic population from $|1\rangle$ to $|2\rangle$ electronic states can be computed as the time integral of an appropriate correlation function, namely

$$k_{1\to 2}(T) = \int_{-\infty}^{\infty} dt\, \mathrm{tr}\{\hat{\rho}_{\beta,1}\mu(\vec{\hat{x}})e^{-i\hat{h}_2 t}\mu(\vec{\hat{x}})e^{i\hat{h}_1 t}\} \qquad (14)$$

[Note: For notational simplicity, we set $\hbar = 1$ throughout in this section.] When the potential energy surfaces $V_{1,2}(\vec{x})$ are strongly displaced from each other and/or the system temperature is sufficiently high, the correlation function on the rhs of eq 14 can be simplified by dropping the kinetic energy terms from the diabatic Hamiltonians $\hat{h}_{1,2}$ which appear in the temporal propagator factors. (Essentially, this amounts to ignoring the noncommutability of momentum and position operators in the evaluation of the correlation function.) This generates the following approximation for the ET rate constant:

$$k_{1\to 2}^{\mathrm{Lax}}(T) = \int_{-\infty}^{\infty} dt\, \mathrm{tr}\{\hat{\rho}_{\beta,1}\mu^2(\vec{\hat{x}})^{-i[V_2(\vec{\hat{x}}) - V_1(\vec{\hat{x}})]t}\} \qquad (15a)$$

$$= \int_{-\infty}^{\infty} dt \int d\vec{x}\, \rho_{\beta,1}(\vec{x})\, \mu^2(\vec{x})^{-i[V_2(\vec{x}) - V_1(\vec{x})]t} \qquad (15b)$$

$$= 2\pi \int d\vec{x}\, \rho_{\beta,1}(\vec{x})\, \mu^2(\vec{x})\, \delta(V_2(\vec{x}) - V_1(\vec{x})) \qquad (15c)$$

where in eq 15b $\rho_{\beta,1}(\vec{x}) = \langle\vec{x}|\hat{\rho}_{\beta,1}|\vec{x}\rangle$ and $\int d\vec{x}$ means integrate over all nuclear coordinate space (from $-\infty$ to $+\infty$ over each coordinate).

Such an approximation was proposed many years ago by Lax,[78] and thus we will term eq 15 the Lax approximation in the following exposition.

Equation 15 can be applied for any diabatic PESs and nonadiabatic coupling function. In the present paper we are concerned with particular functional forms for these quantities. Let us write the ET Hamiltonian of interest to us here as

$$\hat{H} = \begin{pmatrix} \varepsilon & \Delta \\ \Delta & -\varepsilon \end{pmatrix} + \begin{pmatrix} 1 & \kappa\left(\dfrac{\Delta}{\varepsilon}\right) \\ \kappa\left(\dfrac{\Delta}{\varepsilon}\right) & -1 \end{pmatrix} \sum_j \lambda_j \hat{x}_j + \hat{H}_{\mathrm{B}} \qquad (16)$$

where H_{B} the simple harmonic oscillator Hamiltonian $\hat{H}_{\mathrm{B}} = \Sigma_j[\hat{p}_j^2/2 + \omega_j^2\hat{x}_j^2/2]$, the sum being taken over all oscillator modes, and κ is a real-valued parameter in the range $0 < \kappa < 1$. In particular, $\kappa = 0$ corresponds to the Condon approximation and, because of the structure of the diabatic PESs, the canonical spin-boson model; furthermore, $\kappa = 1$ corresponds to the NCE Hamiltonian.

Within this generalized spin-boson model we can explicitly evaluate

$$\mu(\vec{x}) = \Delta\left(1 + \frac{\kappa}{\varepsilon}\sum_j \lambda_j x_j\right)$$

$$V_2(\vec{x}) - V_1(\vec{x}) = -2\varepsilon\left(1 + \frac{1}{\varepsilon}\sum_j \lambda_j x_j\right)$$

When $\kappa = 1$, we see that for all coordinate configurations where $V_2(\vec{x}) - V_1(\vec{x}) = 0$, it is also true that $\mu(\vec{x}) = 0$. Stated alternatively, $\mu(\vec{x}) = 0$ all along the crossing seam of the two diabatic PESs. Since the energy conserving delta function in eq 15c vanishes precisely along the same crossing seam, the Lax approximation to the ET rate constant vanishes, too, i.e., $k_{1\rightarrow2}^{\text{Lax}}(T) = 0$.

Owing to the relative simplicity of the rate constant calculation within the Lax approximation, it behooves us to attempt to compute the corresponding rate constant for any value of κ in the interval $0 < \kappa < 1$. Explicit calculation for nonzero values of κ is most easily carried out by manipulating the Lax time correlation function. Thus, it is useful to define

$$C^{\text{Lax}}(t) = \int d\vec{x}\, \rho_{\beta,1}(\vec{x})\, \mu^2(\vec{x})^{-i[V_2(\vec{x})-V_1(\vec{x})]t} \quad (17)$$

The Lax rate constant is then given by the following time integral over this time correlation function: $k_{1\rightarrow2}^{\text{Lax}} = \int_{-\infty}^{\infty} dt\, C^{\text{Lax}}(t)$. Let us begin with the case that $\mu(\vec{x})$ is a constant, $\mu(\vec{x}) = \Delta$, i.e., the Condon approximation. (Again, this corresponds to the case that $\kappa = 0$, or, equivalently, the standard spin-boson model.) Note that the thermal density matrix is a product of 1D harmonic oscillator mode factors:

$$\rho_{1,\beta}^{(j)}(x_j) =$$
$$\left[\frac{\omega_j \tanh(\beta\omega_j/2)}{\pi}\right]^{1/2} \exp\{-\omega_j \tanh(\beta\omega_j/2)[x_j + \lambda_j/\omega_j^2]^2\}$$

Furthermore, the potential difference term in the exponent of eq 17 is linear in the bath coordinates as noted above. Hence $C^{\text{Lax}}(t)$ factors into 1D Gaussian integrals which can each be performed and then conjoined into the net result:

$$C^{\text{Lax}}(t) =$$
$$\Delta^2 \exp\left\{-t^2 \sum_j \frac{\lambda_j^2}{\omega_j \tanh(\beta\omega_j/2)} - 2it\sum_j \frac{\lambda_j^2}{\omega_j^2} + 2i\varepsilon t\right\}$$
$$(18)$$

which is itself a Gaussian in the time variable. Some insight into the structure of this formula can be obtained by observing that the quantity $E_r = 2\sum_j \lambda_j^2/\omega_j^2$ is the reorganization energy for the electron transfer process, i.e., the potential energy above the minimum energy of V_2 that the system attains when it is (suddenly) transferred to electronic state $|2\rangle$ at the equilibrium configuration of V_1. In a similar spirit, it is useful to note that at high T (s.t. $\beta\omega_j \ll 1$ for all modes in the bath) the coefficient of t^2 also becomes proportional to E_r. Specifically, let us define

$$\sum_j \frac{\lambda_j^2}{\omega_j \tanh(\beta\omega_j/2)} \equiv k_B T_{\text{eff}} E_r \quad (19)$$

Here T_{eff} is an effective temperature which approaches the system temperature T at high temperatures. In terms of these quantities, the Lax correlation function takes the form

$$C^{\text{Lax}}(t) = \Delta^2 \exp\{-E_r k_B T_{\text{eff}} t^2 + it[2\varepsilon - E_r]\}$$

Integrating this in time from $-\infty$ to $+\infty$ gives the Lax rate constant in the Condon approximation (i.e., for the canonical spin-boson model):

$$k_{1\rightarrow2}^{\text{Lax}}(T) = \Delta^2\left[\frac{\pi}{E_r k_B T_{\text{eff}}}\right]^{1/2} \exp\left\{\frac{-(E_r - 2\varepsilon)^2}{4E_r k_B T_{\text{eff}}}\right\} \quad (20)$$

which, in the high temperature limit (s.t. $T_{\text{eff}} \rightarrow T$) becomes the celebrated Marcus formula for the nonadiabatic $|1\rangle \rightarrow |2\rangle$ ET rate constant.[12] A similar analysis, reversing the roles of the two electronic states, yields the corresponding $|2\rangle \rightarrow |1\rangle$ rate constant:

$$k_{2\rightarrow1}^{\text{Lax}}(T) = \Delta^2\left[\frac{\pi}{E_r k_B T_{\text{eff}}}\right]^{1/2} \exp\left\{\frac{-(E_r + 2\varepsilon)^2}{4E_r k_B T_{\text{eff}}}\right\} \quad (21)$$

Given the Lax approximation rate constants relevant to the canonical spin-boson model ($\kappa = 0$) and NCE limit Hamiltonian ($\kappa = 1$), we wish to understand how the rate constant interpolates between its $\kappa = 0$ value, i.e., the standard high-T ET rate constant in the canonical spin-boson model, and its $\kappa = 1$ value, namely, 0. Thus we need to evaluate the integral on the rhs of eq 15a for the case that $\mu(\vec{x}) = \Delta(1 + (\kappa/\varepsilon)\sum_j\lambda_j x_j)$, with $0 < \kappa < 1$. Hence we need to perform the integrals

$$J_p = \int_{-\infty}^{\infty} dt \int d\vec{x}\, \rho_{1,\beta}(\vec{x})\left(\sum_j \lambda_j x_j\right)^p \exp\left\{2i\left(\sum_j \lambda_j x_j + \varepsilon\right)t\right\}$$
$$(22)$$

for $p = 0-2$. The case that $p = 0$ (Condon approximation, or equivalently, the canonical spin-boson model) has been evaluated above. The cases $p = 1, 2$ are new. They can be handled via a generating function method, i.e., by noting that

$$J_p = \frac{1}{(2i)^p}\left[\frac{\partial^p I(\Gamma)}{\partial \Gamma^p}\right]_{\Gamma=0}$$

with $I(\Gamma) \equiv \int_{-\infty}^{\infty} dt\, C(t,\Gamma)$ and

$$C(t,\Gamma) \equiv$$
$$\Delta^2 \int d\vec{x}\, \rho_{g,\beta}(\vec{x}) \exp\left\{2i\left(\varepsilon + \sum_j \lambda_j x_j\right)t + 2i\Gamma\sum_j \lambda_j x_j\right\}$$

Just as in the Condon limit case $\Gamma = 0$ analyzed above, for any value of Γ this correlation function factors into 1D Gaussian integrals (one for each mode), each of which can be performed analytically. Assembling the resultant product of 1D factors yields

$$C(t,\Gamma) = \Delta^2 \exp\left\{ -(t+\Gamma)^2 \sum_j \frac{\lambda_j^2}{\omega_j \tanh(\beta\omega_j/2)} - \right.$$

$$\left. 2i(t+\Gamma)\sum_j \frac{\lambda_j^2}{\omega_j^2} + 2i\varepsilon t \right\}$$

Subsequently, we can integrate this correlation function over all time to give the following simple result for $I(\Gamma)$:

$$I(\Gamma) = \exp\{-2i\varepsilon\Gamma\} k_{1\to2}^{\text{Lax}}(T)$$

where $k_{1\to2}^{\text{Lax}}(T)$ is the Condon limit rate constant noted in eq 20 above. Thus, we evaluate $J_p = (-\varepsilon)^p k_{1\to2}^{\text{Lax}}(T)$, $p = 0, 1, 2, \dots$. Composing the final Lax approximation formula for the rate constant at arbitrary κ:

$$k_{1\to2}^{\text{Lax}}(\kappa,T) = \left[1 + 2\frac{\kappa}{\varepsilon}(-\varepsilon) + \left(\frac{\kappa}{\varepsilon}\right)^2 \varepsilon^2 \right] k_{1\to2}^{\text{Lax}}(T) =$$

$$[1-\kappa]^2 k_{1\to2}^{\text{Lax}}(T) \qquad (23a)$$

Note that this formula interpolates properly between the desired limits at $\kappa = 0$ and $\kappa = 1$. Finally, exchanging the roles of $|1\rangle$ and $|2\rangle$ in the analysis leads to the following Lax approximation to the corresponding reverse rate constant:

$$k_{2\to1}^{\text{Lax}}(\kappa,T) = [1-\kappa]^2 k_{2\to1}^{\text{Lax}}(T) \qquad (23b)$$

Thus for fixed T, the ratio $k_{1\to2}^{\text{Lax}}(\kappa,T)/k_{2\to1}^{\text{Lax}}(\kappa,T)$ is independent of κ.

In Figure 5 we plot $(k_{+-})^{1/2}$ vs κ for system and parameters considered in Figure 1 at two inverse temperatures. [Note: k_{+-} of section 5a corresponds to $k_{1\to2}$ here.] The full quantum time correlation functions (cf. eq 9b) were used to generate the numerical results presented in Figure 5. For $\beta = 0.02$, the Lax limit formulas above should be quantitatively accurate, because the full quantum time correlation functions (TCFs) decay rapidly with time and the temperature is high. Indeed, we find quantitative agreement between the Lax limit rate constant formulas obtained above and numerical results based on the
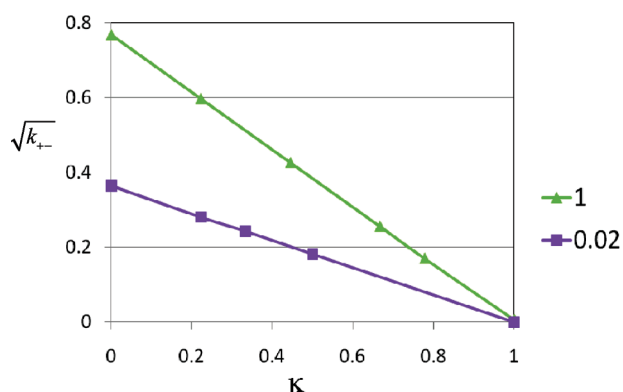
Figure 5. Plot of the square root of the rate constant, $(k_{+-})^{1/2}$, vs κ with bath parameters $\eta = 0.16$ and $\omega_c = 7.5$ using the PN perturbation solution for $\hat{H}_S = \begin{bmatrix} 1 & 0.9 \\ 0.9 & -1 \end{bmatrix}$, where κ in eq 1 is varied from 0 (spin-boson limit) to 1 (NCE limit): $\beta = 1$ (green triangles) and $\beta = 0.02$ (purple squares). Note the linear scaling at both temperatures.

full quantum TCFs in the entire range $0 < \kappa < 1$. Interestingly, we find the *same* scaling for the lower temperature case $\beta = 1$, i.e., $k_{+-}(\kappa,T)/k_{+-}(0,T) = (1 - \kappa)^2$, even though examination of the TCFs for $\kappa = 0$ (not shown) reveals that they do not fall particularly well within the Lax limit (where they would be given by the Gaussian function noted in eq 18). This leads us to conjecture that the scaling of $k_{+-}(\kappa,T)/k_{+-}(0,T)$ just noted holds for *any* set of system and bath parameters (whether they fall within the Lax limit regime or not), although we have not yet succeeded in proving this assertion analytically. The most important point for present purposes is that the Golden Rule rate constants appear to vanish smoothly as $\kappa = 1$ is approached from below (vanishing precisely only at this limit value) for all sets of system and bath parameters within the class of model Hamiltonians under study herein.

6. Conclusions

The focus of this paper has been to develop and test the accuracy of approximate perturbation theory solutions for the reduced dynamics of generalized Hamiltonians where a discrete two-level system is coupled to a condensed-phase bath. These Hamiltonians have been used to study the quantum dynamics of two-level systems beyond the Condon approximation by including off-diagonal system–bath coupling terms linear in the bath coordinates (such terms are excluded in the Condon approximation). Differential equations describing the dynamics of the reduced density matrix have been developed for Hamiltonians of this general form using second-order time-perturbation theory with a small polaron transformation. A scaling term, κ, which quantifies the strength of the non-Condon coupling terms, allows us to study a continuous range systems that lie between two exactly solvable limits: the canonical spin-boson model (for which numerically exact solution procedures exist in certain regions of parameter space) and the exact non-Condon model (NCE) studied recently in the context of electron transfer.

After successfully benchmarking our second-order perturbation theory solutions of the general Hamiltonian in two important limits, we have been able to use these approximate solutions with some confidence to study more general non-Condon Hamiltonians, namely, where the coupling strength to the non-Condon terms interpolates between the two aforementioned limits. These generalized non-Condon Hamiltonians display rich long-time behavior that we have been able to understand using a combination of numerical and analytical tools. Our conclusions are that in general the nonlocal second-order perturbation equations (PN) are quite accurate in both the short-time and long-time limits for a wide range of parameter choices. The local Markovian limit of these equations (PL) is less reliable in terms of capturing the long-time dynamics at the NCE limit; however, it is quite accurate for other values of κ (at least for bath spectral densities and nonadiabatic coupling strengths where the Markovian approximation is valid), where it correctly predicts long-time relaxation to the Boltzmann limit.

The present study highlights an unusual property of the NCE Hamiltonian, namely, that even though the primary (two-level) system is coupled to a large harmonic oscillator bath (reservoir) that is prepared in a thermal equilibrium state at temperature T, long-time Schrödinger dynamics of the system–bath supersystem does *not* generate Boltzmann equilibrium at this temperature T but rather produces a steady state with completely non-Boltzmann properties. Our numerical and analytical studies here suggest that this property holds only for Hamiltonians with precisely the NCE structure, and that even a small perturbation

away from this structure (e.g., κ slightly less than 1) leads to a recovery of long-time Boltzmann populations of the diabatic electronic states. The odd non-Boltzmann "trapping" characteristic of the NCE Hamiltonian appears to stem from the precise vanishing of the forward and backward Golden Rule rate constants, which is in turn connected with the vanishing of the nonadiabatic coupling function along the crossing seam that characterizes the two diabatic potential surfaces.

Appendix

In the Appendix, we evaluate the second-order perturbation solutions explicitly.

The second-order perturbation term is $-(1/\hbar^2)\int_0^t \text{tr}_B[\hat{V}^I(t),[\hat{V}^I(t'),\hat{\bar{\rho}}^I(t')]]\,dt'$. To simplify this term, we must evaluate the second-order commutator $\text{tr}_B[\hat{V}^I(t),[\hat{V}^I(t'),\bar{\rho}^I(t')]]$. If we assume that

$$\hat{\bar{\rho}}^I(t) = \hat{\bar{\rho}}_S^I(t)\hat{\rho}_\beta = \begin{bmatrix} \rho_{11}(t) & \rho_{12}(t) \\ \rho_{21}(t) & \rho_{22}(t) \end{bmatrix}\hat{\rho}_\beta$$

then this term can be found as follows:

$$[\hat{V}^I(t),[\hat{V}^I(t'),\hat{\bar{\rho}}^I(t')]] = \hat{V}^I(t)[\hat{V}^I(t'),\hat{\bar{\rho}}^I(t')] - [\hat{V}^I(t'),\hat{\bar{\rho}}^I(t')]\hat{V}^I(t) =$$

$$\begin{bmatrix} (\hat{\bar{\Delta}}_+(t)\,\hat{\bar{\Delta}}_-(t')\hat{\rho}_\beta\rho_{11} - \hat{\bar{\Delta}}_+(t)\hat{\rho}_\beta\rho_{22}\hat{\bar{\Delta}}_-(t')) & (\hat{\bar{\Delta}}_+(t)\,\hat{\bar{\Delta}}_-(t')\hat{\rho}_\beta\rho_{12} - \hat{\bar{\Delta}}_+(t)\hat{\rho}_\beta\rho_{21}\hat{\bar{\Delta}}_+(t')) \\ (\hat{\bar{\Delta}}_-(t)\,\hat{\bar{\Delta}}_+(t')\hat{\rho}_\beta\rho_{21} - \hat{\bar{\Delta}}_-(t)\hat{\rho}_\beta\rho_{12}\hat{\bar{\Delta}}_-(t')) & (\hat{\bar{\Delta}}_-(t)\,\hat{\bar{\Delta}}_+(t')\hat{\rho}_\beta\rho_{22} - \hat{\bar{\Delta}}_-(t)\hat{\rho}_\beta\rho_{11}\hat{\bar{\Delta}}_+(t')) \end{bmatrix} -$$

$$\begin{bmatrix} (\hat{\bar{\Delta}}_+(t')\hat{\rho}_\beta\rho_{22}\hat{\bar{\Delta}}_-(t) - \hat{\rho}_\beta\rho_{11}\hat{\bar{\Delta}}_+(t')\,\hat{\bar{\Delta}}_-(t)) & (\hat{\bar{\Delta}}_+(t')\hat{\rho}_\beta\rho_{21}\hat{\bar{\Delta}}_+(t) - \hat{\rho}_\beta\rho_{12}\hat{\bar{\Delta}}_-(t')\,\hat{\bar{\Delta}}_+(t)) \\ (\hat{\bar{\Delta}}_-(t')\hat{\rho}_\beta\rho_{12}\hat{\bar{\Delta}}_-(t) - \hat{\rho}_\beta\rho_{21}\hat{\bar{\Delta}}_+(t')\,\hat{\bar{\Delta}}_-(t)) & (\hat{\bar{\Delta}}_-(t')\hat{\rho}_\beta\rho_{11}\hat{\bar{\Delta}}_+(t) - \hat{\rho}_\beta\rho_{22}\hat{\bar{\Delta}}_-(t')\,\hat{\bar{\Delta}}_+(t)) \end{bmatrix}$$

Then, e.g., the (1,1) element of the trace over the bath coordinates of the second-order interaction term is

$$\text{tr}_B\{(\hat{\bar{\Delta}}_+(t)\,\hat{\bar{\Delta}}_-(t')\hat{\rho}_\beta\rho_{11} - \hat{\bar{\Delta}}_+(t)\hat{\rho}_\beta\rho_{22}\hat{\bar{\Delta}}_-(t')) - (\hat{\bar{\Delta}}_+(t')\hat{\rho}_\beta\rho_{22}\hat{\bar{\Delta}}_-(t) - \hat{\rho}_\beta\rho_{11}\hat{\bar{\Delta}}_+(t')\,\hat{\bar{\Delta}}_-(t))\}$$

Since it can be shown that $\langle\hat{\bar{\Delta}}_+(t)\hat{\bar{\Delta}}_-(t')\rangle = \langle\hat{\bar{\Delta}}_+(t')\hat{\bar{\Delta}}_-(t)\rangle^*$, we see that this trace becomes

$$= \rho_{11}[2\text{Re}\langle\hat{\bar{\Delta}}_+(t)\,\hat{\bar{\Delta}}_-(t')\rangle + 2\text{Re}\langle\hat{\bar{\Delta}}_-(t)\,\hat{\bar{\Delta}}_+(t')\rangle] - 2\text{Re}\langle\hat{\bar{\Delta}}_-(t)\,\hat{\bar{\Delta}}_+(t')\rangle$$

Similarly, all the reduced density matrix elements can be obtained by evaluation of the bath correlation functions:

$$\langle\hat{\bar{\Delta}}_+(t)\,\hat{\bar{\Delta}}_+(t')\rangle, \langle\hat{\bar{\Delta}}_+(t)\,\hat{\bar{\Delta}}_-(t')\rangle, \langle\hat{\bar{\Delta}}_-(t)\,\hat{\bar{\Delta}}_+(t')\rangle \text{ and } \langle\hat{\bar{\Delta}}_-(t)\,\hat{\bar{\Delta}}_-(t')\rangle$$

Using standard boson algebra techniques, these correlation functions may be determined from the following general formulas: If $u, v \equiv \pm = \pm 1$, then

$$\text{tr}_B\{\hat{\bar{\Delta}}_u(t)\,\hat{\bar{\Delta}}_v(t')\hat{\rho}_\beta\} \equiv e^{(i/\hbar)2\varepsilon(ut+vt')}\,\text{tr}_B\{e^{(i\tau/\hbar)\hat{H}_B}e^{u\hat{P}_B}(\Delta + d\hat{R}_B)e^{u\hat{P}_B}e^{-(i\tau/\hbar)\hat{H}_B}e^{v\hat{P}_B}(\Delta + d\hat{R}_B)e^{v\hat{P}_B}\hat{\rho}_\beta\}$$

$$= \left\langle\hat{\bar{\Delta}}_u(t)\,\hat{\bar{\Delta}}_v(t')\right\rangle$$

$$= e^{(i/\hbar)2\varepsilon(ut+vt')}[\Delta^2\text{tr}_B\{e^{(i\tau/\hbar)\hat{H}_B}e^{2u\hat{P}_B}e^{-(i\tau/\hbar)\hat{H}_B}e^{2v\hat{P}_B}\hat{\rho}_\beta\} + \Delta d\text{tr}_B\{e^{(i\tau/\hbar)\hat{H}_B}e^{2u\hat{P}_B}e^{-(i\tau/\hbar)\hat{H}_B}e^{v\hat{P}_B}\hat{R}_Be^{v\hat{P}_B}\hat{\rho}_\beta\}+$$

$$d\Delta\text{tr}_B\{e^{(i\tau/\hbar)\hat{H}_B}e^{u\hat{P}_B}\hat{R}_Be^{u\hat{P}_B}e^{-(i\tau/\hbar)\hat{H}_B}e^{2v\hat{P}_B}\hat{\rho}_\beta\} + d^2\text{tr}_B\{e^{(i\tau/\hbar)\hat{H}_B}e^{u\hat{P}_B}\hat{R}_Be^{u\hat{P}_B}e^{-(i\tau/\hbar)\hat{H}_B}e^{v P_B}\hat{R}_Be^{v\hat{P}_B}\hat{\rho}_\beta\}]$$

$$= e^{(i/\hbar)2\varepsilon(ut+vt')}e^{-2\sum_{m=1}^n g_m^2(r_m^2(u^2+2uvf_m^*+v^2)+s_m^2(u^2+2uvf_m+v^2))}[\Delta^2 +$$

$$2\Delta d(u-v)\sum_{k=1}^n G_kg_k[f_ks_k^2 - f_k^*r_k^2]+d^2\sum_k G_k^2(f_k^*r_k^2 + f_ks_k^2) - d^24uv(\sum_{k=1}^n G_kg_k(f_k^*r_k^2 - f_ks_k^2))^2]$$

where $\tau = t - t'$, n is the number of bath modes, and the following definitions have been used:

$$g_j = \frac{cG_j}{\hbar\omega_j} \qquad G_j = \lambda_j\sqrt{\frac{\hbar}{2\omega_j}}$$

$$f_k = e^{it\omega_k} \qquad \bar{n}_k = \frac{1}{e^{\beta\hbar\omega_k} - 1}$$

$$r_k = \sqrt{1 + \bar{n}_k} \quad s_k = \sqrt{\bar{n}_k}$$

It is important to note that this correlation expression is distinguished from that of the analogous small polaron correlation function obtained for the standard spin-boson model[39] by the addition of the three terms involving the parameter d.

References and Notes

(1) Marcus, R. A. *J. Chem. Phys.* **1965**, *43*, 679.
(2) Levich, V.; Dogonadze, R. R. *Dokl. Acad. Nauk SSSR* **1959**, *124*, 123. Levich, V. G.; Dogonadze, R. R. *Dokl. Acad. Nauk SSSR* **1960**, *133*, 158.
(3) Sparpaglione, M.; Mukamel, S. *J. Chem. Phys.* **1988**, *88*, 3263.
(4) Newton, M. D. *Chem. Rev.* **1991**, *91*, 767.
(5) Bader, J. S.; Kuharski, R. A.; Chandler, D. *J. Chem. Phys.* **1990**, *93*, 230.
(6) Gehlen, J. N.; Chandler, D. *J. Chem. Phys.* **1992**, *97*, 4958.
(7) Nitzan, A. *J. Chem. Phys. Lett.* **1972**, *15*, 350.
(8) Nitzan, A.; Jortner, J. *J. Chem. Phys.* **1973**, *58*, 2412–2434.
(9) Mukamel, S.; Oppenheim, I.; Ross, J. *Phys. Rev. A* **1978**, *17*, 1988–1998.
(10) Mukamel, S. *Chem. Phys.* **1979**, *37*, 33–47.
(11) Skourtis, S.; Archontis, G.; Xie, Q. *J. Chem. Phys.* **2001**, *115*, 9444.
(12) Garg, A.; Onuchic, J. N.; Ambegaokar, V. *J. Chem. Phys.* **1985**, *83*, 4491–4503.
(13) Benjamin, I.; Evans, D.; Nitzan, A. *J. Chem. Phys.* **1997**, *106*, 1291.
(14) Benjamin, I.; Evans, D.; Nitzan, A. *J. Chem. Phys.* **1997**, *106*, 6647.
(15) Newton, M. D. *Theor. Chem. Acc.* **2003**, *110*, 307.
(16) Nitzan, A. *Annu. Rev. Phys. Chem.* **2001**, *52*, 681.
(17) Jang, S.; Newton, M. D. *J. Chem. Phys.* **2005**, *122*, 024501.
(18) Small, D. W.; Matyushov, D. V.; Voth, G. A. *J. Am. Chem. Soc.* **2003**, *125*, 7470.
(19) Daizadeh, I.; Medvedev, E. S.; Stuchebrukhov, A. A. *Proc. Natl. Acad. Sci. U.S.A.* **1997**, *94*, 3703.
(20) Toutounji, M. M.; Ratner, M. A. *J. Phys. Chem. A* **2000**, *104*, 8566.
(21) Skourtis, S.; Archontis, G.; Xie, Q. *J. Chem. Phys.* **2001**, *115*, 9444.
(22) Nadeau, J. M.; Liu, M.; Waldeck, D. H.; Zimmt, M. B. *J. Am. Chem. Soc.* **2003**, *125*, 15964.
(23) Voityuk, A. A.; Siriwong, K.; Rosch, N. *Phys. Chem. Chem. Phys.* **2001**, *3*, 5421.
(24) Daub, J.; Engl, R.; Kurzawa, J.; Miller, S. E.; Schneider, S.; Stockmann, A.; Wasielewski, M. R. *J. Phys. Chem. A* **2001**, *105*, 5655.
(25) Marin, T. W.; Homoelle, B. J.; Spears, K. G.; Hupp, J. T.; Spreer, L. O. *J. Phys. Chem. A* **2002**, *106*, 1131.
(26) Hayes, R. T.; Walsh, C. J.; Wasielewski, M. R. *J. Phys. Chem. A* **2004**, *108*, 2375.
(27) Rubtsov, I. V.; Redmore, N. P.; Hochstrasser, R. M.; Therien, M. J. *J. Am. Chem. Soc.* **2004**, *126*, 2684.
(28) Hayes, R.; Wasielewski, M.; Gosztola, D. *J. Am. Chem. Soc.* **2000**, *122*, 5563.
(29) Davis, W.; Ratner, M.; Wasielewski, M. *J. Am. Chem. Soc.* **2001**, *123*, 7877.
(30) Scherer, T.; Vanstokkum, I.; Brouwer, A.; Verhoeven, J. *J. Phys. Chem.* **1994**, *98*, 10539.

(31) Donhauser, Z. J.; Mantooth, B. A.; Kelly, K. F. *Science* **2001**, *292*, 2303.
(32) Coalson, R. D.; Evans, D. G. *Chem. Phys.* **2004**, *296*, 117.
(33) Cook, W. R.; Evans, D. G.; Coalson, R. D. *Chem. Phys. Lett.* **2006**, *420*, 362–366.
(34) Peter, S.; Evans, D. G.; Coalson, R. D. *J. Phys. Chem. B* **2006**, *110* (38), 18758.
(35) Peter, S.; Evans, D. G.; Coalson, R. D. *J. Phys. Chem. B* **2006**, *110* (38), 18764.
(36) Leggett, A. J.; Chakravarty, S; Dorsey, A. T.; Fisher, M.; Garg, A.; Zwerger, W. *Rev. Mod. Phys.* **1987**, *59*, 1.
(37) May, V.; Kuhn, O. *Charge and Energy Transfer Dynamics in Molecular Systems*; Wiley: Berlin, 2000.
(38) Krempl, S.; Winterstetter, M.; Plohn, H.; Domcke, W. *J. Chem. Phys.* **1994**, *100*, 926.
(39) Dumcke, R.; Spohn, H. *Z. Phys. B: Condens. Matter* **1979**, *34*, 419–422.
(40) Petrov, E. G.; May, V.; Hanggi, P. *Chem. Phys.* **2004**, *296*, 251.
(41) Nesi, F.; Paladino, E.; Thorwart, M.; Grifoni, M. *Phys. Rev. B* **2007**, *76*, 15–155323.
(42) Creechley, J.; Dahnovsky, Y. *Chem. Phys.* **2004**, *296*, 171.
(43) Gayen, T.; Mcdowell, K.; Burns, A. *J. Chem. Phys.* **2000**, *112*, 4310–4320.
(44) Pereverzev, A.; Bittner, E. R. *J. Chem. Phys.* **2005**, *123*, 244903.
(45) Kubo, R.; Toyozawa, Y. *Prog. Theor. Phys.* **1955**, *13*, 160–182.
(46) Redfield, A. *Adv. Magn. Reson.* **1965**, *1*, 1.
(47) Jean, J. M.; Friesner, R. A.; Fleming, G. R. *J. Chem. Phys.* **1992**, *96*, 5827–5842. Pollard, W. T.; Felts, A. K.; Friesner, R. A. *Adv. Chem. Phys.* **1996**, *93*, 77–134.
(48) Yang, M.; Fleming, G. R. *Chem. Phys.* **2002**, *282*, 163–180.
(49) Laird, B. B.; Budimir, J.; Skinner, J. L. *J. Chem. Phys.* **1991**, *94*, 4391–4404.
(50) Jang, S.; Cao, J. S.; Silbey, R. J. *J. Chem. Phys.* **2002**, *116*, 2705–2717.
(51) Davies, E. B. *Commun. Math. Phys.* **1974**, *39*, 91–110.
(52) Egorova, D.; Kuhl, A.; Domcke, W. *Chem. Phys.* **2001**, *268*, 105–120.
(53) Zwanzig, R. *Physica* **1964**, *30*, 1109.
(54) Kohen, D.; Marston, C. C.; Tannor, D. J. *J. Chem. Phys.* **1997**, *107*, 5236–5253.
(55) Wilkie, J. *J. Chem. Phys.* **2001**, *114*, 7736–7745.
(56) Yan, Y. J.; Shuang, F.; Xu, R. X.; Cheng, J. X.; Li, X. Q.; Yang, C.; Zhang, H. Y. *J. Chem. Phys.* **2000**, *113*, 2068–2078.
(57) Rackovsky, S.; Silbey, R. *Mol. Phys.* **1973**, *25*, 61.
(58) Silbey, R. *Annu. Rev. Phys. Chem.* **1976**, *27*, 203.
(59) Coalson, R. D.; Evans, D. G.; Nitzan, A. *J. Chem. Phys.* **1994**, *101*, 436.
(60) Cho, M. H.; Silbey, R. J. *J. Chem. Phys.* **1995**, *103*, 595.
(61) Jang, S.; Jung, Y. J.; Silbey, R. *J. Chem. Phys.* **2002**, *275*, 319–332.
(62) Harris, R. A.; Silbey, R. *J. Chem. Phys.* **1983**, *78*, 7330.
(63) Silbey, R.; Harris, R. A. *J. Chem. Phys.* **1984**, *80*, 2615.
(64) Parris, P. E.; Silbey, R. *J. Chem. Phys.* **1985**, *83*, 5619.
(65) Silbey, R.; Harris, R. A. *J. Phys. Chem.* **1989**, *93*, 7062–7071.
(66) Suarez, A.; Silbey, R.; Oppenheim, I. *J. Chem. Phys.* **1992**, *97*, 5101–5107.
(67) Reichman, D. R.; Silbey, R. J. *J. Chem. Phys.* **1996**, *104*, 1506.
(68) Skinner, J. L.; Hsu, D. *J. Phys. Chem.* **1986**, *90* (21), 4931–4938.
(69) Golosov, A. A.; Friesner, R. A.; Pechukas, P. *J. Chem. Phys.* **1999**, *110*, 138–146.
(70) (a) Golosov, A. A.; Reichman, D. R. *J. Chem. Phys.* **2001**, *115*, 9848. (b) Golosov, A. A.; Reichman, D. R. *J. Chem. Phys.* **2001**, *115*, 9862.
(71) Blum, K. *Density Matrix Theory and Applications*, 2nd ed.; Plenum Press: New York, 1996.
(72) Schatz, G. C.; Ratner, M. A. *Quantum Mechanics in Chemistry*; Dover Publications: Mineola, NY, 2002.
(73) Makarov, D. E.; Makri, N. *Chem. Phys. Lett.* **1994**, *221*, 482–491.
(74) Weiss, U. Quantum Dissipative Systems; World Scientific: Singapore, 2001.
(75) Zwanzig, R. *Nonequilibrium Statistical Mechanics*; Oxford University Press: Oxford, U.K., 2001.
(76) Makri, N.; Makarov, D. E. *J. Chem. Phys.* **1995**, *102*, 4600–4610.
(77) Makri, N.; Makarov, D. E. *J. Chem. Phys.* **1995**, *102*, 4611–4618.
(78) Lax, M. *J. Chem. Phys.* **1952**, *20*, 1752–1760.