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Classical Approximation to Nonradiative Electronic Relaxation in Condensed Phase Systems

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We present a study of the classical limit of nonradiative electronic relaxation in condensed phase systems. The discrete Hamiltonian representing an impurity in a condensed phase environment is mapped onto a continuous form using the Meyer−Miller approach. The classical electronic relaxation rate is obtained within the framework of the reactive flux formalism and is compared to the fully quantum mechanical result, and to a mixed quantum−classical approximation. Similar to the case of vibrational relaxation, we find that the fully classical treatment is closer to the fully quantum mechanical rate than the mixed quantum−classical treatment. We provide a time domain analysis of the results.

I. Introduction

Nonradiative relaxation in condensed phases plays an important role in many processes of scientific and technological interest, including the operation of lasers and chemical reactions in solutions.[1−3] Radiationless decay is most conveniently introduced by contrasting it to radiative relaxation, where the system goes from the excited state to the ground state by emitting a photon of the same energy as the gap between the two states involved in the transition. In radiationless relaxation, the excitation energy of the system is not transferred to the electromagnetic field, but instead is dissipated into other forms of motion, such as heat. Particular examples of nonradiative decay include electronic relaxation of ionic impurity centers in solids, vibrational relaxation of molecules in crystals and in solutions, intramolecular vibrational energy redistribution in large polyatomic molecules, energy transfer processes, etc. It is often the case that the amount of energy transferred from the impurity to the host exceeds by many times the typical energy associated with the thermal motion of the solvent. Clearly, in contrast to radiative decay, many quanta of bath excitations need to be created in this process, which is generally referred to as multiphonon relaxation (MPR).

Most theoretical treatments of MPR are based on the time-dependent perturbation theory, where the relaxation rate is expressed in terms of the appropriate time correlation function. A fully quantum mechanical evaluation of this time correlation function is a daunting task that is achievable only for highly simplified models, such as the harmonic bath model. The latter model would be appropriate for treating radiationless decay in a low-temperature solid, but is inadequate for problems involving liquid hosts.[4−6] Given the extreme difficulty of calculating quantum time correlation functions in liquids, a common approach is to obtain the relaxation rates from mixed quantum−classical simulations, where the two discrete states of the impurity are treated quantum mechanically, while the solvent degrees of freedom are treated classically.[7,8] In our recent work,[9,10] we have highlighted the problems associated with such mixed treatment by considering an exactly solvable model Hamiltonian. It was shown that for large energy gaps of the impurity, that are typical for the electronic energy relaxation, the rates obtained within the mixed quantum−classical treatment can differ by several orders of magnitude from the exact quantum results.[9,10]

The mixed quantum−classical approximation was also discussed in the context of vibrational energy relaxation,[11,12] and vibronic absorption spectra.[13,14] For the vibrational energy relaxation it was found that in certain cases the mixed quantum−classical approximation can underestimate the vibrational relaxation rate by several orders of magnitude.[11,12] One important difference between the treatments of electronic and vibrational energy relaxation processes concerns the model Hamiltonian for the solute itself. In the former case, due to the large electronic energy gaps, it is usually sufficient to consider only two states of the impurity (ground and excited), while in the latter case the whole vibrational manifold can be involved in the process. It is straightforward to formulate the problem of vibrational energy relaxation *fully classically*, *provided* one calculates the overall energy relaxation rate for the whole vibrational manifold of the solute, rather than state-to-state transition rates. In fact, it has been found that such a fully classical treatment provides consistently more accurate results for overall vibrational relaxation rates compared to the mixed quantum−classical approach.[11,12]

In view of the above finding, we became interested in performing a fully classical treatment of the electronic relaxation problem. Since a typical model for the electronic relaxation involves two discrete solute electronic states (with two distinct solvent PES associated with them), it is more difficult to formulate a fully classical treatment of this model than in the vibrational relaxation case. One possibility is to employ the method of Meyer and Miller,[15−17] which provides a classical analogue for a system involving discrete quantum states. To study the 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 most convenient way to obtain the rate in this approach is to use the reactive−flux method,[18−22] which was generalized

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to the quantum mechanical case by Miller, Schwartz, and Tromp.[23] This approach has recently been applied to the unbiased spin−boson problem by Miller and coworkers.[24,25] As will become clear in the next Section, our Hamiltonian is more general, but the model we employ is still exactly solvable quantum mechanically (within the lowest order perturbation theory), which will allow us to compare the fully quantum and fully classical results for the electronic relaxation rates. Since the quantum mechanical rates are obtained within the lowest order perturbation theory while the fully classical rates are obtained from the non-perturbative reactive flux approach, we limit the magnitude of the nonadiabatic coupling terms to the range where the Fermi golden rule is valid.

We consider two routes for computing the classical limit of the electronic relaxation rates. In both cases the propagation of all degrees of freedom is done classically. The two classical limits differ with respect to choice of the mapping of the quantum mechanical operators that appear in the reactive flux formalism. In the fully classical approximation we follow the quasi-classical mapping and sampling of initial conditions,[15] while in the other approach we perform a Wigner−Weyl[26,27] transform of the relevant operators. In semiclassical language, the latter approach is often referred to as the Wigner phase space method,[28] or the linearized semiclassical initial value representation (linearized SC-IVR or LSC-IVR).[29]

The organization of the paper is as follows: in Section II we introduce our model Hamiltonian and provide a summary of the quantum mechanical reactive flux method.[23] In Section III we describe the mapping of the discrete model Hamiltonian onto the continuous Meyer−Miller form.[15,17] We also outline the details of the implementation of the LSC-IVR and the fully classical approximation to the reactive flux formalism. The results of our calculations using this formalism are given in Section IV, where the classical electronic relaxation rates are compared with the exact quantum rates. In Section V we conclude.

II. Model Hamiltonian and Nonradiative Relaxation Rate

The model Hamiltonian used in this work is identical to the one we used in our previous study of mixed quantum−classical approximations to nonadiabatic electronic relaxation.[9] We consider an impurity embedded in a condensed phase environment, which we model as a harmonic bath. The impurity has two relevant quantum levels which we label as $|0\rangle$ and $|1\rangle$ for the ground and excited states with energies E_0 and E_1, respectively. The most convenient, yet completely general, form of the Hamiltonian is given by[9]

$$H = (H_b + \Delta + E_0)|0\rangle\langle 0| + (H_b + E_1)|1\rangle\langle 1| + V_{01}|0\rangle\langle 1| + V_{10}|1\rangle\langle 0| \quad (1)$$

where H_b is the bath Hamiltonian which we take to be a sum over harmonic mass-weighted normal modes Q_α with frequencies ω_α and conjugate momenta P_α:

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

The diagonal coupling term, Δ, is taken to be a quadratic function of the bath degrees of freedom[30−32]

$$\Delta = \sum_\alpha \omega_\alpha^2 \delta_\alpha Q_\alpha + \frac{1}{2}\sum_\alpha \omega_\alpha^2 \delta_\alpha^2 + \sum_{\alpha\alpha'} g_{\alpha\alpha'} Q_\alpha Q_{\alpha'} \quad (3)$$

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. It reduces to the form used by Miller and coworkers[24,25] 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 procedure of obtaining the coupling constant δ_α and $g_{\alpha\alpha'}$ was described in our recent work.[9]

For simplicity we limit the discussion here to the static-coupling (crude Born−Oppenheimer) approach in which the off-diagonal coupling matrix elements, V_{01} and V_{10}, are taken to be real constants, i.e., they are independent of the bath degrees of freedom,[9] $V_{01} = V_{10} = V_c$. In our previous work we have also considered a more general form of the off-diagonal coupling matrix elements.[9]

As mentioned in the Introduction, we obtain the nonradiative relaxation rate using the reactive flux formalism.[18−21] The quantum mechanical rate is given in terms of the time integral over the symmetrized flux−flux correlation function[23]

$$k_{0\leftarrow 1} = \frac{1}{Z_r}\int_0^\infty \mathrm{d}t\, C_f(t) \quad (4)$$

where Z_r is the partition function of the reactants, and the flux−flux correlation function is given by

$$C_f(t) = \mathrm{Tr} F_\beta F(t) \quad (5)$$

In the above, F_β is the Boltzmannized flux operator ($\beta = 1/k_B T$ is the inverse temperature)

$$F_\beta = e^{-\beta H/2}\, F e^{-\beta H/2} \quad (6)$$

and the symmetrized flux operator, F, can be expressed in terms of a commutator between the Hamiltonian (H) and a projection operator on the products ($P_0 = |0\rangle\langle 0|$)[23]

$$F = \frac{i}{\hbar}[H,P_0] = \frac{i}{\hbar}(V_{10}|1\rangle\langle 0| - V_{01}|0\rangle\langle 1|) \quad (7)$$

The fully quantum mechanical calculation of the flux−flux time correlation function is not feasible for most many-body systems. Recently, Miller and coworkers[24,25,29,33] have introduced a semiclassical method based on a linear approximation to the Van Vleck propagator.[34,35] In the following section we will provide a brief description of their semiclassical method and make the connection to our model.

III. The Classical Approximation

A. Meyer−Miller Hamiltonian. To obtain a consistent classical description of the nonradiative relaxation rate we need to represent the Hamiltonian in eq 1 with a set of continuous degrees of freedom. One convenient approach to reduce the discrete representation of the Hamiltonian to a continuous one is based on the early work of Meyer and Miller (sometimes referred to as the Meyer−Miller Hamiltonian).[15] Recently, Stock and Thoss[17] have shown that the Meyer−Miller Hamiltonian can be obtained by extending the formulation due to Schwinger. In their derivation, the mapping relation between the basis set and the harmonic oscillator creation and annihilation operators, a_n and $a_m^\dagger$, with commutation relations $[a_n, a_m^\dagger] = \delta_{nm}$, is given by

$$|n\rangle\langle m| \rightarrow a_n^\dagger a_m \tag{8}$$

Using the identity $|0\rangle\langle 0| + |1\rangle\langle 1| = 1$ along with the above specified map (cf. eq 8), the Hamiltonian in the continuous representation reads

$$H = E_0 a_0^\dagger a_0 + E_1 a_1^\dagger a_1 + H_b + \Delta a_0^\dagger a_0 + V_{01} a_0^\dagger a_1 + V_{10} a_1^\dagger a_0 \tag{9}$$

with H_b and Δ given by eqs 2 and 3, respectively. Introducing the position

$$q_n = \frac{1}{\sqrt{2}}(a_n^\dagger + a_n)$$

and momentum

$$p_n = \frac{i}{\sqrt{2}}(a_n^\dagger - a_n)$$

operators, the corresponding Hamiltonian takes the form

$$H = \frac{1}{4}\hbar\omega_{\mathrm{el}}(p_1^2 + q_1^2 - 1) - \frac{1}{4}\hbar\omega_{\mathrm{el}}(p_0^2 + q_0^2 - 1) + H_b + \frac{1}{2}\Delta(p_0^2 + q_0^2 - 1) + \frac{1}{2}(V_{01} + V_{10})(q_0 q_1 + p_0 p_1) \tag{10}$$

where $\hbar\omega_{\mathrm{el}} = E_1 - E_0$, and we have set the zero of energy to be halfway between the two states. The fully quantum mechanical dynamics generated by the Hamiltonian in eq 10 is exactly the same as those generated by the Hamiltonian in eq 1. The advantage of eq 10 is that it can be used as a starting point for a rigorous classical as well as semiclassical approximations.

B. Classical Nonradiative Relaxation Rate. We discuss two classical approximations to the electronic relaxation rates. The first is based on a linearized approximation to the SC-IVR propagator[36−43] introduced by Miller and coworkers,[29] which is referred to as the linearized SC-IVR approach (LSC-IVR). In many ways this approach is identical to the Wigner phase space method due to Heller.[28] It is not a pure classical limit in the sense that the relevant operators are replaced with the corresponding Wigner−Weyl transforms.[26,27] However, both the electronic and the bath degrees of freedom are propagated classically in this approach, i.e., $q_n(t)$, $p_n(t)$, $Q_\alpha(t)$, and $P_\alpha(t)$ are classical dynamic variables. The LSC-IVR flux−flux correlation function is given by[29]

$$C_f(t) = \frac{1}{(2\pi\hbar)^f}\int d\mathbf{q}d\mathbf{p}d\mathbf{Q}d\mathbf{P}F_{w\beta}(\mathbf{q},\mathbf{p},\mathbf{Q},\mathbf{P})F_w(\mathbf{q}(t),\mathbf{p}(t)) \tag{11}$$

where **q** and **p** label the electronic phase space variables, **Q** and **P** label the bath phase space variables, and f is the total number of degrees of freedom. We approximate F_β in eq 6 by $F_\beta = Fe^{-\beta H_b}$ which is equivalent to neglecting the diagonal coupling term, Δ, for the initial distribution,[25] an approximation not always justified. The Wigner−Weyl form of F_β is then given by

$$F_\beta^w(\mathbf{q},\mathbf{p},\mathbf{Q},\mathbf{P}) = F^w(\mathbf{q},\mathbf{p})\rho_\beta^w(\mathbf{Q},\mathbf{P}) \tag{12}$$

where

$$F^w(\mathbf{q},\mathbf{p}) = 16V_c(p_1 q_0 - p_0 q_1)e^{-(q_0^0+p_0^2+q_1^2+p_1^2)} \tag{13}$$

and

$$\rho_b^w(\mathbf{Q},\mathbf{P}) = \prod_\alpha \frac{1}{\cosh(\beta\hbar\omega_\alpha/2)} \exp\left\{-\frac{2\tanh(\beta\hbar\omega_\alpha/2)}{\hbar\omega_\alpha}\left[\frac{P_\alpha^2}{2} + \frac{\omega_\alpha^2 Q_\alpha^2}{2}\right]\right\} \tag{14}$$

In the other classical approach, the Wigner−Weyl form of the operators is replaced with the purely classical form, and the quantum mechanical partition function, Z_r, needed to obtain the electronic relaxation rate is also replaced with its classical counterpart. The flux−flux correlation function is obtained in a similar way to the LSC-IVR with

$$F^w(\mathbf{q},\mathbf{p}) = V_c(p_1 q_0 - p_0 q_1) \tag{15}$$

and ρ_b^w is replaced by the classical distribution function, i.e., by taking the limit $\hbar \rightarrow 0$ in eq 14.

One technical point we would like to make before we discuss the results is related to the sampling of the initial distribution of the electronic degrees of freedom. In the LSC-IVR, the Wigner form of the Boltzmannized flux operator suggests a Gaussian sampling of the electronic phase space variables, according to eq 13, and each trajectory carries a weight of $p_1q_0 - p_0q_1$. On the other hand, the classical form of the flux operator is given only in terms of the weight $p_1q_0 - p_0q_1$. Thus, in the fully classical approach we adopt the quasiclassical prescription,[15] where the population of the two states ($N_n = (q_n^2 + p_n^2 - 1)/2$) is sampled randomly in the interval 0−1 such that the total population is unity, and the conjugate angle, $\phi_n = \tan^{-1}(p_n/q_n)$, is sampled randomly between the interval $0-2\pi$. As before, each trajectory carries a weight of $p_1q_0 - p_0q_1$.

IV. Results

To demonstrate the limitations of the classical approximations we consider a simple model studied by Stock and Thoss,[17] which is the well known spin−boson model[44] with only one vibrational mode. Specifically, the model consists of two coupled electronic states with a Hamiltonian $H_{sb} = (Q^2 + P^2)/20 + (q_1^2 + p_1^2)/2 + (p_0p_1 + q_0q_1)/5 + Q(q_0^2 + p_0^2 - q_1^2 - p_1^2)/40$. In Figure 1 we show the time dependence of the ground state population. The full-blown SC-IVR for this model is in very good agreement with the fully quantum mechanical result (not shown).[17] It captures both the period of the oscillations as well as the dephasing and rephasing of the ground state population. The LSC-IVR and the classical approximation are in good agreement with the SC-IVR for short times; however, they fail to capture the rephasing of the ground state population.[17] The LSC-IVR does a somewhat better job compared to the classical approximation. We note that in the classical approximation shown, we have used a Wigner form for the initial distribution, i.e., the electronic and nuclear degrees of freedom were sampled from a Wigner distribution. However, the Wigner−Weyl transform of the population operator was employed only for the LSC-IVR approach and not for the classical approximation. To be more specific, the classical ground state population was given by

$$P_{\mathrm{classical}} = \frac{1}{2}(q_0^2 + p_0^2 - 1) \tag{16}$$

and in the LSC-IVR the ground state population was given by

$$P_{\mathrm{LSC-IVR}} = 8({q^2}_0 + p_0^2 - 1/2)e^{{q^2}_0+{p^2}_0+{q^2}_1+{p^2}_1} \tag{17}$$

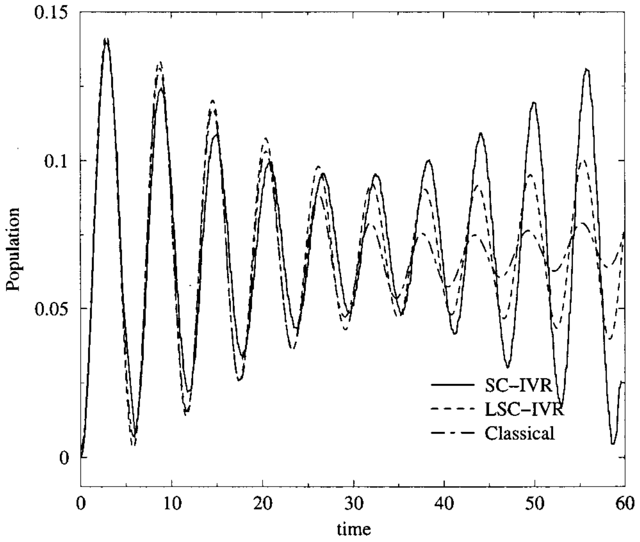

Figure 1. Plot of the time dependence of the ground state population for a spin−boson model with only one vibrational mode. The solid, dashed, and dashed-dotted lines are the SC-IVR, LSC-IVR, and classical approximations, respectively. The SC-IVR is in very good agreement with the fully quantum mechanical result (not shown).

The lesson to be learned from the above model is that the LSC-IVR and the classical approximation are reliable only for relatively short times, and they fail to capture the rephasing phenomena.[33] Moreover, the Wigner−Weyl transform of the relevant operators improves the agreement at long times, but is still not sufficient to capture the full SC-IVR rephasing. Thus, the success of these classical approximations in condensed phase systems depends mainly on the time scale of the decay of the correlation function associated with the relevant observable. In the case that the correlation function decays on a short time scale, and rephasing is not important, they are expected to provide reasonable results.[24,25] Such a situation is likely to occur in condensed phase problems.

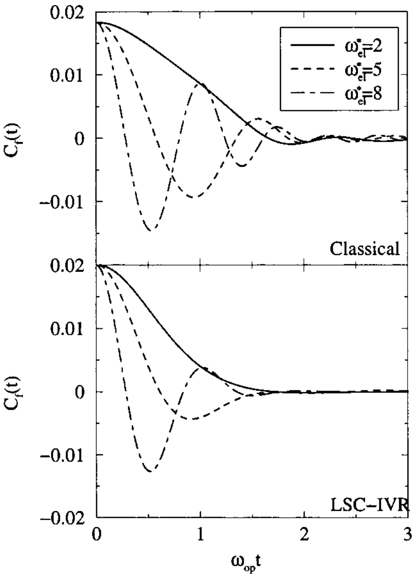

Figure 2. Plots of the flux−flux correlation function for the LSC-IVR (lower panel) and the classical approximation (upper panel) versus time. Note that as the electronic gap increases, the flux−flux correlation function become oscillatory, reflecting the recrossing of the dividing surface.

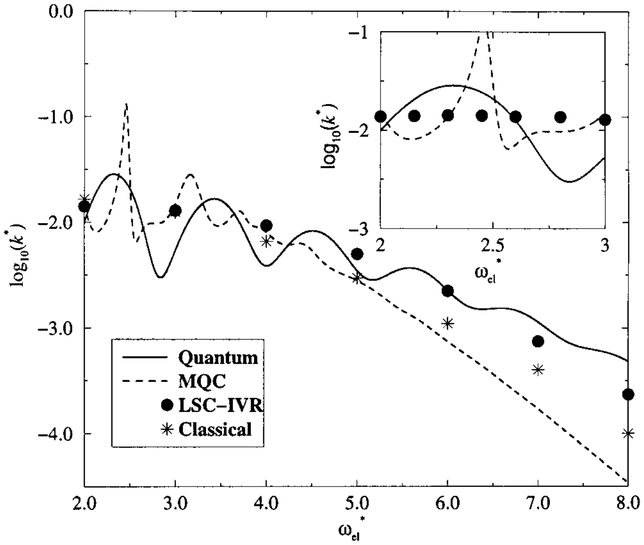

Figure 3. Semilog plot of the electronic relaxation rate as a function of the reduced electronic gap. The fully quantum mechanical (solid line) and the mixed quantum−classical (dashed line) results were obtained using the Fermi golden rule. The LSC-IVR (●) and the fully classical (∗) results were obtained using the reactive flux formalism. The LSC-IVR provides the best overall agreement, but fails to reproduce the oscillation (see the inset).

In view of the above, we have performed a test of the classical and LSC-IVR approaches for a non-trivial many-body problem defined by the Hamiltonian given in eq 10. The above model is completely specified by the two spectral densities—$J_0(\omega)$ and $J_1(\omega)$—corresponding to the ground and excited states of the impurity, respectively. The procedure for obtaining the coefficients δ_α and $g_{\alpha\alpha'}$ in eq 3 from these spectral densities is outlined in ref 9. Since we are primarily interested in the electronic nonradiative relaxation processes characterized by large energy gaps, we assume that the dominant contribution to the relaxation rate comes from the high-frequency optical phonons. In order to model the corresponding spectral density, we have chosen a Gaussian form centered at ω_{op} with the width parameter σ and the normalization constant λ[30]

$$J_{0,1}(\omega) = \frac{\lambda_{0,1}}{(2\pi\sigma^2)^{1/2}} \exp[-(\omega-\omega_{op}^{0,1})^2/2\sigma^2] \qquad (18)$$

where the labels 0 and 1 refer to the ground and excited state of the impurity, respectively. Since optical phonons are characterized by a narrow dispersion, we have limited ourselves to the case $\sigma/\omega_{op}^{0,1} \ll 1$ (from now on we employ atomic units), which, in addition, allows us to avoid the nonphysical contributions arising from the tail of the Gaussian function extending to negative frequencies. Specifically, we have chosen the following values of the parameters: $\sigma = 0.1$, $\omega_{op}^{0} = 1.1$, $\omega_{op}^{1} = 1.0$, $\lambda_0 = 0.05$, and $\lambda_1 = 0.125$. With the above spectral densities, we have calculated the flux−flux correlation function using the LSC-IVR method and the classical approach, as discussed in the previous section. The results of our calculations are shown in Figure 2 for three values of the dimensionless electronic energy gap $\omega^*_{el} = \omega_{el}/\omega_{op}$. One sees that with increasing energy gap the flux−flux correlation function in both methods becomes more oscillatory and is therefore likely to become less accurate. Note also that for a given energy gap the oscillations are less pronounced in the LSC-IVR result compared to the fully classical method.

The results for the electronic relaxation rates are shown in Figure 3 on a semilog plot versus the dimensionless electronic energy gap. Also shown are the fully quantum mechanical and mixed quantum−classical (the so called dynamic classical limit

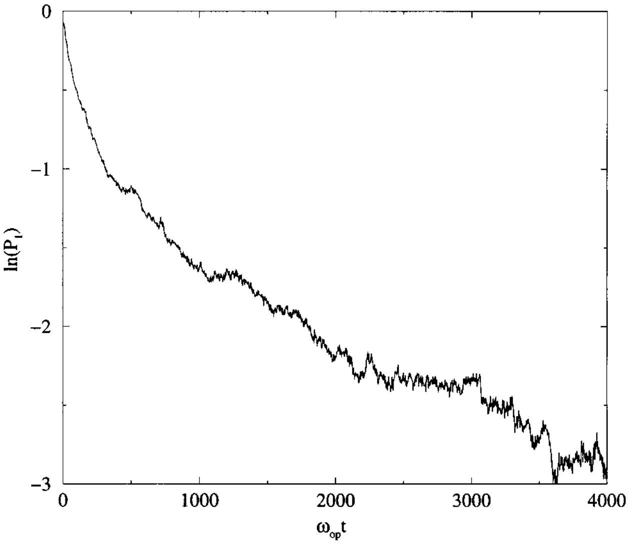

Figure 4. Semilog plot of the time dependence of the excited state population ($P_1(t) = {}^1/_2(q_1^2 + p_1^2 - 1)$) for the classical approximation. The LSC-IVR is identical to the classical result within the noise level of the computation, and thus is not shown.

(DCL) which was described in detail in ref 9) results, both obtained within the low order perturbation theory.[9] One sees that for small electronic energy gaps the LSC-IVR approach does not capture the oscillations present in the quantum result, which is reminiscent of the static classical method.[45] These oscillations are absent even when the Wigner−Weyl transform of the flux operator is used (LSC-IVR). Thus, it is the classical treatment of the *dynamics* of the electronic degrees of freedom which fails to reproduce the resonances.[33]

For large energy gaps, the performance of the classical methods is better compared to the mixed quantum−classical approximation, similar to the situation for vibrational energy relaxation.[11,12] The LSC-IVR provides the best overall agreement among the approximations considered in this work. We would like to emphasize that going from the classical to LSC-IVR treatment involves the Wigner−Weyl transform not only of the initial distribution, but also of the flux operators, and the transformation of the flux operator turns out to be important for the calculation of the electronic relaxation rate.

An alternative approach to obtain the electronic relaxation rates is based on a nonequilibrium approach, where the system is initiated in the excited state, and the rate is obtained from the long time decay of the excited state population. The fully quantum mechanical rate obtained using this approach should be in agreement with the rate obtained via the fully quantum mechanical reactive flux formalism. The strength of the reactive flux approach is that the rate is obtained from relatively short time information, while the approach based on the time dependent population requires a consideration of much longer times. As we have shown, the classical limit of the reactive flux approach is a good approximation of the quantum result. It might be thought that one could equally well determine the rate by using the Meyer−Miller dynamics to generate the long time decay of the population. Unfortunately, this is not the case, as is illustrated in Figure 4, where we show a semilog plot of the classical excited state population for an inverse temperature $\beta = 2$. From the long decay of the excited state population one would determine a rate constant much smaller than that found from the reactive flux approach. The reason for this is that the classical approach presented in this work was derived from a semiclassical approximation, which is known to deviate from the exact quantum dynamics at long times.

V. Conclusions

Motivated by recent work on vibrational energy relaxation in condensed phases, which has shown that a fully classical treatment of the problem is superior to the mixed quantum−classical approach,[11,12] we have performed a fully classical calculation of the electronic energy relaxation rates. We have employed the reactive flux formalism combined with the method of mapping of discrete quantum degrees of freedom onto the classical ones proposed two decades ago by Meyer and Miller[15] and recently modified by Stock and Thoss.[17] We have considered two implementations of the method: a fully classical approximation and a linearized semiclassical initial value representation, that involves a Wigner−Weyl transform of the initial distribution and the flux operator.

In calculating the electronic relaxation rates for an impurity coupled to a condensed phase environment, we have employed a model studied previously by us,[9] where an impurity is represented by a two-level system, and all the nuclear (bath) degrees of freedom are treated in the harmonic approximation. In the earlier study of this model, we have treated it both quantum mechanically and in the mixed quantum−classical approximation. The results of the present work have demonstrated that, similarly to the case of vibrational relaxation, a fully classical treatment produces better agreement with the fully quantum mechanical rates than the mixed quantum−classical approach. Furthermore, the rates obtained within LSC-IVR method are closer to the exact quantum rates than the fully classical results. However, the LSC-IVR approach requires performing Wigner−Weyl transformations which are difficult to obtain for a general system, and even for the present application several approximation were introduced. In addition, both classical methods performed rather poorly for small electronic energy gaps, where they failed to reproduce the resonances present in the exact quantum rates.

In more general terms, one can mention the following feature that makes a fully classical approach more robust compared to the mixed quantum−classical approximation. Namely, the time propagation of the classical degrees of freedom in the fully classical approach is unique, while the mixed quantum−classical propagation approach suffers from nonuniqueness,[9,10] i.e., there is freedom in the choice of the Hamiltonian used to propagate the classical degrees of freedom in the mixed quantum classical approach. 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. However, the criteria for choosing the optimal propagation scheme must be established for a general system where the bath is not taken in the harmonic approximation.

Both the classical treatment and the mixed quantum classical approximation lend themselves to a systematic improvement, that would involve going from classical to a full-blown semiclassical approximation for the degrees of freedom that were treated classically. It seems to be imperative to use the fully SC-IVR in order to reproduce the resonances mentioned earlier. However, the latter approach is not yet practical for the many-body system.[46,47]

Finally, we can draw one more conclusion from the present study, namely, that it is always advantageous to employ the framework where the required time-correlation functions are characterized by a fast decay. We have illustrated this point by showing that the classical results obtained from the flux−flux correlation function were far superior to those obtained from the analysis of the population decay.

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