FEATURE ARTICLE

On the Adequacy of Mixed Quantum-Classical Dynamics in Condensed Phase Systems

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A detailed study of mixed quantum-classical approximations for radiative and nonradiative processes in condensed phase systems is presented and each approximation is compared to exact fully quantum mechanical dynamics. The problems are formulated in terms of a quantum mechanical time correlation function, and the corresponding mixed quantum-classical descriptions are obtained following the general methodology of Wigner−Kirkwood based on the expansion in powers of Planck's constant. Illustrative examples of the performance and applicability of mixed quantum-classical treatments include vibrational and electronic energy relaxation processes, and the calculation of vibronic absorption spectrum.

I. Introduction

One of the longstanding problems in chemistry and physics is the quantum mechanical treatment of dynamical properties of arbitrary condensed phase systems. Unfortunately, direct solution of the time-dependent Schrödinger equation is computationally nonfeasible due to the exponential scaling with the number of degrees of freedom. In Feynman's path integral formulation, the exact numerical solution of this problem is extremely complicated due to the well-known phase cancellations (the sign problem). At the present time, one of the viable alternatives to the exact quantum mechanical solution is the use of mixed quantum-classical treatments, where a small subset of highly "quantum" modes is treated quantum mechanically while the remaining degrees of freedom are treated classically. The major issue in these mixed approaches is self-consistent dynamical treatment of the quantum and classical degrees of freedom: the motion of the classical particles and the concomitant time-dependence of the Hamiltonian triggers quantum transitions, while the latter alter the potential energy surface and thereby change the forces that act on the classical particles.

In the situation where the energies of the classical particles are larger than the spacings between the quantum states, the back-reaction of the quantum subsystem on the classical one can be neglected; such approach is taken in the classical path methods[1−3] and in the Redfield theory.[4] However, in most cases of chemical interest, it is necessary to properly describe the feedback between quantum and classical degrees of freedom. To achieve this goal, two major attempts have been undertaken, the mean field approach based on the Ehrenfest work[5] and the Preston−Tully surface hopping method.[6]

The Ehrenfest approach led to the development of the most widely used mixed quantum-classical method which is a classical version of the fully quantum time dependent self-consistent field (TDSCF) method.[7−10] The main limitation of this approach is that the classical trajectories evolve on a mean potential energy surface (PES), and there are certain physical situations where such a single configuration TDSCF approach is inadequate. The above shortcoming of the single configuration TDSCF is remedied in the surface hopping approach,[6,11−25] which originated in the pioneering work of Preston and Tully,[6] and it is the classical analogue of a multiconfiguration generalization of the TDSCF.[10] Tully uses the word "analogue"[10] because surface hopping is not a rigorous classical limit. In recent years, several groups have attempted to derive surface hopping from first principles,[10,26,27] although some uncontrolled approximations are still unavoidable.

Various extensions and modifications of the above two mixed quantum-classical schemes have been proposed over the recent years. On the basis of early work of Pechukas,[28−30] Rossky et al.[31] have developed a nonadiabatic molecular dynamics method and applied it to the study of electron solvation in various liquids.[32−35] It was later shown that surface hopping can be presented as a short time approximation to the Pechukas formulation.[18] Thirumalai, Bruskin, and Berne[36] have also derived a mixed quantum-classical approximation based on the semiclassical theory of Pechukas,[28−30] but they applied it to the case where the initial and final quantum states are the same. Their final mixed quantum-classical approximation is identical to the TDSCF ansatz, yet it was derived within the stationary phase approximation. In the original work, they combine the mixed quantum-classical approximation with the Gaussian wave-

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packet method[37,38] to determine the electronic spectra of a diatomic molecule embedded in a rare gas matrix. Ben-Nun et al. developed a mixed quantum-classical method and applied it to study the dynamics of I_2 in rare gas solvents.[39,40] Gerber and co-workers have introduced the classical separable potential (CSP) approximation which was used to study the dynamics of halogens in rare gas clusters.[41,42]

A more systematic approach to treating dynamical processes in condensed phases is based on the semiclassical propagator originally written down by Van Vleck,[43,44] which is the stationary phase approximation to the exact quantum mechanical propagator.[45] The root search is the bottleneck of this method in its original formulation, and it has been circumvented by transforming to the initial value representation.[46−56] Due to the unfavorable system size scaling, the semiclassical initial value representation (SC-IVR) methods have been primarily applied to systems with few degrees of freedom. Several approximations have been introduced to extend the applicability of semiclassical methods to many-body systems. Neria and Nitzan[57,58] have applied the frozen Gaussian approximation[37,38] to calculate the nonradiative relaxation rate for model systems and for solvated electron. Miller and co-workers[59−61] used a "linearized" approximation to the SC-IVR propagator to study nonadiabatic transitions of a quantum system coupled to a bath of harmonic oscillators. Makri and Thompson[62,63] have combined the forward and backward paths of the bath to compute a semiclassical version of Feynman−Vernon[64] influence functional.

Despite the fact that SC-IVR approach has a more sound theoretical foundation than the mixed quantum-classical methods, it is also more computationally demanding. Therefore, we limit the scope of the present review to the mixed quantum-classical treatments. As already discussed, a wide variety of these methods have been developed and have been applied to numerous problems. However, all these methods involve various levels of approximations. In view of that, it is of great importance to assess the accuracy of mixed quantum-classical methods by performing tests on exactly solvable (but still realistic) models. Most such tests reported in the literature to date have been confined to few particle systems,[65−70] one of the notable exceptions being the study of the spin-boson problem[71] by Müller and Stock.[72]

Motivated by the widespread use of mixed quantum-classical simulations and the lack of information on their accuracy for many-body problems, in a recent series of papers[73−77] we have undertaken a comprehensive study of reliability of mixed quantum-classical methods for a wide variety of models and physical processes. In particular, we have looked at the problems involving a single PES (in the context of vibrational energy relaxation in condensed phases)[73,74] and at the situations where several PES are necessary for describing the process of interest.[75−77] In the latter case, we considered both radiative processes[75,76] (taking vibronic absorption spectrum of a chromophore coupled to a condensed phase environment as a test case) and at the nonradiative relaxation processes[77] (specifically, electronic relaxation of an impurity in a bath).

In all cases studied, it has been assumed that the coupling between the relevant quantum states in the quantum subsystem (guest or solute or chromophore) is small. Thus, the lowest order perturbation theory can be applied to calculate the property of interest, such as the energy relaxation rate, dephasing time or spectrum. Since it was imperative for us to be able to obtain the exact quantum mechanical result for each problem studied, the condensed phase environment was always modeled as a collection of harmonic oscillators (in some cases we were able to take the limit of infinite number of bath modes). In addition to the fully quantum mechanical solution, for each problem we have formulated the corresponding mixed quantum-classical description, where the bath degrees of freedom (and, in certain cases, the nuclear degrees of freedom of the impurity) were treated classically.

In providing such a description, we have followed the general methodology of Wigner−Kirkwood based on the expansion in powers of Planck's constant of the relevant quantum mechanical time-correlation function (TCF).[78] We would like to emphasize that the above expansion is unique only for the problems involving a single PES,[79,80] and it is somewhat arbitrary for the case of several PESs.[81,82] We address this issue of nonuniqueness and attempt to provide a prescription for an optimal mixed quantum-classical representation.

Our methodology is somewhat different from the aforementioned mixed quantum-classical treatments, where certain ad hoc approximations are unavoidable. It remains an open question whether those mixed quantum-classical treatments agree with our mixed quantum-classical results in the regime where lowest order perturbation theory is valid, i.e., the weak coupling limit. Since the main concern of this article is to assess the accuracy of mixed quantum-classical treatments in condensed phases, we will not return to this issue herein.

By providing a methodology for obtaining both exact quantum mechanical and mixed quantum-classical treatments for all studied models, we were able to address the following major issues: 1. Can mixed quantum-classical methods provide an accurate description of dynamical processes in condensed phase systems? What is the range of their applicability in terms of the physical parameters characterizing the system (temperature, characteristic energies, etc.)? 2. What are the criteria for choosing the most accurate propagation scheme for our mixed quantum-classical treatment (recall the arbitrariness mentioned above in the case of multiple PESs)? 3. Are there ways to infer the quantum dynamical information from the results of classical or mixed quantum-classical simulations by applying certain "quantum corrections"? 4. How *do fully* classical treatments compare to mixed quantum-classical approaches in terms of approximating the exact quantum results?

The article is structured as follows: in section II we provide a general formulation of our mixed quantum-classical approach. We start by writing the exact quantum mechanical expression for the observable of interest in terms of the relevant time correlation function. Next, we expand it in powers of Planck's constant, and retain the terms up to (and including) the term of order $\hbar^0$. We note that in certain cases terms containing inverse powers of $\hbar$ are present in the expansion, which generally leads to a nonuniqueness of the mixed quantum-classical result (see the discussion of Mukamel on the semiclassical treatment of spectroscopic observables[81,82]).

In section III we provide comparisons between the fully quantum mechanical and mixed quantum-classical results for various physical problems. We start by considering vibrational energy relaxation in condensed phases. As was shown by Sakun,[83] and Berkowitz and Gerber,[84] the dominant contribution to the relaxation rate in this case comes from the dependence of the off-diagonal system−bath coupling on the bath coordinates. We consider both the linear coupling case which allows only single-phonon processes[73] and the nonlinear coupling case which is necessary for multiphonon relaxation.[74] Next we consider a quantum subsystem that contains electronic degrees of freedom.[77] In this case the system−bath interactions depend strongly on the quantum state of the system, and thus one is forced to consider several (at least two) PESs. Section IV provides the last test case which involves the vibronic absorption spectrum of a diatomic chromophore in a condensed phase environment, where both electronic transitions and vibrational relaxation are important.[75,76]

In Section V we discuss the results for the different models presented in sections III and IV. We try to delineate the various relevant parameters that govern the success or failure of mixed quantum-classical approximations to time correlation functions. We discuss the static and dynamical contributions to the properties of interest for several limiting cases. Finally, in section VI we provide our view of future direction in the study of mixed quantum-classical dynamics in many-body systems.

II. Model Hamiltonian and Mixed Quantum-Classical Theory

In what follows, we will focus on two particular states of the quantum subsystem, which we label as $|0\rangle$ and $|1\rangle$. All other degrees of freedom (apart from those of the quantum subsystem) will be generally treated within the classical approximation when a mixed quantum-classical treatment is imposed. Thus we refer to them as the "nuclear" degrees of freedom, and label their positions and momenta with **Q** and **P**, respectively. We are interested in radiative and nonradiative transitions between these two quantum states and write the general total Hamiltonian as follows:

$$H_{\text{tot}} = H_0|0\rangle\langle 0| + H_1|1\rangle\langle 1| + V_{01}|0\rangle\langle 1| + V_{10}|1\rangle\langle 0| \qquad (1)$$

where $H_0 = E_0 + H'_b + \Delta_0$ and $H_1 = E_1 + H'_b + \Delta_1$; H'_b, Δ_0, Δ_1, V_{01} and V_{10} are operators in the Hilbert space of the nuclear variables **Q** and **P**. In the study of vibronic absorption spectrum the off-diagonal coupling matrix elements V_{01} and V_{10} will depend also on the time t.

As will become clear below, it is convenient to perform the following transformation of the total Hamiltonian: we add and subtract $\Delta_0|1\rangle\langle 1|$ in eq (1) and use the identity $|0\rangle\langle 0| + |1\rangle\langle 1| = 1$ to obtain

$$H_{\text{tot}} = (H_b + E_0)|0\rangle\langle 0| + (H_b + \Delta + E_1)|1\rangle\langle 1| + V_{01}|0\rangle\langle 1| + V_{10}|1\rangle\langle 0| \equiv H + V \qquad (2)$$

where $H_b = H'_b + \Delta_1$ and $\Delta = \Delta_1 - \Delta_0$. In eq 2 we have also used the following definitions

$$H = (H_b + E_0)|0\rangle\langle 0| + (H_b + \Delta + E_1)|1\rangle\langle 1| \qquad (3)$$

and

$$V = V_{01}|0\rangle\langle 1| + V_{10}|1\rangle\langle 0| \qquad (4)$$

With the above form of the total Hamiltonian, it is clear that the Hamiltonian corresponding to the state $|0\rangle$ is given by $H_0 = H_b + E_0$, while the Hamiltonian corresponding to state $|1\rangle$ is given by $H_1 = H_b + \Delta + E_1$. Δ is the difference between the two PESs in the dressed picture, i.e., when the constant terms (E_0 and E_1) are omitted. This form of the Hamiltonian is the most convenient choice for the present problems, yet it is completely general.

As discussed in the Introduction, we use the lowest order perturbation theory (the Fermi golden rule) to calculate the property of interest (relaxation rate, dephasing time, or absorption spectrum). In what follows, we will treat the off-diagonal coupling V between the two quantum states within the perturbation approximation. In the time-domain formulation of the Fermi golden rule, this property is related to a real-time correlation function of the form:

$$C(t) = \text{Tr}[\rho_0(\beta) V\, e^{iHt/\hbar} V\, e^{-iHt/\hbar}] \qquad (5)$$

where the thermal averaging is performed with the distribution appropriate to the initial quantum state, i.e., we assume that the system has equilibrated under H_0:

$$\rho_0(\beta) = \frac{1}{Z(\beta)}\, e^{-\beta H_0}|0\rangle\langle 0| \qquad (6)$$

and the partition function $Z(\beta)$ is given by

$$Z(\beta) = \text{Tr}[e^{-\beta H_0}|0\rangle\langle 0|] \qquad (7)$$

Similarly, the real-time correlation function can be written as

$$C(t) = \text{Tr}[\rho_0(\beta) V(0) V(t)] \qquad (8)$$

In the above equations $\beta = 1/k_B T$ is the inverse temperature, the symbol Tr(...) denotes the trace over all degrees of freedom, and V is given in eq 4.

We next perform the trace over the two quantum states $|0\rangle$ and $|1\rangle$ to obtain

$$C(t) = \frac{1}{Z(\beta)} \text{Tr}_{\mathbf{Q}}\, [e^{-\beta H_0} V_{01}\, e^{iH_1 t/\hbar} V_{10}\, e^{-iH_0 t/\hbar}] \qquad (9)$$

where $\text{Tr}_{\mathbf{Q}}$ (...) denotes the trace over the nuclear degrees of freedom, and the partition function $Z(\beta)$ is now given by

$$Z(\beta) = \text{Tr}_{\mathbf{Q}}\, [e^{-\beta H_0}] \qquad (10)$$

Applying the interaction representation, eq 9 can be written in the form of a time-ordered exponential[85]

$$C(t) = \left\langle e^{i\omega_{10}t} V_{01}(0) \exp_{-}\left(\frac{i}{\hbar}\int_0^t dt' \Delta(t')\right) V_{10}(t) \right\rangle \qquad (11)$$

where $\langle ... \rangle \equiv \text{Tr}_{\mathbf{Q}}\, [e^{-\beta H_0} ...]/Z(\beta)$ denotes a quantum mechanical ensemble average over Hamiltonian H_0, and $\omega_{10} = (E_1 - E_0)/\hbar$. The negative time ordered exponential, $\exp_{-}(...)$, is defined in the usual way.[86] $\Delta(t)$, $V_{01}(t)$, and $V_{10}(t)$ are the Heisenberg form for the operators Δ, V_{01}, and V_{10}, respectively, and are given by

$$\Delta(t) = e^{iH_0 t} \Delta e^{-iH_0 t} \qquad (12)$$

$$V_{ss'}(t) = e^{iH_0 t} V_{ss'} e^{-iH_0 t} \qquad (13)$$

where s and s' take the values of 0 or 1.

The mixed quantum-classical limit of eq 11 is obtained in two steps: (a) We replace the quantum mechanical trace over the nuclear degrees of freedom **Q** with a phase-space integral over a corresponding classical distribution function. (b) We replace the quantum mechanical operators $V_{10}(t)$, $V_{10}(t)$, and $\Delta(t)$ with the corresponding classical dynamical variables. In doing so we also drop the time ordering since the classical dynamical variable $\Delta(t)$ commutes with itself at all times.[81]

Thus, eq 11 reduces to a mixed quantum-classical time correlation function of the form

$$C_{mqc}(t) = \left\langle V_{01}(0) \exp\left(\frac{i}{\hbar}\int_0^t dt' \Delta(t')\right) V_{10}(t) \right\rangle_{\text{cl}} \qquad (14)$$

where $\langle ... \rangle_{\text{cl}} \equiv \int d\mathbf{Q} d\mathbf{P}\, (e^{-\beta H_0(\mathbf{Q},\mathbf{P})} ...)/Z_{\text{cl}}(\beta)$ denotes a classical ensemble average over the classical Hamiltonian $H_0(\mathbf{Q}, \mathbf{P})$, and

$Z_{\mathrm{cl}}(\beta)$ is the classical partition function given by

$$Z_{\mathrm{cl}}(\beta) = \frac{1}{(2\pi\hbar)^f}\int \mathrm{d}\mathbf{Q}\mathrm{d}\mathbf{P}\mathrm{e}^{-\beta H_0(\mathbf{Q},\mathbf{P})} \tag{15}$$

Equation 11 can be rewritten in various different (but *equivalent*) forms by making different choices for the Hamiltonian under which $\Delta(t)$, $V_{01}(t)$, and $V_{10}(t)$ are propagated. In other words, one is not restricted to using H_0 in transforming to the interaction picture. However, after carrying out steps a and b outlined above, the resulting mixed quantum-classical time correlation functions are *not* equivalent to each other. This is precisely the nonuniqueness of the mixed quantum-classical approximation mentioned in the Introduction. In the case where the Hamiltonians associated with the two quantum states are the same (i.e., when $\Delta = 0$), the time-ordered exponentials in eq 11 disappear, and the mixed quantum-classical approximation becomes unique.

Equation 14 is perfectly suited for evaluation in a simulation by propagating classical trajectories on the Hamiltonian specified by the interaction picture used. The mixed quantum-classical TCF is obtained by monitoring the time-dependent potential energy difference between the two PESs ($\Delta(t)$) and averaging over the appropriate initial conditions. The applications reported in this article were obtained for a model system where an analytic expression for the correlation function was derived, and thus there was no need for performing simulations. We did perform a convergence test and found that typically 1000 trajectories were enough to obtain converged results for the correlation function.

Before we discuss the application and performance of the mixed quantum-classical approximation we would like to emphasize that the above mixed quantum-classical approach is *not* identical to the so called mean-field approach (i.e., mixed quantum-classical TDSCF). Since we obtain the relevant property of interest within the framework of lowest order perturbation theory, the mixed quantum-classical approach does not include the feedback between the classical subsystem and the quantum subsystem.

III. Nonradiative Processes

In this section we discuss the application of the general results obtained above to various physical problems involving nonradiative relaxation. Depending on the specific problem, different mechanisms will give the dominant contribution to the relaxation rate. For example, in the case of vibrational energy relaxation, the solvent is not affected significantly by the change of the solute vibrational state,[83,84] and the dominant relaxation mechanism arises from the dependence of the solute-solvent coupling term on the solvent coordinates.[74,87−102] In the language of the previous section, this means that we set $\Delta = 0$. On the other hand, electronic relaxation is generally accompanied by a significant change in the solute−solvent interaction,[88] and one needs to introduce different PESs for different solute electronic states. A common model involves shifted/distorted surfaces, where Δ is a linear/quadratic function of the bath coordinates.[87,88,103−111] Since the dominant mechanisms of vibrational and electronic relaxation are different, we will discuss these two problems separately.

We model the condensed phase environment in both vibrational and electronic relaxation processes as a harmonic bath, which constitutes the nuclear degrees of freedom in our system. Thus, we take H_b in eq 2 to be a sum over harmonic mass-weighted normal modes Q_α with frequencies ω_α and conjugate momenta P_α:

$$H_b = \frac{1}{2}\sum_\alpha (P_\alpha^2 + \omega_\alpha^2 Q_\alpha^2) \tag{16}$$

A. Vibrational Energy Relaxation. Numerous processes in condensed phases involve dissipation of energy from vibrationally excited modes. Thus, a profound microscopic understanding of vibrational energy relaxation is of major importance.[112−120] In theoretical treatments of vibrational energy relaxation based on the low-order perturbation theory the total Hamiltonian is generally partitioned into three terms: the Hamiltonian for the vibrational mode of the solute, the Hamiltonian for the solvent degrees of freedom, and the interaction between these two subsystems, which induces the transitions between the solute vibrational states. Within this formalism, the state-to-state transition rates are determined by the Fourier transform (at the vibrational frequency of the solute) of the TCF for the force exerted by the solvent on the solute vibrational mode. When studying vibrational energy relaxation in low-temperature solids, this TCF can be evaluated quantum mechanically. At the same time, a full quantum treatment of dynamics in liquid hosts is not feasible, and a common approach is to treat the translational degrees of freedom in liquids classically. However, for certain experimental conditions (e.g., vibrational relaxation of molecular oxygen in liquid mixtures with argon in the temperature range 60−90 K)[101,121] a classical treatment of the solvent may be questionable. In other words, the mixed quantum-classical treatment outlined in the previous Section is likely to break down. In this subsection we present the mixed quantum-classical treatment of vibrational energy relaxation, and review the previous theoretical work concerning its range of validity.

In order to apply the general theoretical framework outlined in the previous section to the problem of vibrational energy relaxation, we make the following identifications: $|0\rangle$ and $|1\rangle$ are the two vibrational states of the solute for which we calculate the transition rate (in what follows, we treat the solute vibrational degree of freedom q in the harmonic approximation, however the theoretical treatment is not limited to this choice[122]).

As mentioned earlier, we assume that the bath Hamiltonian is the same for all solute vibrational states, i.e., we set $\Delta = 0$. V is the perturbation that couples the solute vibrational mode q to the solvent degrees of freedom $\mathbf{Q}$. We take it to be linear in q and assume it to be a function of a certain collective solvent coordinate Q, that is, some (linear) combination of the modes comprising the set $\mathbf{Q}$, i.e. we write $V = qF(Q)$. Thus $V_{01} = \langle 0|q|1\rangle = q_{01}$ and $V_{10} = \langle 1|q|0\rangle = q_{10}$. Two functional forms for $F(Q)$ have been considered previously: (1) case of bilinear solute−solvent coupling ($V \propto qQ$) has been treated in detail by Bader and Berne[73] and (2) case where the solute−solvent interaction is modeled with an exponential function of the bath collective coordinate has been analyzed by Egorov and Berne.[74] The former case allows for single phonon relaxation processes while the latter is appropriate for describing multiphonon relaxation.

As stated above, the transition rate from state $|1\rangle$ to state $|0\rangle$ is proportional to the Fourier transform (at the solute vibrational frequency $\omega_{\mathrm{vib}} = (E_1 - E_0)/\hbar$) of the TCF for the force $F(\mathbf{Q})$. The quantum mechanical expression for the state-to-state transition rate then reads

$$k_{0\to 1} = \frac{|q_{01}|^2}{\hbar^2}\int_{-\infty}^{\infty} \mathrm{d}t \exp(i\omega_{\mathrm{vib}}t)\,\langle F(0)F(t)\rangle \tag{17}$$

TABLE 1: Vibrational Energy Relaxation Rates for the Quantum Mechanical, Mixed Quantum-Classical, and Classical Treatments Taken from the Work of Bader and Berne[73]

	classical solvent	quantum solvent
classical solute	T_1^{-1}	$T_1^{-1}\,\beta\hbar\omega/2\coth\beta\hbar\omega/2$
quantum solute	$T_1^{-1}2/\beta\hbar\omega\tanh\beta\hbar\omega/2$	T_1^{-1}

The mixed quantum-classical approximation to $k_{0\to1}$ is obtained by applying the procedure outlined in the previous section.

As indicated by Bader and Berne,[73] in the case of bilinear solute−solvent coupling the fully quantum and mixed quantum-classical results for the rate are related by

$$k_{0\to1}^{qm} = \frac{\beta\hbar\omega_{\mathrm{vib}}}{2}\coth\left(\frac{\beta\hbar\omega_{\mathrm{vib}}}{2}\right)k_{0\to1}^{mqc} \tag{18}$$

The above relation is exact, and holds for an arbitrary (not necessarily harmonic) model for the internal vibration of the solute. When the solute vibrational mode *is harmonic*, Bader and Berne[73] have shown that the above relation also holds for the overall energy relaxation rate T_1^{-1}

$$(T_1^{-1})^{qm} = \frac{\beta\hbar\omega_{\mathrm{vib}}}{2}\coth\left(\frac{\beta\hbar\omega_{\mathrm{vib}}}{2}\right)(T_1^{-1})^{mqc} \tag{19}$$

At the same time, the fully classical treatment of the relaxation rate T_1^{-1}, is *identical* to the fully quantum one for this particular model (harmonic oscillator bilinearly coupled to the harmonic bath). The above results are summarized in Table 1.

Within the low-order perturbation theory, the model studied by Bader and Berne can only produce single-phonon transitions, and thus is mainly applicable to study the relaxation of the low-frequency solute vibrational modes. On the other hand, vibrational energy relaxation of high-frequency modes is dominated by multiphonon processes. In order to account for multiphonon relaxation, one needs to consider the solute−solvent coupling that is nonlinear in the solvent coordinates **Q**. This case has been considered in the work of Egorov and Berne[74] where the solute−bath interaction was modeled with an exponential function of a collective solvent coordinate. A semilog plot of the comparison between the fully quantum mechanical, mixed quantum-classical, and classical relaxation rates (scaled by a typical phonon frequency of the bath) versus the vibrational frequency (scaled by the same value) is shown in Figure 1.

It is clearly seen that in contrast to the case of linear coupling studied by Bader and Berne, where the fully quantum and the fully classical results are identical, in the case of exponential solute−bath interaction, the fully classical treatment significantly underestimates the relaxation rate. The mixed quantum-classical result for the relaxation rate is always below the classical result, i.e., the fully classical treatment gives consistently better results for the relaxation rate than the mixed quantum-classical one (although the classical rates are still off from the quantum rates by several orders of magnitude). Note that, as the vibrational frequency of the solute increases, the disagreement between the classical/mixed quantum-classical and the quantum results becomes worse.

In addition, we also show the results of the quantum correction to the classical relaxation rate as given by eq 16 of ref 74. Unlike the case of bilinear coupling studied by Bader and Berne, there is no exact analytic relation between the mixed quantum-classical and quantum mechanical rate. On the basis of stationary phase method Egorov and Berne derived an approximate correction to the mixed quantum-classical relaxation rate. It was found that the quantum correction is accurate over a wide range of relevant system−bath parameters as shown in the figure. The important point is that in the high frequency limit this quantum correction depends exponentially on the solute vibrational frequency, and thus the ratio of the fully quantum to the mixed quantum-classical rate becomes very large.

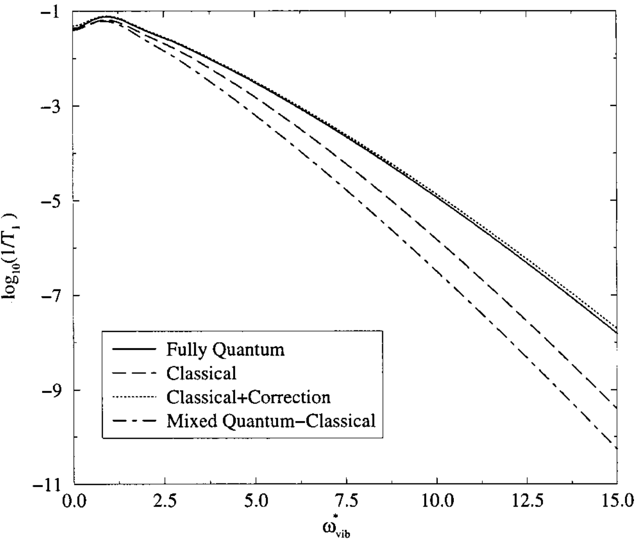

Figure 1. A semilog plot of the vibrational relaxation rate versus the solute vibrational frequency for the exponential solute−solvent interaction. The solid, dashed, dotted, and dashed−dotted lines are for the fully quantum mechanical, classical, corrected, and mixed quantum-classical relaxation rates, respectively.

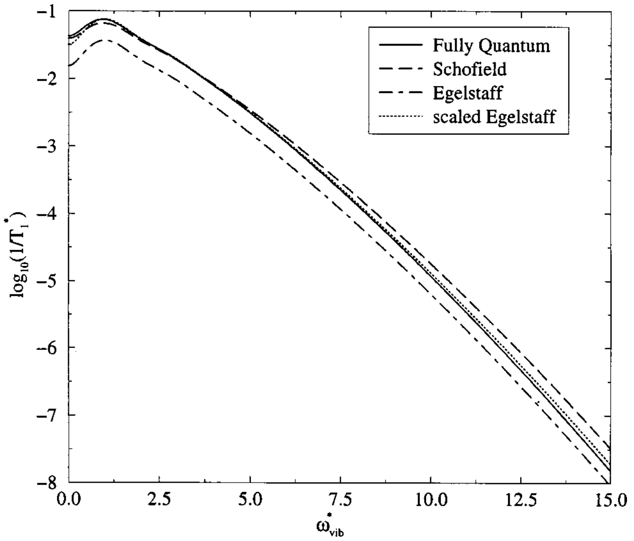

Figure 2. A semilog plot of the vibrational relaxation rate versus the solute vibrational frequency for the exponential solute−solvent interaction. The solid line is for the fully quantum mechanical relaxation rate. The dashed, dashed−dotted and dotted lines are for the Schofield, Egelstaff, and scaled Egelstaff empirical corrections.

It is also of interest to compare the results obtained with the quantum correction factor to other approximations suggested in the literature.[123−125] These approximations have been discussed in the context of vibrational relaxation and rigid rotors[126,127] and more recently in the context of a general time correlation function.[74,128] The results of the application of the Schofield, Egelstaff, and “scaled” Egelstaff empirical corrections to the present problem are shown in Figure 2 along with the exact quantum mechanical relaxation rate. One sees that the

Schofield transformation overestimates the quantum correction somewhat (especially at the higher frequencies), the Egelstaff approximation gives the rates which are too low, and the "scaled" Egelstaff procedure is generally as accurate as the approximate correction shown in Figure 1 (see also eq 16 of ref 74).

In summary, the problem of vibrational energy relaxation in the present formulation provides a convenient test case where a unique mixed quantum-classical approximation to the quantum time correlation function can be obtained. We have considered two models for the solute−solvent coupling (bilinear and exponential), and have analyzed the relation between the fully quantum, mixed quantum-classical and classical vibrational relaxation rates. In both cases, the classical treatment provides more accurate relaxation rates, than the mixed quantum-classical approximation. However, in the case of nonlinear coupling it can still underestimate the rate significantly in the high frequency limit.

B. Nonradiative Electronic Relaxations. Nonradiative electronic relaxation is an important step in numerous chemical and physical processes, such as internal conversion, electron transfer reactions, etc.[87,92,129−133] Radiationless electronic relaxation processes in condensed phases involve energy transfer from electronically excited impurities to the host, and it is often the case that the amount of energy transferred exceeds by many times the typical energy associated with the thermal motion of the solvent. Clearly, many quanta of the bath excitations must be created in this process.

Most theoretical treatments of electronic multiphonon relaxation are based on the time-dependent perturbation theory. Due to some arbitrariness in defining the zeroth-order Hamiltonian and the coupling term, various routes to nonradiative decay are possible. Here we consider two different routes: the adiabatic (Born−Oppenheimer) and the "static-coupling" (crude Born−Oppenheimer) methods. In the present formulation both methods involve shifts and/or distortions between the two PESs corresponding to the two electronic states. In the language of section II, Δ is taken to be a quadratic function of the nuclear degrees of freedom $\mathbf{Q}$. This is very different from the case of vibrational relaxation discussed in the previous subsection, where the two PESs were taken to be identical, i.e., $\Delta = 0$. Due to these shifts/distortions of PESs, both the adibatic and the static coupling descriptions allow for multiphonon processes in the lowest order perturbation theory. The difference between the adiabatic approach and static coupling approach is in the form of the off-diagonal coupling matrix elements V_{01} and V_{10}. In the adiabatic approach the off-diagonal coupling depends on the momentum operators of the nuclear degrees of freedom $\mathbf{P}$, while in the static coupling approach the off-diagonal coupling matrix elements are taken to be constants. In solid-state theory, both approaches were employed by Kubo and Toyozawa,[134] Perlin,[135] Miyakawa and Dexter,[136] and others.[87,88,103−111,137−141] Recently, they have become widely used in the field of liquid phase chemistry in the context of calculating nonradiative relaxation rates of solvated electrons.[57,142,143]

As in the case of vibrational relaxation, we now focus on assessing the accuracy of a mixed quantum-classical treatment in the calculation of the electronic relaxation rate. We consider an impurity embedded in a condensed phase environment and concentrate on the nonradiative transitions between the initial electronic state $|0\rangle$ and the final electronic state $|1\rangle$ of the impurity. As before, the bath (which constitutes the nuclear degrees of freedom) is taken in the harmonic approximation, cf. eq 16. Regarding the diagonal coupling term Δ, we write it as a quadratic form in the bath coordinates:

$$\Delta = \sum_{\alpha} \omega_{\alpha}^{2}\delta_{\alpha}Q_{\alpha} + \frac{1}{2} + \frac{1}{2}\sum_{\alpha} \omega_{\alpha}^{2}\delta_{\alpha}^{2} + \sum_{\alpha\alpha'} g_{\alpha\alpha'}Q_{\alpha}Q_{\alpha'} \qquad (20)$$

This form of diagonal coupling would arise when the two potential energy surfaces corresponding to the two electronic states can be described by two multidimensional harmonic surfaces with different equilibrium positions and different frequencies with the additional possibility of mode mixing between the two states. The first two terms in Δ are due to the displacements of the equilibrium positions of the normal modes, while the last term corresponds to the frequency shifts and Duschinsky rotations of the normal modes between the two electronic states. The procedure of obtaining the coupling constant δ_{α} and $g_{\alpha\alpha'}$ is given in our recent work.[77]

Under the assumption of the constant off-diagonal coupling (static coupling approach), the quantum mechanical expression for the transition rate reduces to the Fourier transform (evaluated at the frequency ($\omega_{\mathrm{el}} = (E_1 - E_0)/\hbar$) of the thermal average of the time-ordered exponential:

$$k_{0\to1} = \frac{|V_{01}|^2}{\hbar^2}\int_{-\infty}^{\infty} \mathrm{d}t\, \mathrm{e}^{i\omega_{\mathrm{el}}t}\left\langle \exp_{-}\left\{\frac{i}{\hbar}\int_0^t \mathrm{d}t'\Delta(t')\right\}\right\rangle \qquad (21)$$

As discussed in the previous section, in order to obtain a mixed quantum-classical approximation to the above result, one needs to replace the quantum mechanical average with the classical one, neglect the time ordering, and treat $\Delta(t)$ as a function of dynamic classical variables. In addition, one needs to specify the Hamiltonian used for the propagation of the nuclear degrees of freedom, i.e., the form of the interaction picture used. Here we will limit ourselves to the following two propagation schemes: (a) the dynamic classical limit is obtained by propagating $\Delta(t)$ on the initial Hamiltonian H_0 and (b) the average classical limit is obtained by propagating $\Delta(t)$ on the arithmetic averaged Hamiltonian $^1/_2(H_0 + H_1)$ (both mixed quantum-classical approximations are very different from the mixed quantum-classical TDSCF approach).

The fully quantum mechanical results are calculated by employing the density matrix formalism of Kubo and Toyozawa,[134] which is based on Gaussian integrals. (Equivalently, one could use the boson algebra technique of Balian and Brezin,[144] which allows evaluation of the thermal averages of exponentiated quadratic functions of phonon operators.[145−147]) The method to obtain the mixed quantum-classical result is based on phase space Gaussian integrals, and the details can be found in our recent work.[75] In all cases, the calculations can be done only for a finite number of bath modes (convergence tests have shown that 100 bath modes is always sufficient to obtain converged results for the relaxation rate). Interested readers may consult ref 77 for explicit expressions of the relaxation rate in the exact quantum mechanical case and in the various mixed quantum-classical approximations.

The results of our calculations are shown in Figure 3, where we present a semilog plot of the transition rate (scaled by a typical phonon frequency of the bath) versus the energy gap (scaled by the same frequency). One sees that for the largest energy gap considered, the dynamic classical approximation underestimates the transition rate by nearly two orders of magnitude, while the average classical approximation is nearly one order of magnitude smaller than the quantum mechanical rate.

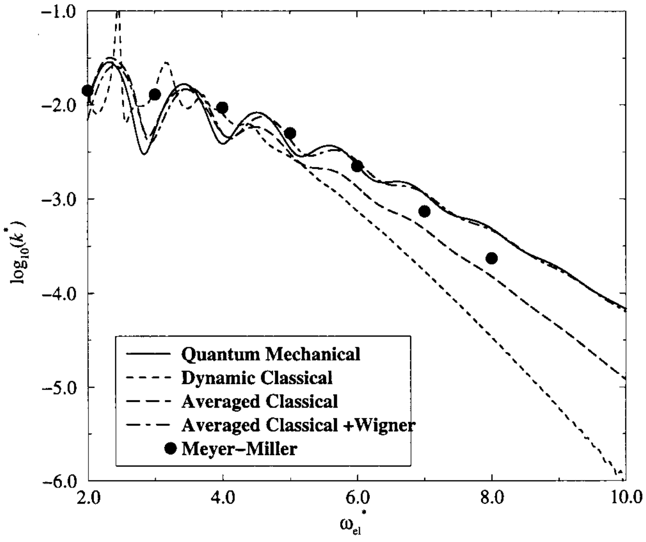

Figure 3. A semilog plot of the electronic relaxation rate versus the electronic energy gap for the static coupling approach. The solid, dotted, dashed, and dashed−dotted lines are the results of the electronic relaxation rate for the quantum mechanical, dynamic classical limit, averaged classical limit, and averaged classical limit with a Wigner initial distribution respectively. The filled circles are the electronic relaxation rate calculated within the Meyer−Miller Hamiltonian approach (see the text for more details).

Motivated by the work of Shemetulskis and Loring,[148] we have analyzed the Wigner form of the time correlation function appearing in the static coupling approach (see eq 21), and have arrived at the conclusion that a mixed quantum-classical treatment should employ the average Hamiltonian for the propagation of the nuclear degrees of freedom.[75,77] Therefore, the somewhat better performance of the average classical propagation scheme is hardly surprising. However, we emphasize that the above conclusion is only valid for the static coupling scheme, i.e., for *constant* off-diagonal coupling matrix elements. It no longer holds when these matrix elements depend on the nuclear coordinates and/or momenta, as will be shown below.

Our analysis of the Wigner form of the time correlation function has suggested performing thermal averaging with the Wigner form of the initial distribution. As can be seen from Figure 3, the results of the above approximation are in excellent agreement with the exact quantum mechanical relaxation rates. Once again, such good agreement is not expected in the case of momentum-dependent coupling (the adiabatic approach, see below).

Recall that in the case of vibrational energy relaxation a fully classical treatment provides more accurate results than the mixed quantum-classical approximation. Motivated by this finding, we became interested in performing a fully classical treatment of the electronic relaxation problem. Since our model for the electronic relaxation involves two discrete states (two distinct PESs), this is more difficult to formulate compared to the vibrational relaxation case. One possibility is to employ the method of Meyer and Miller,[149,150] which provides a classical analog for a system involving on several electronic states. In the Meyer−Miller method, the Hamiltonian of the discrete system is mapped to a continuous one, and the dynamics of the electronic degrees of freedom and the bath degrees of freedom are treated classically. The mapping procedure for the present problem is described in detail in our recent publication.[151] We note in passing that Stock and Thoss[152] have shown that the Meyer−Miller Hamiltonian can be obtained by taking the classical limit of a more general Hamiltonian obtained by using second quantization formalism.

To study the fully classical limit of the nonradiative electronic relaxation we will treat the electronic degrees of freedom and the bath degrees of freedom in the Meyer−Miller Hamiltonian classically. The only nonclassical feature of this computation involves the use of the Wigner form of the appropriate initial distribution.[60,153] In semiclassical language, this approximation is referred to as the linearized SC-IVR.[60]

The most convenient way to obtain the rate in this approach is to use the reactive−flux method,[154−157] which was generalized to the quantum mechanical case by Miller, Schwartz, and Tromp.[158] This approach has been recently applied to the unbiased spin−boson problem by Miller and co-workers.[59,61] Our Hamiltonian is more general and reduces to their model when Δ is taken to be a linear function of the bath modes and E_0 is taken to be equal to E_1. The implementation details for applying the reactive−flux method to our model Hamiltonian will be reported elsewhere.[151]

The results for the electronic relaxation rate of the Meyer−Miller reactive−flux calculations are also shown in Figure 3. Due to the fact that the method is computationally quite demanding, the relaxation rates were calculated only for a few selected values of the electronic energy gaps. We find that the results for the electronic relaxation rate are in good agreement with the exact quantum results. In addition, we would like to point out that in contrast to the mixed quantum-classical approximation, the transformation of the Hamiltonian into the Meyer−Miller form does not suffer from nonuniqueness. Therefore, we believe that this treatment is more robust to the aforementioned mixed quantum-classical approximations.

We now proceed to discuss the adiabatic approach to electronic relaxation processes. In this case, the off-diagonal coupling term depends linearly and quadratically on the bath momenta. Following Kubo and Toyozawa,[134] we neglect the quadratic term and make the Condon approximation in the remaining linear term. The diagonal coupling term Δ is given by eq 20 and is the same as in the static coupling approach. The quantum mechanical expression for the transition rate is given by the Fourier transform (evaluated at the frequency ($\omega_{el} = (E_1 - E_0)/\hbar$) of the thermal average of the time-ordered exponential:

$$k_{0\to 1} = \frac{1}{\hbar^2}\int_{-\infty}^{\infty} \mathrm{d}t\, \mathrm{e}^{i\omega_{el}t} \left\langle \mathbf{S}\cdot\mathbf{P}(0)\exp_-\left(\frac{i}{\hbar}\int_0^t \mathrm{d}t'\Delta(t')\right)\mathbf{S}\cdot\mathbf{P}(t)\right\rangle \tag{22}$$

where according to the Condon approximation the nonadiabatic coupling vector **S** is taken to be independent of the bath coordinates.[77] The quantum mechanical result and various mixed quantum-classical approximations (dynamical classical, averaged classical, and averaged classical with the Wigner initial distribution) for the relaxation rate are then calculated using the same procedures as in the case of static coupling. Interested readers may consult ref 77 for the details.

The results of our calculations are shown in Figure 4, where we present a semilog plot of the transition rate (scaled by a characteristic phonon frequency) versus the dimensionless energy gap (scaled by the same frequency). For the largest energy gap considered, the dynamical classical approximation underestimates the transition rate by several orders of magnitude, while the averaged classical result is about 2 orders of magnitude smaller than the quantum mechanical rate. The averaged classical result with the Wigner initial distribution still provides

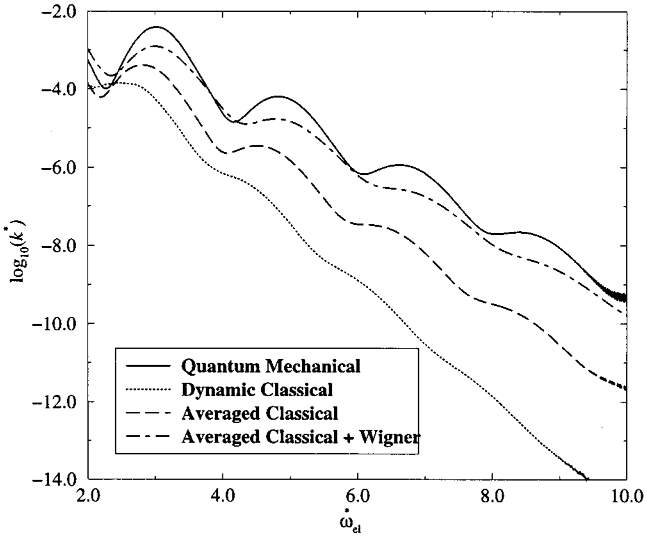

Figure 4. A semilog plot of the electronic relaxation rate versus the electronic energy gap for the adiabatic approach. The solid, dotted, dashed, and dashed−dotted lines are the results of the electronic relaxation rate for the quantum mechanical, dynamic classical limit, averaged classical limit, and averaged classical limit with a Wigner initial distribution respectively.

the best approximation to the exact quantum result, although in the present case it is less accurate compared to the case of the static coupling scheme. Note that we did not present the fully classical approximation in the form of the Meyer−Miller Hamiltonian for the adiabatic approach since the momentum coupling introduces a technical complication into this method.

In summary, the major difference between the electronic relaxation case and the vibrational relaxation (in its present formulation) lies in the nonuniqueness of the mixed quantum-classical approximation. While worrisome, this nonuniqueness can be actually turned into an advantage: one can improve the results of mixed quantum-classical treatment by choosing the optimal propagation scheme. We have illustrated this point by performing the analysis of the Wigner form of the time correlation function in certain cases studied. The outcome of this analysis has allowed us to formulate the optimal propagation scheme, and thereby to improve the agreement of the mixed quantum-classical treatment with the exact quantum result.

IV. Radiative Processes

In addition to nonradiative relaxation processes, quantum time correlation functions are of major importance in calculating various types of spectra.[82,159] The effect of nuclear dynamics of the bath particles on the line shape reveals itself in the shift and broadening of individual spectral lines comprising the gas phase electronic absorption spectrum of the chromophore. As such, the absorption spectrum of a molecule embedded in a crystal or in a liquid provides valuable information about the structure and dynamics of the host and the chromophore perturbed by the host.

Quantum mechanical calculations of electronic absorption spectra in condensed phases are extremely difficult in view of the large number of degrees of freedom involved. For any realistic system this many-body problem can only be solved approximately. The simplest approximation would be to retain the quantum nature of the electronic degrees of freedom only, and to treat all nuclear degrees of freedom (including those of the chromophore) classically.[75,76,81,160−163] This approximation is equivalent to the mixed quantum-classical treatment of the electronic relaxation, and thus is not unique. In due course we will discuss the results of different propagation schemes.

When the nuclear coordinates of the primary system are strongly perturbed by the electronic transition, it would seem appropriate to extend the quantum methodology to these degrees of freedom, and to couple their quantum dynamics in some way to the classical dynamics of the bath particles.[75,76] For this purpose we have formulated a Feynman path integral description of the vibronic absorption spectrum where the primary nuclear degrees of freedom of the chromophore are treated quantum mechanically. The effect of the bath on the spectrum in this approach is entirely given by the influence functional of Feynman and Vernon,[64] which was generalized for the present problem.[75] The mixed quantum-classical approximation is then obtained by taking the classical limit of the influence functional. We note that this classical limit, like many others, does not preserve detailed balance per se. More recently, Makri and Thompson[62,63] studied a semiclassical limit of an influence functional for a different physical problem. Their approach is likely to provide a more accurate solution than the fully classical limit (in the case of a harmonic bath, the semiclassical limit of the influence functional is exact).

We calculate the electronic spectrum within the Fermi golden rule and the electric dipole approximation.[164] We also adopt the Condon approximation where the electric dipole μ does not depend on the nuclear coordinates. Hence, the off-diagonal coupling term is given by

$$V = \epsilon e^{i\omega t}\mu_{01}|0\rangle\langle 1| + \epsilon^* e^{-i\omega t}\mu_{10}|1\rangle\langle 0| \qquad (23)$$

where $\mu_{01} = \langle 0|\mu|1\rangle$ and $\mu_{10} = \langle 1|\mu|0\rangle$ are independent of the nuclear coordinates; ϵ and ω are the amplitude and the frequency of the field coupling the two electronic states, respectively. The normalized electronic absorption spectrum is given by the Fourier transform of the normalized real-time dipole autocorrelation function:

$$I(\omega) = \frac{1}{2\pi}\int_{-\infty}^{\infty} dt\, \exp(i(\omega_{10} - \omega)t)\left\langle \exp_{-}\left\{\frac{i}{\hbar}\int_0^t dt'\Delta(t')\right\}\right\rangle \qquad (24)$$

where $\omega_{10} = (E_1 - E_0)/\hbar$. Here we consider a more particular quadratic form for the diagonal coupling term Δ to model a primary diatomic mode (q) treated in the harmonic approximation and bilinearly coupled to the harmonic bath:

$$\Delta = \frac{1}{2}(\omega_{m1}^2(q - \delta)^2 - \omega_{m0}^2 q^2) + \sum_{\alpha}(g_{\alpha}^1(q - \delta) - g_{\alpha}^0 q)Q_{\alpha} \qquad (25)$$

Note that our model accounts for different vibrational frequencies of the primary mode (ω_{m0} and ω_{m1}) and different solute−bath coupling strength (g_{α}^0 and g_{α}^1) in the two electronic states. The procedure of obtaining the coupling constant $g_{\alpha}^{0,1}$ is described in ref 75.

We calculate the fully quantum mechanical vibronic spectrum and also the dynamic and averaged mixed quantum-classical approximations to it using the techniques mentioned in the previous section. (Recall that the dynamic classical approximation involves propagation with the initial Hamiltonian, while in the averaged classical approximation the propagation is done using the arithmetic average Hamiltonian.) As mentioned earlier, we have also obtained another mixed quantum-classical prescription in which the primary mode (the vibrational mode of

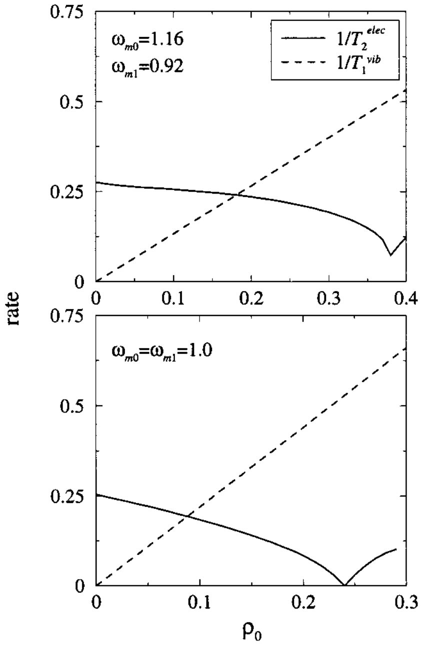

Figure 5. A plot of the electronic dephasing rate $1/T_2^{\mathrm{elec}}$ and the vibrational relaxation rate on the ground electronic state $1/T_1^{\mathrm{vib}}$ versus the coupling strength in the ground electronic state, ρ_0 and for $\rho_1 = 0.24$ (see our original work[76] for the definitions of $\rho_{0,1}$). Note that $1/T_2^{\mathrm{elec}}$ decreases with ρ_0 until a minimum is reached, and then it increases with ρ_0, while $1/T_2^{\mathrm{vib}}$ scales linearly with the coupling strength.

the molecule) is treated quantum mechanically, based on taking a classical limit of the appropriate influence functional.[75]

Within our model, the two important time scales in calculating the vibronic spectrum are the vibrational relaxation rate for the primary mode ($1/T_1^{\mathrm{vib}}$) and the electronic dephasing rate ($1/T_2^{\mathrm{elec}}$). The two rates have very different dependencies on the temperature and on other physical parameters specifying the model. In general, the electronic dephasing rate increases with the magnitude of the *difference* between the system−bath coupling strengths in the two electronic states, while the vibrational relaxation rate in each of these states is proportional to the magnitude of the coupling strength. Thus, by adjusting these parameters, one can achieve the situation where the electronic dephasing is faster than vibrational relaxation ($1/T_2^{\mathrm{elec}} > 1/T_1^{\mathrm{vib}}$) or vice versa, as illustrated in Figure 5. On the basis of the discussion of mixed quantum-classical treatments of vibrational energy relaxation in the bilinear coupling case, one may anticipate that the optimal mixed quantum-classical scheme would be different for these two situations.

In our work, we have considered both the case of $1/T_2^{\mathrm{elec}} > 1/T_1^{\mathrm{vib}}$ and the opposite case when $1/T_2^{\mathrm{elec}} > 1/T_1^{\mathrm{vib}}$.[75,76] The performance of various mixed quantum-classical approximations was indeed found to be markedly different in the two cases. In Figure 6 we present the exact quantum mechanical vibronic absorption spectrum and various mixed quantum-classical approximations to it for the case when the electronic dephasing is much faster than vibrational relaxation. One sees immediately that the dynamic classical approximation captures only the envelope of the exact spectrum but not the vibronic structure, similar to the classical Franck−Condon result.[165] We note that this failure of the dynamic classical approximation is related to a rather specific choice of parameters; in a more general case, the performance of this method is somewhat better, as will be shown below. The averaged classical treatment provides a good approximation to the absorption spectrum, albeit somewhat misplaces the positions of individual vibronic features. The best agreement is obtained using the mixed quantum-classical treatment in which both the two states and the primary mode are treated quantum mechanically and the bath is treated classically. This approximation captures the position and very slightly overestimates the width of the individual lines.

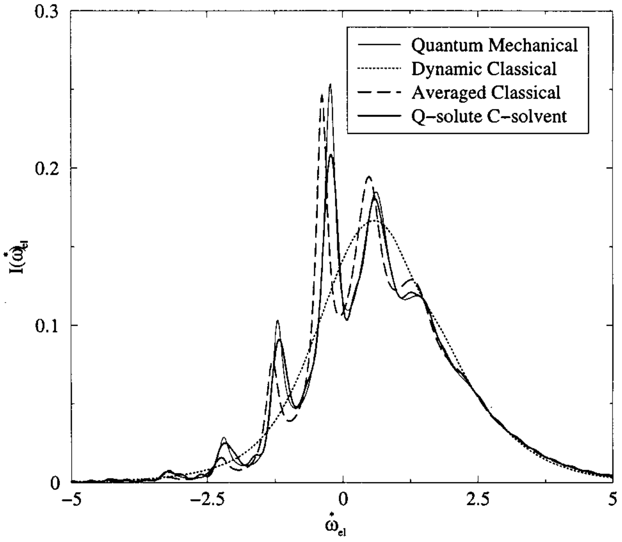

Figure 6. The vibronic absorption spectrum of a diatomic molecule coupled to a harmonic bath in the limit of fast electronic dephasing. The thin solid line is the fully quantum mechanical result. The dotted and dashed lines are the dynamic and average classical approximations, respectively. The thick solid line is the result of the mixed quantum-classical treatment where the primary mode is treated quantum mechanically and the bath is treated classically (Q-solute, C-Solvent).

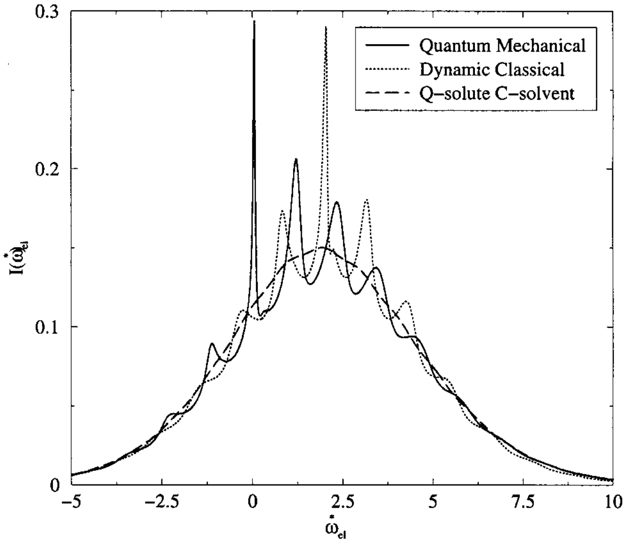

Figure 7. The vibronic absorption spectrum of a diatomic molecule coupled to a harmonic bath in the limit of fast vibrational relaxation. The thin solid line is the fully quantum mechanical result. The dotted line is the dynamic classical approximation. The dashed line is the result of the mixed quantum-classical treatment where the primary mode is treated quantum mechanically and the bath is treated classically (Q-solute, C-Solvent). The results of the averaged classical limit agree with the fully quantum mechanical result and thus are not shown.

We now turn to the case when the vibrational relaxation is faster than the electronic dephasing. The corresponding results for the absorption spectra are presented in Figure 7; the relevant parameters are given in the caption. Since we have seen that for the problem of vibrational relaxation the mixed quantum classical treatment is inferior to the fully classical one, in the present case one would anticipate a breakdown of the ap-

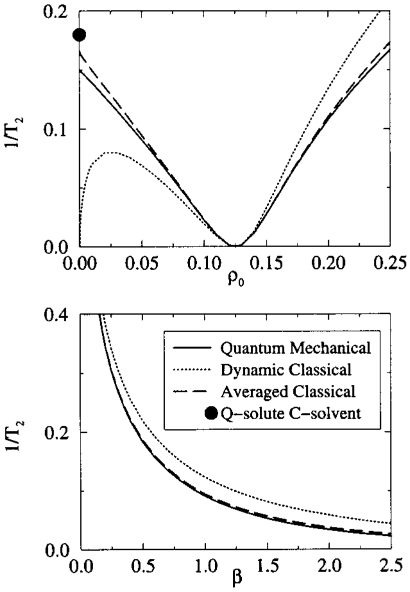

Figure 8. Plots of the temperature and coupling dependence of the dephasing rate $1/T_2^{\mathrm{elec}}$. Shown are the fully quantum mechanical result (solid line), dynamic classical approximation (dotted line), average classical approximation (dashed line), and the result of the mixed quantum-classical treatment where the primary mode is treated quantum mechanically and the bath is treated classically (●, Q-solute, C-solvent).

proximation where the primary mode is treated quantum mechanically and the bath is treated classically. As can be clearly seen from Figure 7, this is indeed the case: the above approximation captures only the envelope of the spectrum, and fails to predict the individual vibronic features. As expected from the work of Bader and Berne,[73] the problems with this method are somewhat less pronounced at higher temperatures. In contrast to the case of fast electronic dephasing, for the present choice of parameters the dynamic classical approximation does capture the overall shape and width of individual vibronic features; however, they are shifted with respect to the exact quantum result. Finally, the averaged classical result is essentially indistinguishable from the fully quantum spectrum, and therefore is not shown in Figure 7. As in the case of nonradiative electronic relaxation, performing the averaging with the Wigner initial distribution is expected to improve the performance of mixed quantum-classical treatments. However, the major improvement occurs at high frequencies, i.e., in the tails of the spectra, where the magnitude of the spectra are rather small, and therefore the improvement is not noticeable.

As is clear from the above discussion, one of the major deficiencies of mixed quantum-classical treatments in calculating vibronic spectra is that they produce incorrect results for the positions and widths of individual vibronic features. The above quantities are given by the frequency shifts and dephasing rates which, in turn, are determined by the long-time behavior of the corresponding time-correlation functions. In order to address this issue, we have adopted and generalized the theory of Skinner and Hsu[166−168] which allowed us to calculate the frequency shifts and the dephasing rates for the fully quantum mechanical case and for the dynamic and averaged classical approximations. The results of our calculations are presented in Figure 8. The dynamic classical treatment underestimates the dephasing rates severely as the coupling strength in the initial electronic state goes to zero, while the averaged classical approximation reproduces the quantum dephasing rates reasonably well over the whole range of the coupling strengths. For the approximation where the primary mode is treated quantum mechanically and the solvent is treated classically, we can only calculate the dephasing rate analytically in the absence of coupling in the initial electronic state, the result is also shown in Figure 8, it is slightly larger than the quantum dephasing rate.

To summarize this Section, we have considered the vibronic absorption spectrum of a diatomic molecule (taken in the harmonic approximation) bilinearly coupled to a harmonic bath (with *different* equilibrium positions, coupling strengths, and molecular vibrational frequencies for the two electronic states), and tested various mixed quantum-classical approximations. We considered separately two situations: the case when the electronic dephasing is fast compared to vibrational relaxation, and the opposite case—the vibrational relaxation is faster than the electronic dephasing. We have found that in the first case the approximation where the primary mode is treated quantum mechanically and the solvent is treated classically provides the best overall agreement with the quantum mechanical spectrum. In the second case, the best mixed quantum-classical approximation is provided by the averaged classical treatment. These findings are consistent with the results from the previous Section on the vibrational energy relaxation in the case of bilinear coupling.

One final remark is that all spectra in our work were calculated within the Franck−Condon approximation, and the averaged classical method was generally found to give highly accurate results. However, if one goes beyond the Franck−Condon approximation, the off-diagonal matrix elements of the dipole operator acquire a dependence on the bath coordinates, and the analysis of the Wigner form of the corresponding time correlation function would no longer suggest classical propagation with the average Hamiltonian. In other words, the averaged classical method then can no longer be expected to provide accurate results. This is similar to our findings on the electronic relaxation rates calculated in the adiabatic approximation presented in the previous Section.

V. Discussions and Conclusions

The problem of obtaining accurate quantum mechanical time correlation functions in many-body systems is of primary importance for calculating numerous observables of interest in physics and chemistry. Unfortunately, at the present time the exact solution to the above problem is possible only for highly simplified models, such as harmonic baths. As an alternative, various mixed quantum-classical treatments have been widely used over the past several decades. In these methods, the full many-body system is generally divided into a few highly quantum degrees of freedom (for which the characteristic energies are higher than the temperature), and the remaining modes, for which the characteristic energies are lower than the temperature, and which are treated classically. However, the above criterion for selecting the classical modes does not necessarily guarantee the accuracy of the mixed quantum-classical treatments, since it is imperative to achieve a consistent dynamical treatment of quantum and classical degrees of freedom, and to properly describe the feedback between the two subsystems.

The above goals are achieved in different ways depending on a particular realization of the mixed quantum-classical approximation, but in most cases certain ad hoc assumptions and uncontrollable approximations are unavoidable. Therefore, it is of great importance to assess the accuracy and the range of validity of the mixed quantum-classical treatments by comparing their predictions to the quantum mechanical results for exactly solvable models. It also would be advantageous to adopt a systematic approach for developing mixed quantum-classical treatments, since it would allow not only the systematic improvement of the results for the observables of interest, but would also elucidate the mechanisms for the processes under consideration. One such systematic procedure—expansion of the quantum time correlation functions in powers of Planck's constant—forms the basis of our recent work, which has been reviewed in the present article.

Starting with a general harmonic Hamiltonian, we have specialized it and adopted it to study various physical processes, including both radiative and nonradiative transitions of impurities (solutes) in condensed phase environments (baths). We have calculated the observables such as vibronic absorption spectra, electronic dephasing rates, and electronic and vibrational energy relaxation rates. In each case, our major interest was to compare the exact quantum result for a given observable with a mixed quantum-classical approximation to it, where (generally) the solute is treated quantum mechanically, and the bath classically. For that reason, we have always modeled the condensed phase environment as a harmonic bath.

A. Vibrational Energy Relaxation. For the problem of vibrational energy relaxation, we have considered two specific models for the system-bath coupling—bilinear and exponential—and have found that in both cases a fully classical treatment gives more accurate results than the mixed quantum-classical one.

In the case of bilinear coupling (i.e., single-phonon relaxation) the error in the mixed quantum-classical approximation is entirely due to the incorrect thermal averaging, since classical and quantum dynamics for this model are the same. Concomitantly, the fully classical result for the relaxation rate in this case agrees exactly with the quantum mechanical one. This suggests that, for single-phonon processes, it is enough to correct only the initial distribution with which the averaging is performed. However, in highly anharmonic systems this may not be sufficient.

In the case of highly nonlinear system−bath coupling (that is appropriate for multiphonon relaxation processes) the most severe breakdown of mixed quantum-classical and fully classical treatments occurs at high solute vibrational frequencies, where these treatments can underestimate the relaxation rates by several orders of magnitude. This situation has been recently illustrated with a particular physical example by Everitt et al.,[101] who studied vibrational energy relaxation in liquid oxygen, where the vibrational frequency of the solute exceeds the temperature of the solvent and its typical translational frequency by more than 30 times. The above breakdown of mixed quantum-classical approximation is a consequence of both incorrect thermal averaging and incorrect dynamics, with the latter factor accounting for the major part of the error. More specifically, the high-frequency vibrational relaxation rates are mostly sensitive to the short-time behavior of the relevant time correlation function. It can be shown that the mixed quantum-classical treatment produces large errors in the short-time expansion coefficients of TCFs, which, in turn, leads to the errors in the relaxation rates. The above errors arise primarily due to the incorrect treatment of the dynamics, and to a much lesser extent to the incorrect thermal averaging. Thus, employing a Wigner initial distribution is not expected to improve the results significantly. One possible way of improving the results of mixed quantum-classical treatment is to perform a systematic expansion of the first few time-series expansion coefficients of the quantum time correlation function in powers of Planck's constant and to incorporate this information into correcting the results of the mixed quantum-classical approximation. Another way is to resort to semiclassical methods, such as the aforementioned linearized SC-IVR which implies a Wigner−Weyl transform of the correlation function, or to its fully-blown version which would also partially correct part of the incorrect dynamics.

We have also considered various empirical quantum corrections (such as those due to Schofield and Egelstaff) in the context of vibrational energy relaxation in condensed phases. A common feature in these empirical prescriptions is the replacement of the time argument in the classical time-correlation function by a different argument, which depends on time, temperature, and Planck's constant. As a result, the moments of this modified TCF get closer to the true quantum values. However, such prescriptions are ad hoc in nature, i.e., they cannot be derived in a rigorous and *systematic* way. Indeed, our studies have shown that none of these procedures is robust enough to provide accurate results for vibrational relaxation rates for different solute−solvent interaction potential.

B. Nonradiative Electronic Relaxation. For the problem of electronic energy relaxation, we have considered a model with two PESs, corresponding to the two electronic states of the solute. Due to a finite energy spacing between these two states, the relevant time correlation function retains some quantum character, and the mixed quantum-classical approximation is not unique. Specifically, there is a certain arbitrariness in the choice of the Hamiltonian that is used to propagate the classical degrees of freedom.

We have considered a Wigner form for the appropriate time correlation function, and have shown that the above arbitrariness can be used to some advantage, i.e. one can attempt to find an optimal propagation scheme for the classical degrees of freedom that produces the best agreement with the quantum results. For the case of static coupling between the two PESs (i.e., coupling independent of nuclear coordinates and momenta) we have shown that for our model the optimal propagation scheme involves an arithmetic average of the nuclear Hamiltonians associated with the initial and final electronic states. In the case when the two multidimensional harmonic surfaces corresponding to the two electronic states differ only with respect to the equilibrium positions of individual modes (but the frequencies of these modes are the same and there is no mode mixing involved), the above averaged quantum-classical treatment produces the exact quantum result for the rate *provided* it is combined with the thermal averaging performed with the Wigner distribution. Once again, the error in the standard mixed quantum-classical approximation (i.e., the one based on the initial state classical propagation) arises both due to the incorrect treatment of the dynamics (which can be fixed by choosing the optimal propagation scheme) and due to the incorrect averaging (which can be fixed by using the Wigner distribution). In contrast to the case of vibrational energy relaxation, both factors contribute nearly equally (about 1 order of magnitude for the case studied) to the error in the electronic relaxation rate. Given the importance of performing thermal averaging with the Wigner distribution, we note that for anharmonic systems this can be achieved approximately by employing the same methodology as the one used in the semiclassical initial value representation method to treat the time dependence. However, the success of the Wigner method for anharmonic systems is still open for future investigations, and the overall good performance for the present *harmonic* system is likely to break down.

For the case of adiabatic (i.e., momentum-dependent) coupling, the analysis of the Wigner form of the time correlation function is considerably more involved. The only conjecture we can make at this point is that the optimal propagation scheme is likely to be different from the averaged Hamiltonian, however the later propagation scheme provides reasonably good agreement for the quantum mechanical relaxation rates.

Motivated by the finding that for vibrational relaxation problem in the case of bilinear coupling a fully classical treatment provided more accurate results than the mixed quantum-classical approximation, we performed a fully classical treatment of the electronic relaxation problem. We have formulated the problem using the Meyer−Miller Hamiltonian, which we treated classically, in combination with the Wigner form of the appropriate initial distribution. The results for the rates obtained with the above method were in good agreement with the exact quantum results, though the performance of the averaged classical propagation combined with the Wigner distribution was somewhat better. However, the success of this particular mixed quantum-classical scheme (the averaged propagation scheme) might be limited to the case of harmonic models, and for anharmonic systems the fully classical treatment may well prove to be superior. In addition, we would like to point out that in contrast to the mixed quantum-classical approximation, the transformation of the Hamiltonian into the Meyer−Miller scheme does not suffer from nonuniqueness. Therefore, we believe that this treatment is superior to the mixed quantum-classical approximations.

While our primary interest in considering nonradiative electronic processes was the calculation of multiphonon energy relaxation rates (i.e., large gap limit), we note that the same methodology can be applied to study electron transfer reactions in condensed phases. However, in the latter case the energy gaps involved are typically smaller than those involved in the electronic energy relaxation processes. Therefore, the appropriate criterion for choosing the best mixed quantum-classical approximation for electron transfer reactions should be based on its performance at small and intermediate energy gaps rather than at large energy gaps. We will return to this point below after the discussion of radiative processes.

C. Vibronic Absorption Spectrum. We have also assessed the accuracy of mixed quantum-classical approximations in treating radiative processes in condensed phases, taking as a test case the calculation of the vibronic absorption spectrum of a diatomic molecule bilinearly coupled to a harmonic bath. To establish contact with our work on nonradiative processes, we have considered separately two situations: the case when the electronic dephasing is fast compared to vibrational relaxation, and the opposite case of vibrational relaxation faster than the electronic dephasing. We have found that in the first case the approximation where the primary (diatomic) nuclear mode is treated quantum mechanically and the solvent is treated classically provides the best overall agreement with the quantum mechanical spectrum. This is expected since in the case of an isolated molecule (i.e., for vanishing system−bath coupling), it is necessary to treat all degrees of freedom quantum mechanically to obtain the proper Franck−Condon overlaps. Hence, for small system−bath coupling, when the electronic dephasing dominates the absorption spectrum, a fully quantum treatment of the subsystem is required. In the second case, the best mixed quantum-classical approximation is provided by the averaged classical treatment, and the quantum-solute−classical-solvent approximation breaks down completely.

The above conclusions are consistent with our findings on vibrational energy relaxation in the case of bilinear system−bath coupling. Specifically, in the case of fast vibrational energy relaxation, the vibrational relaxation rates contribute significantly to the widths of individual spectral features, and the mixed quantum-classical treatment (quantum-solvent−classical-solvent) can be expected to give inaccurate results similar to the vibrational relaxation model of Bader and Berne. On the other hand, in the case of the fast electronic dephasing the widths of spectral features are dominated by low-frequency two phonon processes, as can be easily seen by transforming the Hamiltonian for the nuclear coordinates into the normal mode representation. It turns out that, in this case, the widths of individual spectral features (which are dominated by the electronic dephasing rate) are given sufficiently accurately by all mixed quantum-classical treatments. However, the performance of the different methods is very different in determining the peak positions (or the shifts) of the vibronic spectral features. The dynamic classical treatment displaces the spectral features significantly compared to the quantum results, while the other two approximations provide fairly accurate results.

Turning now to the ramifications of our findings on radiative processes for realistic physical systems, we can make the following remarks. Firstly, when the experimentally measured spectrum is featureless (which is likely to occur for high temperatures and/or strong system−bath couplings), any of the mixed quantum-classical treatments will produce sufficiently accurate results. Secondly, when the vibronic structure is clearly pronounced in the spectrum, the choice of the best mixed quantum-classical approximation is dictated by the relative magnitude of vibrational relaxation and electronic dephasing rates. It would be safe to conjecture that in the majority of physical systems the electronic dephasing will dominate over vibrational relaxation, and the mixed (quantum primary mode−classical solvent) treatment would be the optimal one. However, the above two rates differ markedly in their temperature dependence, and it is conceivable that for certain temperatures and system-bath couplings the opposite situation will be realized, in which case the averaged classical treatment (at least for harmonic systems) is the method of choice.

Finally, going back to our remark on the electron transfer reactions, we note that the rates for these processes can be calculated using the same methodology as the one employed to calculate the vibronic absorption spectrum. Hence, the mixed (quantum primary mode−classical bath) treatment is generally likely to give the most accurate results for the electron transfer rates.

VI. Future Directions

In this article we have reviewed our recent work on the validity of mixed quantum-classical approximations for treating dynamical processes in condensed phases. Our results have demonstrated that these approximations have to be used with extreme caution. For problems involving a single potential energy surface (such as vibrational energy relaxation) the mixed quantum-classical approximation is unique, and for solute frequency large compared to the thermal energy it fails to provide accurate results. For problems with multiple surfaces (such as electronic relaxation and vibronic spectra) the mixed quantum-classical approximations are not uniquely defined, and due to the arbitrariness in the choice of the propagation scheme, the accuracy of the mixed quantum-classical treatment can be improved. However, in order to achieve accurate results, one needs to perform thermal averaging with the Wigner initial distribution instead of the classical one. While for harmonic systems considered in the present work this can be readily done, for anharmonic systems this is a highly nontrivial problem.

The present study has been based entirely on the Fermi golden rule, and therefore the later treatment neglects the feedback between the quantum and classical subsystems. One possible way to go beyond the lowest order perturbation theory and include the feedback is provided by the surface hopping technique.[12] However, similar to the approximate treatments considered in this work, the surface hopping method also relies on the mixed quantum-classical description of the system. When the coupling between the quantum states involved is weak, the perturbation theory is valid, and therefore the results from the surface hopping calculations are expected to be similar to those obtained from the mixed quantum-classical perturbative approach taken in this work. The methods for improving these results (i.e., “mixed state propagation” and thermal averaging with the Wigner distribution) can be readily incorporated into a surface hopping method, although the same limitations as discussed in the previous Section would also apply.

In the case where mixed quantum-classical approximations fail, one needs to resort to a higher level of approximation such as the semiclassical methods. One such possibility is to employ the linearized semiclassical initial value representation method.[60] We have applied this method to the calculation of electronic relaxation rates based on the reactive-flux approach and obtained very good agreement with the fully quantum mechanical result even for large energy gaps.[151] The use of the reactive-flux formalism implies that the method is not limited to the weak coupling regime. The main limitation of this approach is that it requires the knowledge of the Wigner distribution, which is difficult to obtain for anharmonic systems. Another possibility is the rigorous forward−backward semiclassical formulation of many-body dynamics.[62] More work is needed before this approach will become practical for many-body systems.

Finally, we would like to mention that there exists and is currently being developed an entirely different approach to quantum dynamics in condensed phases that is based on performing the fully quantum simulations in imaginary time (thus obviating the sign problem), and performing an analytic continuation to the real time using various methods,[169] such as maximum entropy,[170−172] singular value decomposition,[173,174] etc. The above analytic continuation is a well known ill- defined problem, which makes it extremely difficult to obtain accurate real-time information from the simulated quantum imaginary-time data with realistic levels of noise. To achieve this goal, much further work is required.

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