Quantum Dissipative Dynamics of Electron Transfer Reaction System: Nonperturbative Hierarchy Equations Approach

Midori Tanaka and Yoshitaka Tanimura[*]

Department of Chemistry, Graduate School of Science, Kyoto University, Kyoto 606-8502

A multistate displaced oscillator system strongly coupled to a heat bath is considered a model of an electron transfer (ET) reaction system. By performing canonical transformation, the model can be reduced to the multistate system coupled to the Brownian heat bath defined by a non-ohmic spectral distribution. For this system, we have derived the hierarchy equations of motion for a reduced density operator that can deal with any strength of the system bath coupling at any temperature. The present formalism is an extension of the hierarchy formalism for a two-state ET system introduced by Tanimura and Mukamel into a low temperature and multistate system. Its ability to handle a multistate system allows us to study a variety of problems in ET and nonlinear optical spectroscopy. To demonstrate the formalism, the time-dependent ET reaction rates for a three-state system are calculated for different energy gaps.

Electron transfer (ET) processes play an important role in many fields in physics, chemistry, and biology.[1] Most ET processes occur in condensed phases where the surrounding molecules provide the energetic fluctuations and dissipations needed in the reactions. In the case of ET in a polar solvent, the interaction energy that consists of the solvent–solute interaction energy and solvent dipole–dipole energy is used as the ET reaction coordinate.[2–4] The ET reaction is then characterized by parabolic free-energy surfaces for the reactant and product states as a function of the reaction coordinate. Although ET rates are commonly studied using free-energy surfaces, the ultrafast dynamics of ET processes is investigated using the potential energy surfaces as a function of molecular coordinates.[5,6] This potential energy description is similar to that used in nonlinear ultrafast spectroscopy.[7,8] By adopting this description, one may study ET processes by nonlinear optical measurements.[9,10] A variety of approaches that have been developed to study not only ET processes but also nonlinear optical responses are used to investigate ET dynamics.[5–14]

Unlike most of the above-mentioned approaches based on the perturbative treatment of nonadiabatic transitions, the reduced equation of motion approach that describes the dynamics of density matrix of an ET system coupled to the environment can handle any strength of nonadiabatic coupling. This approach is successful in a classical case characterized by free-energy surfaces,[5,6,15] but it has to employ crucial assumptions such as rotating wave approximation and perturbative system–bath interaction in a quantum case. This strongly limits its applicability. Meanwhile, it was found that the hierarchy equation approach is a powerful means of describing a system strongly coupled to a bath without using rotating wave approximation and white-noise (Born or Van Hove) approximation.[16–21] This approach was introduced to investigate the connection between the phenomenological stochastic Liouville equation theory and dynamical Hamiltonian theory.[22–25] Most

studies that use this approach are limited to the case in which the spectral distribution function is given by the ohmic form with the Lorentzian cutoff. One can extend the hierarchy equation approach to a non-ohmic case by employing a multiplex hierarchy for a nonexponential decay noise.[17]

In this letter, we describe a Brownian spectral distribution case that is suitable for modeling the ET system. Although the former hierarchy equations for a two-state ET system developed by Tanimura and Mukamel[26] cannot be applied to a low-temperature system, where the quantum transition plays a major role, the present ones have no temperature restriction. This is due to the low-temperature correction method developed in the ohmic case.[16–18,23] Moreover, we formulated the equations of motion for a multistate system, where a variety of problems in ET and nonlinear optical spectroscopy can be modeled.

We consider a molecular system with electronic states denoted by $|j\rangle$. The Hamiltonian of the system is

$$\hat{H}_{A} = \sum_{j} \hbar\Omega_{j}|j\rangle\langle j| + \sum_{j\neq k} \hbar\Delta_{jk}|j\rangle\langle k|. \tag{1}$$

The system is strongly coupled to a single harmonic mode described by the coordinate, momentum, mass, and frequency denoted by Q, P, M, and ω_{0}. This mode is in turn coupled to a bath of harmonic oscillators described by x_{j}, p_{j}, m_{j}, and ω_{j} for the jth mode. The coupling strength to the jth mode is given by c_{j}. The Hamiltonian for a single harmonic mode and the oscillator bath with the system–bath interaction is then expressed as[11,26]

$$\hat{H}_{int} = \frac{\hat{P}^{2}}{2M} + \sum_{j} \frac{1}{2}M\omega_{0}^{2}\left(\hat{Q} - \frac{d_{j}D}{2}|j\rangle\langle j|\right)^{2}$$
$$+ \sum_{j}\left[\frac{\hat{p}_{j}^{2}}{2m_{j}} + \frac{1}{2}m_{j}\omega_{j}^{2}\left(\hat{x}_{j} - \frac{c_{j}}{m_{j}\omega_{j}^{2}}\hat{Q}\right)^{2}\right], \tag{2}$$

where D is the characteristic scale of the system and d_{j} is the dimensionless coupling constant between the state $|j\rangle$ and the oscillator mode. By using the canonical transformation,

[*]E-mail: tanimura@kuchem.kyoto-u.ac.jp

the above Hamiltonians can be transformed into the multi-state spin-Boson Hamiltonian as

$$\hat{H}_A + \hat{H}_{\text{int}} = \sum_j \hbar\Omega_j |j\rangle\langle j| + \sum_{j\neq k} \hbar\Delta_{jk} |j\rangle\langle k|$$
$$+ \sum_j \left\{ \frac{\hat{p}_j'^2}{2m_j'} + \frac{1}{2}m_j'\omega_j'^2 \left(\hat{x}_j' - \frac{c_j'}{m_j'\omega_j'^2}\hat{V} \right)^2 \right\}, \quad (3)$$

where

$$\hat{V} = \sum_j d_j |j\rangle\langle j|. \quad (4)$$

The spectral distribution function $J(\omega) \equiv \sum_j (c_j'^2/2m_j'\omega_j')\delta(\omega - \omega_j')$, which contains all information on the bath, is given by the Brownian spectral distribution:[11]

$$J(\omega) = \frac{2\hbar\lambda}{\pi} \frac{\gamma\omega_0^2\omega}{(\omega_0^2 - \omega^2)^2 - \gamma^2\omega^2}. \quad (5)$$

Here, we chose $\lambda = MD^2\omega_0^2/2\hbar$ with the fixed D and assume the friction function $\gamma(\omega) \equiv \sum_j (c_j'^2/2m_j'\omega_j'^2)\delta(\omega - \omega_j')$, in the frequency-independent form as $\gamma(\omega) = \gamma$. The bath degrees of freedom defined by eq. (3) can be reduced by performing the path integrals for the coordinate x_j', which leads to the influence functional in the form[12]

$$F = \exp\left\{ -\frac{1}{\hbar} \int_{t_0}^t ds \int_{t_0}^s du\, V^\times(s) \right.$$
$$\left. \times (-iL_1(s-u)V^\circ(u) + L_2(s-u)V^\times(u)) \right\}, \quad (6)$$

where $V^\times(s) \equiv V(\{\psi(s)\}) - V(\{\psi'(s)\})$ and $V^\circ(s) \equiv V(\{\psi(s)\}) + V(\{\psi'(s)\})$ are the commutator and anticommutator of $\hat{V}$ expressed in the coherent state representation of sets of Grassmann numbers $\{\psi(s)\}$ and $\{\psi'(s)\}$ that describe the states of the system, $|j\rangle$ and $\langle k|$. The time-dependent kernels corresponding to the fluctuation $L_1(t) \equiv \langle[Q(t),Q]\rangle/\hbar$ and dissipation $L_2(t) \equiv \langle Q(t)Q + QQ(t)\rangle/2\hbar$ induced by the bath are expressed by the spectral distribution as $L_1(t) = \int_0^\infty d\omega\, J(\omega)\sin(\omega t)$ and $L_2(t) = \int_0^\infty d\omega\, J(\omega)\coth(\beta\hbar\omega/2)\cos(\omega t)$, respectively.[12,16,22] For eq. (5), we have

$$L_1(t) = \frac{\hbar\lambda\omega_0^2}{2i\zeta}\left\{ \exp\left[-\left(\frac{\gamma}{2}-i\zeta\right)t\right] - \exp\left[-\left(\frac{\gamma}{2}+i\zeta\right)t\right] \right\} \quad (7)$$

and

$$L_2(t) = -\frac{4\lambda\gamma\omega_0^2}{\beta}\sum_{k=1}^\infty \frac{\nu_k}{(\omega_0^2+\nu_k^2)^2 - \gamma^2\nu_k^2}e^{-\nu_k t}$$
$$+ \frac{\hbar\lambda\omega_0^2}{2\zeta}\exp\left[-\left(\frac{\gamma}{2}-i\zeta\right)t\right]\coth\left[\frac{\beta\hbar}{2}\left(\zeta+i\frac{\gamma}{2}\right)\right]$$
$$- \frac{\hbar\lambda\omega_0^2}{2\zeta}\exp\left[-\left(\frac{\gamma}{2}+i\zeta\right)t\right]\coth\left[\frac{\beta\hbar}{2}\left(-\zeta+i\frac{\gamma}{2}\right)\right], \quad (8)$$

where $\zeta = \sqrt{\omega_0^2 - \gamma^2/4}$ and $\nu_k = (2\pi/\beta\hbar)k$ with $2\pi/\beta\hbar$ being the Matsubara frequency. The reduced density operator $\hat{\rho}_A(t)$ is expressed as $\int D[\{\psi(t)\}] \int D[\{\psi'(t)\}]e^{iS_A/\hbar}Fe^{-iS_A'/\hbar}$, where $\int D[\cdots]$ represents the functional integral of the Grassmann variables and S_A is the action for $\hat{H}_A$. The equation of motion for the reduced density operator can be derived by evaluating the time derivative of the left- and right-hand-side wave

functions and the influence functional.[16-19,22-25] If the time derivative of eq. (6) is in a convenient form, we can arrange the equations of motion for the reduced density operator in a closed form. We rearrange part of the influence functional $(-1/\hbar)(-iL_1(s-u)V^\circ(u) + L_2(s-u)V^\times(u))$ as

$$\sum_\pm e^{-(\gamma/2\pm i\zeta)(s-u)}\Theta_\pm(u) + \sum_{k=1}^\infty e^{-\nu_k(s-u)}\Psi_k(u), \quad (9)$$

where $\Theta_\pm(u)$ and $\Psi_k(u)$ are readily derived from eqs. (6)–(8) in the functions of $V^\times(u)$ and $V^\circ(u)$ and their explicit expressions will be given in the operator form as eqs. (12) and (13).

Aside from the factor $(V^\times(t))^N$, the Nth-order derivative of the influence functional is expressed in terms of the functional

$$F_{j_1,j_2,\ldots}^{(n,m)} = \left\{ \int_{t_0}^t du\, \Theta_-(u)\exp\left[-\left(\frac{\gamma}{2}-i\zeta\right)(t-u)\right] \right\}^n$$
$$\times \left\{ \int_{t_0}^t du\, \Theta_+(u)\exp\left[-\left(\frac{\gamma}{2}+i\zeta\right)(t-u)\right] \right\}^m$$
$$\times \prod_{k=1}^\infty \left(\int_{t_0}^t du\, \Psi_k(u)e^{-\nu_k(t-u)} \right)^{j_k} F, \quad (10)$$

for a set of nonnegative integers $\{n, m, j_1, j_2, \ldots\}$ with $N \equiv n + m + \sum_k j_k$. The production over k continues to infinity, but, in practice, we can truncate it for a large $k = K$ that satisfies $\nu_K \gg \max\{\Omega_i - \Omega_j\}$, where $\Omega_i - \Omega_j$ is the transition frequency between the system states $|i\rangle$ and $|j\rangle$, since we have $\nu_k e^{-\nu_k t} \simeq \delta(t)$ for all k values $> K$. We now introduce a set of reduced density operators $\hat{\rho}_{j_1,\ldots,j_K}^{(n,m)}(t)$ for $\int D[\{\psi(t)\}] \int D[\{\psi'(t)\}]e^{iS_A/\hbar}F_{j_1,\ldots,j_K}^{(n,m)}e^{-iS_A'/\hbar}$ by regarding eq. (10) as the generalized influence functional. As eq. (10) implies, the set of integers $\{n, m, j_1, \ldots, j_K\}$ relates to a characteristic relaxation rate $n(\gamma/2 - i\zeta) + m(\gamma/2 + i\zeta) + \sum_k j_k\nu_k$, and the 0th member corresponds to $\hat{\rho}_A(t) = \hat{\rho}_{0,\ldots,0}^{(0,0)}(t)$.

Then, starting from $\hat{\rho}_{0,\ldots,0}^{(0,0)}(t)$, we can construct the hierarchy equations of motion by evaluating the time derivative of $\hat{\rho}_{j_1,\ldots,j_K}^{(n,m)}(t)$ as

$$\frac{\partial}{\partial t}\hat{\rho}_{j_1,\ldots,j_K}^{(n,m)}(t) = -\left[\frac{i}{\hbar}\hat{H}_A^\times + \frac{(n+m)\gamma}{2} - i(n-m)\zeta \right.$$
$$\left. + \sum_{k=1}^K j_k\nu_k - \hat{\Xi}\right]\hat{\rho}_{j_1,\ldots,j_K}^{(n,m)}(t)$$
$$+ \hat{V}^\times\hat{\rho}_{j_1,\ldots,j_K}^{(n+1,m)}(t) + n\hat{\Theta}_-\hat{\rho}_{j_1,\ldots,j_K}^{(n-1,m)}(t)$$
$$+ \hat{V}^\times\hat{\rho}_{j_1,\ldots,j_K}^{(n,m+1)}(t) + m\hat{\Theta}_+\hat{\rho}_{j_1,\ldots,j_K}^{(n,m-1)}(t)$$
$$+ \sum_{k=1}^K \hat{V}^\times\hat{\rho}_{j_1,\ldots,j_k+1,\ldots,j_K}^{(n,m)}(t)$$
$$+ \sum_{k=1}^K j_k\nu_k\hat{\Psi}_k\hat{\rho}_{j_1,\ldots,j_k-1,\ldots,j_K}^{(n,m)}(t), \quad (11)$$

where

$$\hat{\Theta}_\pm = \frac{\lambda\omega_0^2}{2\zeta}\left\{ \mp\hat{V}^\circ \pm \coth\left[\frac{\beta\hbar}{2}\left(\mp\zeta + i\frac{\gamma}{2}\right)\right]\hat{V}^\times \right\}, \quad (12)$$

$$\hat{\Psi}_k = \frac{4\lambda}{\beta\hbar}\frac{\gamma\omega_0^2}{(\omega_0^2+\nu_k^2)^2 - \gamma^2\nu_k^2}\hat{V}^\times, \quad (13)$$

and $\hat{\Xi} = \hat{V}^\times \sum_{k=K+1}^\infty \hat{\Psi}_k$. Here, we denote $\hat{O}^\times\hat{f} \equiv \hat{O}\hat{f} - \hat{f}\hat{O}$

and $\hat{O}^\circ \hat{f} \equiv \hat{O}\hat{f} + \hat{f}\hat{O}$ for any operators $\hat{O}$ and $\hat{f}$. As can be seen from the form of equations, the $(n, m, j_1, \ldots, j_K)$th member of the hierarchy is coupled to the lower- and higher-order members as $\hat{\rho}_{j_1,\ldots,j_K}^{(n\pm 1,m)}$, $\hat{\rho}_{j_1,\ldots,j_K}^{(n,m\pm 1)}$, $\hat{\rho}_{j_1\pm 1,\ldots,j_K}^{(n,m)}$, etc. In this approach, the 0th member of the hierarchy is the exact solution of the total Hamiltonian [eqs. (1) and (2)] defined by $\hat{\rho}_{0,\ldots,0}^{(0,0)}(t) = tr_{Q,x_j}\{\hat{\rho}_{tot}(t)\}$ and it includes all orders of the system–bath interactions. Then the order of system–bath interactions in $\hat{\rho}_{j_1,\ldots,j_K}^{(n,m)}(t)$ is lower than that in $\hat{\rho}_{0,\ldots,0}^{(0,0)}(t)$ by N ($N \equiv n + m + \sum_k j_k$), since we defined the time derivative of F in eq. (10) by excluding the factor $(V^\times)^N$. Thus, the present approach conceptually differs from conventional perturbative expansion approaches; in such approaches, the 0th member includes no system–bath interactions and thus higher members take into account higher-order system–bath interactions.[16] Because of this hierarchical structure, we can handle strong system–bath interactions and non-white-noise baths.

For the condition $n + m + \sum_{k=1}^{K} j_k \gg \max\{\Omega_i - \Omega_j\}/\min(\gamma/2, \nu_1)$, this infinite hierarchy can be truncated by the terminator as

$$\frac{\partial}{\partial t}\hat{\rho}_{j_1,\ldots,j_K}^{(n,m)}(t) \simeq -\left[\frac{i}{\hbar}\hat{H}_A^\times - i(n-m)\zeta - \hat{\Xi}\right]\hat{\rho}_{j_1,\ldots,j_K}^{(n,m)}(t). \quad (14)$$

The set of eqs. (11)–(14), a main result of this study, is the extension of the former result of a two-state system for a high-temperature bath[26] to a multistate system coupled to the Brownian bath at any temperature. These equations can be numerically evaluated using the matrix expressions of the system and interaction, $\hat{H}_A$ and $\hat{V}$, since they become simultaneous differential equations for matrix elements.

To demonstrate our method, we employ a three-state model illustrated in Fig. 1 and calculate ET reaction rates from the initial state $|1\rangle$ to the final state $|3\rangle$ mediated by a midway state $|2\rangle$ discussed in refs. 27 and 28. All of the former approaches could not handle the present model under the physical conditions below. The Hamiltonian for the three-state displaced oscillators system is denoted by

$$\hat{H}_A = \hbar \begin{bmatrix} \Omega_1 & \Delta_{12} & 0 \\ \Delta_{12} & \Omega_2 & \Delta_{23} \\ 0 & \Delta_{23} & \Omega_3 \end{bmatrix}, \quad (15)$$
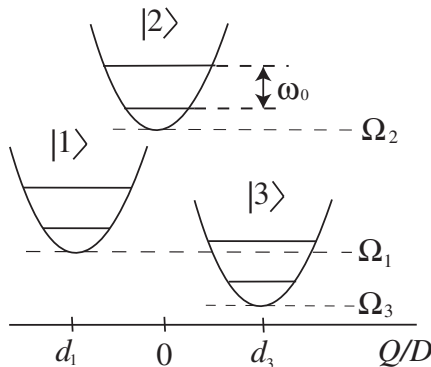

Fig. 1. Schematic view of a three-state system coupled to a harmonic mode. The displacements of the potentials are denoted by the dimensionless parameter d_1 and d_3 with $d_2 = 0$. Here, Ω_2 is chosen to illustrate a case in the normal region.

where Δ_{jk} represents the nonadiabatic coupling between the j and k states.

We computationally carry out a linear response experiment to obtain the rate in the three-state ET reaction in the same manner to obtain the Kubo transformed reactive flux correlation function for a double-well potential system.[23,24] We introduce a perturbation into the third state as $\Omega_3 = \Omega_3 + \epsilon$, where ϵ represents the perturbation. By turning on the perturbation for a sufficient time and by numerically integrating the hierarchy equations, the state of the system comes to a perturbed equilibrium state. After the perturbation is turned off (this defines $t = 0$), the populations return to the unperturbed equilibrium state. This change can be monitored by introducing the difference in population into the third state defined by $\delta\mathcal{N}(t) \equiv \rho_{33}(t) - \rho_{33}(\infty)$, where $\rho_{33}(t)$ is the density matrix element of the third state and $\rho_{33}(\infty)$ is the equilibrium distribution without the perturbation. ET reaction rate (flux correlation function) is then expressed as $k(t) = -\delta\dot{\mathcal{N}}(t)/\delta\mathcal{N}(t)$. Since $\delta\mathcal{N}(t)$ and $\delta\dot{\mathcal{N}}(t)$ are expected to be proportional to the perturbation ϵ, $k(t)$ does not depend on ϵ.

ET reaction rate is calculated for different intermediate energies $\Omega_2 = -4\omega_0, -2\omega_0, 0, 2\omega_0$, and $4\omega_0$ for fixed $\Omega_1 = \omega_0$ and $\Omega_3 = 0$. The displacements between the first and second states and those between the second and third states are respectively defined by $d_1 = -0.5$ and $d_3 = 0.5$, with $d_2 = 0$. The nonadiabatic couplings are set by $\Delta_{12} = \Delta_{23} = 0.5\omega_0$. The bath parameters are chosen to be $\lambda = 15\omega_0$, $\gamma = 0.5\omega_0$, and $\beta\hbar\omega_0 = 0.6$, which correspond to those in the case of $\omega_0 = 800\,\text{cm}^{-1}$ ($1/\omega_0 = 41.7\,\text{fs}$) at $T = 305\,\text{K}$. Since $\gamma/2 < \omega_0$, the harmonic mode is underdamped with the frequency $\zeta = 0.97\omega_0$. Although the coupling between the harmonic mode and the bath γ is weak, we cannot employ the perturbative approach, since the coupling between the system and the harmonic mode λ is strong. Thus, we need to treat the reduced bath mode described by $\hat{p}_j'$ and $\hat{x}_j'$ nonperturbatively. The depth of the maximum hierarchy is $N = 15$ with the number of Matsubara frequencies $K = 3$. The accuracies are checked by changing N and K.

Figure 2 shows ET reaction rate as a function of time for different Ω_2 values. As in the case of the reaction rates of double-well potential, ET reaction rate starts from zero and quickly increases in a quantum case owing to the uncertainty of population states around the crossing points.[23] ET rate shows an oscillation feature up to about $t = 15/\omega_0$ because of the interference of transition between the discrete energy states at different potentials.[24] In a classical picture, the oscillation feature is interpreted as the recrossing of the population between the potentials caused by the electron that is not trapped. After the temporal motions ended owing to the dissipation arising from the bath, ET rate reached plateau values. These plateau values correspond to the relaxation rates denoted by k_{rxn}. ET rate increases with a decrease in Ω_2, since the intermediate state acting as a barrier for ET reaction decreases for small Ω_2 and since the potentials of the second and third states do not reach the inverted region in this parameter range.[1] Here, we showed the results under the limited condition for demonstration purposes. Detailed analyses of ET problems in the context of nonlinear optics for a variety of conditions are left for future work.
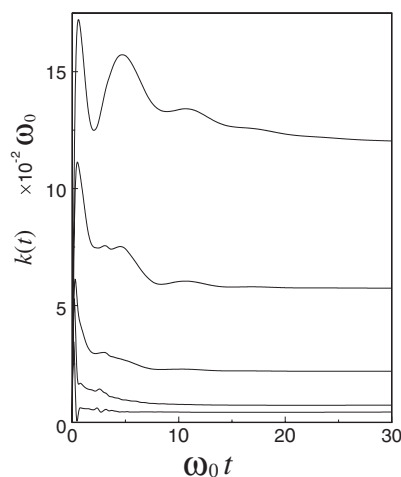
Fig. 2. ET reaction rate defined by the flux-flux correlation function is plotted for different values of Ω_2 as a function of t. The lines correspond to $\Omega_2 = -4\omega_0$, $-2\omega_0$, 0, $2\omega_0$, and $4\omega_0$ from top to bottom.

In this study, we derived the hierarchy of equations of motion for an ET system modeled by displaced oscillators coupled to a bath. Our approach can treat any strength of nonadiabatic coupling and activation energy, and the bath coupling at any temperature. In addition, the present approach requires less CPU power than other hierarchy approaches based on molecular coordinate descriptions; numerical calculations using this approach converge more than 10^2 times faster than those using other approaches. This formulation can be extended to multimode Brownian oscillator systems characterized by multiple baths by modifying the dimension of hierarchy elements.

In conclusion, the present formalism provides a powerful means for the study of various ET reaction processes as well as nonlinear optical responses in which quantum effects play a major role.

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