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Nonadiabatic chemical reactions

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Abstract

A mixed quantum-classical approach where the environment is treated classically and the reactive degrees of freedom are considered to be quantum mechanical can be used to describe many chemical reactions, such as proton and electron transfer processes. We present reactive flux correlation function expressions for the rate constants of nonadiabatic chemical reactions occurring in quantum-classical systems. By means of a two-state model coupled to a classical bath, we illustrate an efficient method of computation, based on a sequential short step propagation, which is applicable to quantum systems interacting with general classical condensed phase environments.

Keywords: Rate constants; Nonadiabatic; Quantum-classical

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1. Introduction

The computation of reaction rates in condensed phase systems presents a number of challenges for simulation. Often rate processes are activated events requiring methods to sample rarely visited regions of configuration space. If the reaction has a quantum character, as in electron or proton transfer processes, one must deal with the fact that several quantum states can participate in the reactive event, introducing new effects that must be accounted for in simulation schemes [1].

In this article we consider the computation of the rates of nonadiabatic chemical reactions using a surface-hopping scheme that simulates the solution to the quantum-classical Liouville equation. We begin with an outline of quantum-classical dynamics [2] and the derivation of reactive-flux correlation expressions for rate constants that include nonadiabatic effects [3]. The main focus of this work is on the use of the sequential short-time propagation algorithm [4] for the simulation of the reaction rate. The use of this algorithm allows us to obtain results with much greater computational efficiency than those reported previously [3] using a direct computation of the Dyson series for the quantum-classical evolution. We present the results of a calculation on a model system comprising a reactive two-level system coupled to a large bath of harmonic oscillators.

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2. Quantum-classical nonadiabatic rate constants

Consider a quantum system in a classical bath described by the time-independent Hamiltonian operator, $\hat{H}_W(R,P) = P^2/(2M) + \hat{p}^2/(2m) + \hat{V}_W(\hat{q},R)$, which is the sum of the classical kinetic energy $P^2/2M$, a quantum kinetic energy operator $\hat{p}^2/2m$ and a potential energy operator $\hat{V}_W(\hat{q},R)$. The subscript W is used to indicate that the quantum-classical description can be derived from a fully quantum one by means of a partial Wigner transform. The quantum-classical Liouville equation for the density matrix $\hat{\rho}_W$ is

$$\frac{\partial \hat{\rho}_W(R,P,t)}{\partial t} = -\mathrm{i}\mathcal{L}_W \hat{\rho}_W(t) = -\big(\hat{H}_W, \hat{\rho}_W(t)\big). \tag{1}$$

The quantum-classical Liouville operator $\mathrm{i}\hat{\mathcal{L}}$ is defined in terms of the quantum-classical bracket $(\hat{H}_W, \hat{A}_W) = \frac{\mathrm{i}}{\hbar}[\hat{H}_W, \hat{A}_W] - (1/2)(\{\hat{H}_W, \hat{A}\} - \{\hat{A}, \hat{H}_W\})$, where, for any operators $\hat{A}_W$ and $\hat{B}_W$, $[\hat{A}_W, \hat{B}_W]$ is the commutator and $\{\hat{A}_W, \hat{B}_W\}$ is the Poisson bracket. The quantum-classical Liouville equation (1) can be derived from the quantum Liouville equation by performing a partial Wigner transform on the bath degrees of freedom in scaled variables.

An expression for the reaction rate can be derived by considering the quantum-classical system subject to external time-dependent affinities that couple to microscopic variables $\hat{\chi}_{Wi}$ that characterize the chemical species. The chemical rate law follows from the calculation of the non-equilibrium average by evaluating the density matrix to linear order in the affinities. Following the standard development of linear response theory, the response function obtained from such an analysis can be related to the linear phenomenological Onsager coefficients that characterize the transport processes [5] (in this case the chemical relaxation) in the system. In simulations it is convenient to consider the time-dependent Onsager coefficients, from which the true phenomenological coefficients may be determined from the plateau value of this expression, should such a plateau exist.

3. Nonadiabatic chemical reaction model

We now turn to the use of this formalism and compute the rate constant for a model nonadiabatic reacting system. We consider a reacting system comprising a two-level system directly coupled to a classical nonlinear oscillator with mass M_0 and phase space coordinates (R_0, P_0), which is in turn coupled to a bath of independent harmonic oscillators. The system Hamiltonian in the diabatic representation is

$$\mathbf{H} = \begin{pmatrix} +\hbar\gamma_0 R_0 & -\hbar\Omega \\ -\hbar\Omega & -\hbar\gamma_0 R_0 \end{pmatrix} + \left(\sum_{j=0}^{N} \frac{P_j^2}{2M_j} + V_b(R)\right)\mathbf{I}, \tag{2}$$

where

$$V_b(R) = V_n(R_0) + \sum_{j=1}^{N}\big(M_j\omega_j^2/2\big) \times \big(R_j - c_j R_0/\big(M_j\omega_j^2\big)\big)^2.$$

The nonlinear oscillator has a quartic potential energy function, $V_n(R_0) = aR_0^4/4 - bR_0^2/2$. The linear coupling to the two-level system is given by $-\hbar\gamma_0 R_0 = \hbar\gamma(R_0)$. The classical nonlinear oscillator is bilinearly coupled, in turn, to a bath of N independent harmonic oscillators labeled $j = 1, \ldots, N$ with masses M_j and frequencies ω_j. The bilinear coupling between the quartic oscillator and harmonic bath is characterized by an Ohmic spectral density. See Refs. [6,7] for details and Ref. [3] for specific parameter values. We use the notation $(R,P) = (R_0, R_1, \ldots, R_N, P_0, P_1, \ldots, P_N)$ for the point in the $2(N+1)$-dimensional phase space of the model. We report results in dimensionless variables $\tilde{R}_j = (M_j\omega_c/\hbar)^{1/2}R_j$, $\tilde{P}_j = (\hbar M_j\omega_c)^{-1/2}P_j$, $\tilde{\beta} = \hbar\omega_c\beta = \hbar\omega_c/k_B T$ and $\tilde{t} = t\omega_c$. The results presented below are for a system with $N = 100$ harmonic oscillators in the bath (unless otherwise noted) and dimensionless parameter values: $\omega_{\max} = 3$ (the cutoff frequency in the Ohmic spectral density), $\xi = 4$, $\Omega = 0.2$, $\gamma_0 = 1$, $a = 3$, $b = 1.8008$ and $\beta = 6$.

The adiabatic eigenstates and eigenvalues in terms of which the calculations were carried out were obtained by diagonalization of the two-level system Hamiltonian (2). When the harmonic oscillator coordinates are integrated out, the ground state adiabatic free energy has a double-well form while the excited state adiabatic free energy has a single minimum with an avoided crossing at $R_0 = 0$. Thus, there are two metastable states, A and B, when the system is on the ground state surface but passage between these states can be influenced by nonadiabatic transitions to the excited state, C. We may write operators that define the chemical species variables as $\hat{N}_A = |1; R_0\rangle\Theta(R_0)\langle 1; R_0|$, $\hat{N}_B = |1; R_0\rangle\Theta(-R_0)\langle 1; R_0|$, and $\hat{N}_C = |2; R_0\rangle\langle 2; R_0|$, where $\Theta(\pm R_0)$ is the Heaviside function selecting the right or left wells and $|I; R_0\rangle\langle I; R_0|$ is a projector onto the adiabatic state $|I; R_0\rangle$.

Given this picture, the chemical reactions $I \rightleftharpoons J$, ($I \neq J = A, B, C$), characterized by the transition probabilities k_{IJ}, occur among the three species. Only two of the three reactions are independent. We may formulate the irreversible thermodynamics for this case in terms of two independent species and the corresponding affinities. We may identify the phenomenological coefficients as $L_{IJ} = (k_{JI} - \delta_{JI})\bar{n}_J^{\mathrm{eq}}$. We have the relations $L_{AA}(\bar{n}_A^{\mathrm{eq}})^{-1} = k_{AA} - 1 = -(k_{AB} + k_{AC})$, which describes the net decay of species A, and $L_{BA}(\bar{n}_A^{\mathrm{eq}})^{-1} = k_{AB}$, with similar relations for L_{BB} and L_{AB}. In view of the symmetry of the model there are only two independent rate constants which may be expressed in terms of the two Onsager coefficients L_{AA} and L_{BA}. Specializing the general expressions for the Onsager coefficients to this reactive case we have $\beta L_{IJ}(t) = -\mathrm{Tr}' \int \mathrm{d}R\,\mathrm{d}P\,\hat{\chi}_{WI}(t)(\hat{\chi}_{WJ}, \hat{\rho}_{We})$, where $\hat{\chi}_I = \hat{N}_I - \langle \hat{N}_I \rangle$. This is a microscopic expression for the time-dependent Onsager coefficient in terms of a quantum-classical progress variable $\hat{\chi}_{W,I}(t)$ and the quantum-classical bracket of the progress variable at time zero with the stationary density matrix. To simplify the notation we drop the W subscript on species variables. To calculate $L_{BA}(\bar{n}_A^{\mathrm{eq}})^{-1} = k_{AB}$ we use the adiabatic basis and have

$$k_{AB}(t) = -\left(\beta\bar{n}_A^{\mathrm{eq}}\right)^{-1} \times \sum_{\alpha\alpha'} \int \mathrm{d}R\,\mathrm{d}P\,\chi_B^{\alpha'\alpha}(t)(\hat{\chi}_A, \hat{\rho}_{We})_{\alpha\alpha'}, \quad (3)$$

with a similar expression for $k_{AC}(t)$.

To calculate the rate coefficients, we must evaluate the quantum-classical brackets and use the form of the equilibrium density matrix which, to order $\hbar$, is given by [5] $\rho_{We}^{\alpha\alpha'} \approx \rho_{We}^{(0)\alpha}\delta_{\alpha\alpha'} - \mathrm{i} f_{We}^{\alpha\alpha'}(1 - \delta_{\alpha\alpha'})$, with $\rho_{We}^{(0)\alpha} = Z_0^{-1}\exp(-\beta H_W^{\alpha})$ where Z_0 is the partition function and $f_{We}^{\alpha\alpha'} = P_0 \cdot d_{\alpha\alpha'}\rho_{We}^{(0)\alpha}(\beta(1 + \exp[-\beta E_{\alpha'\alpha}])/2 + (1 - \exp[-\beta E_{\alpha'\alpha}])/E_{\alpha\alpha'})$, where the nonadiabatic coupling matrix element is $d_{\alpha\alpha'} = \langle\alpha; R_0|\partial/\partial R_0|\alpha'; R_0\rangle$. The diagonal and off-diagonal contributions to the density matrix lead to a decomposition of the time-dependent rate coefficient as the sum of two contributions: $k_{AB}(t) = k_{AB}^d(t) + k_{AB}^o(t)$. For example, the contribution coming from the diagonal part of the density matrix is given by

$$k_{AB}^d(t) = -\left(n_A^{\mathrm{eq}}\right)^{-1} \times \int \mathrm{d}R\,\mathrm{d}P\,N_B^{11}(R, P, t)\delta(R_0)\frac{P_0}{M_0}\rho_{We}^{11}. \quad (4)$$

Eq. (4) has the same form as the classical reactive flux formula except that the time evolution must be carried out using quantum-classical dynamics.

4. Computation of the rate constant

In the adiabatic basis the quantum-classical Liouville operator has matrix elements, $\mathrm{i}\mathcal{L}_{\alpha\alpha',\beta\beta'} = (\mathrm{i}\omega_{\alpha\alpha'} + \mathrm{i}L_{\alpha\alpha'})\delta_{\alpha\beta}\delta_{\alpha'\beta'} - J_{\alpha\alpha',\beta\beta'} \equiv \mathrm{i}\mathcal{L}_{\alpha\alpha'}^0\delta_{\alpha\beta}\delta_{\alpha'\beta'} - J_{\alpha\alpha',\beta\beta'}$, where $\omega_{\alpha\alpha'}(R) = [E_\alpha(R) - E_{\alpha'}(R)]/\hbar$ is the quantum frequency and $\mathrm{i}L_{\alpha\alpha'} = (P/M)\cdot\partial/\partial R + (1/2)(F_W^{\alpha} + F_W^{\alpha'})\cdot\partial/\partial P$, is the classical Liouville operator that involves the mean of the Hellmann–Feynman forces corresponding to the adiabatic states α and α'. The operator $J_{\alpha\alpha',\beta\beta'}$ is responsible for nonadiabatic transitions and corresponding bath momentum changes and has the form

$$\begin{aligned} J_{\alpha\alpha',\beta\beta'} &= -(P/M)\cdot d_{\alpha\beta}\big(1 + (S_{\alpha\beta}/2)\cdot(\partial/\partial P)\big)\delta_{\alpha'\beta'} \\ &\quad - (P/M)\cdot d_{\alpha'\beta'}^*\big(1 + (S_{\alpha'\beta'}^*/2)\cdot(\partial/\partial P)\big)\delta_{\alpha\beta}, \end{aligned}$$

where $S_{\alpha\beta} = \Delta E_{\alpha\beta}(R)d_{\alpha\beta}(\frac{P}{M}\cdot d_{\alpha\beta})^{-1}$ with $\Delta E_{\alpha\beta}(R) = E_\alpha(R) - E_\beta(R)$.

In order to construct, a formulation of the dynamics in terms of surface-hopping trajectories, we divide the time interval t into N segments of lengths $\Delta t_j = t_j - t_{j-1}$ so that

$$\left(\mathrm{e}^{\mathrm{i}\mathcal{L}t}\right)_{\alpha_0\alpha_0',\alpha_N\alpha_N'} = \sum_{(\alpha_1\alpha_1'),\ldots,(\alpha_{N-1}\alpha_{N-1}')} \prod_{j=1}^{N}\left(\mathrm{e}^{\mathrm{i}\mathcal{L}(t_j - t_{j-1})}\right)_{\alpha_{j-1}\alpha_{j-1}',\alpha_j\alpha_j'}. \quad (5)$$

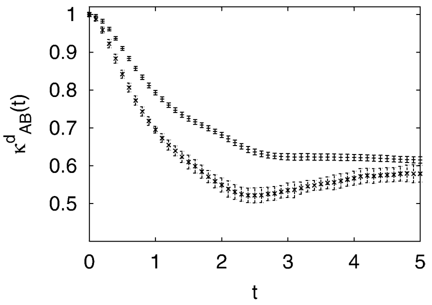

Fig. 1. Transmission coefficient $\kappa^d_{AB}(t)$ versus t from nonadiabatic dynamics coming from k^d_{AB} including up to $n = 2$ quantum transitions (lower curve). For comparison, the upper curve shows the adiabatic transmission coefficient.

If Δt is sufficiently small, in each time interval the system may either stay on the same energy surface or make a transition to a new state. The sequential short-time algorithm may be implemented easily. The total time of the calculation is divided into a fixed number of time slices, the most natural choice being to take the molecular dynamics integration time step Δt as the length of the slice. Thus, one obtains adiabatic propagation of the phase space coordinates for a single time step together with the corresponding phase factor $\mathcal{W}$. At the end of each time step the probabilities, $\Pi = |P \cdot d/M|\Delta t(1 + |P \cdot d/M|\Delta t)^{-1}$ and $\Sigma = 1 - \Pi$ are respectively used for acceptance or rejection of a quantum transition. In the simulations reported below we used the momentum-jump approximation to evaluate J [8].

We computed the adiabatic time dependent transmission coefficient $\kappa_{AB}(t) = k_{AB}(t)/k^{TST}_{AB}$ versus time for several values of N. For $N > 100$ no further change in the value of the transmission coefficient is observed and, therefore, $N = 100$ was used in the simulations reported here. In Fig. 1 we show $\kappa_{AB}(t)$. One can see that the transmission coefficient evolves rapidly to a slowly decaying "plateau" value which, when extrapolated to $t = 0$, determines the rate constant. Nonadiabatic effects modify the value of the transmission coefficient by only a small amount for the chosen model parameters although there are significant differences at short times.

5. Conclusion

The simulation results demonstrate that nonadiabatic rate constants can be computed within the quantum-classical Liouville equation framework. The short-time sequential algorithm yielded results with greater computational efficiency than those obtained earlier using a different algorithm that simulates the individual contributions in the Dyson expansion of the solution of the quantum-classical Liouville equation. In the activated rate process we investigated here, most nonadiabatic transitions occur in the vicinity of the free energy barrier top where trajectories originate. The short-time sequential algorithm is able to capture this dynamics. The full description of nonadiabatic effects for this reaction model requires a knowledge of the rates for the $A \rightleftharpoons B$, $B \rightleftharpoons C$ and $A \rightleftharpoons C$ microscopic transition processes. The nonadiabatic reactive flux formalism and simulation schemes developed earlier and applied to the model reactive system here provide a basis for investigating nonadiabatic effects on chemical reactions in realistic models of physical systems.

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