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On the transition from nonadiabatic to adiabatic rate kernel: Schwinger's stationary variational principle and Padé approximation

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For a two state system coupled to each other by a nonzero matrix element Δ and to the bath arbitrarily, the generalized master equation is derived by applying the well-known projection operator techniques to the quantum Liouville equation. The time-dependent rate kernel is expressed by an infinite summation of the perturbative terms in Fourier–Laplace space. The Schwinger's stationary variation principle in Hilbert space is extended to Liouville space and then applied to the resummation of the rate kernel. The Cini–Fubini-type trial state vector in Liouville space is used to calculate the variational parameters. It is found that the resulting stationary value for the rate kernel in Fourier–Laplace space is given by the [N,N-1]–Padé approximants, in the N-dimensional subspace constructed by the N perturbatively expanded Liouville space vectors. The (first-order) simplest approximation satisfying the variational principle turns out to be equal to the [1,0] Padé approximant instead of the second-order Fermi golden rule expression. Two well-known approximations, the noninteracting blip approximation (NIBA) and nonadiabatic approximation, are discussed in the context of the [1,0] Padé approximant, is also briefly discussed. © 1997 American Institute of Physics. [S0021-9606(97)50107-3]

I. INTRODUCTION

The role of solvent dynamics in the electron transfer reaction in condensed phases has been studied extensively by using various models for the bath.^{1–12} For example, the spinboson model where the two-state system is linearly coupled to the bosonic bath was shown to be one of the most useful models in studying the effect of the dynamical properties of solvent on the electron transfer reaction (or tunneling process in condensed phases).^{8,10,11,13-15} Usually the electron transfer system is assumed to consist of two electronic states, i.e., electron donor and acceptor, and the two states are coupled by the nonzero electron exchange matrix element, Δ . Furthermore, the energy of each state fluctuates in time by the interactions between the two electronic states and the bath degrees of freedom. Since the two energy levels are assumed to be coupled to a common bath, the fluctuation of the energy difference, instead of the fluctuation of each state, is fully responsible for the dynamic effect of the bath on the reaction rate. In this reaction, there are two important timescales determining the reaction rate which are the inverse of the electron exchange matrix element and the correlation time of the bath fluctuation. If the coupling matrix element Δ is very small, the nonadiabatic electron transfer rate, that is, the Fermi golden rule expression, is quantitatively acceptable. However, the above statement is not entirely correct, in general, because the timescale of the bath is another important factor determining the adiabaticity of the reaction rate.⁴ If the time scale of the bath is sufficiently fast, the wave packet created on the curve crossing (or transition state) region, where the Franck-Condon factor becomes a maximum, can be quickly relaxed into an equilibrium state on the potential energy surface of the product state. This means that the survival probability of the created wave packet on the transition state region is very small.^{6,7,12} In this case the second-order Fermi golden rule can indeed be useful in calculating the reaction rate, and the rate is proportional to the square of the electron exchange matrix element. On the other hand, if the bath correlation time is very slow, the reaction rate is now determined by the solvation process. Consequently, the rate does not depend on the electron exchange matrix element. Perhaps Zusman⁴ was the first one who obtained a theoretical expression connecting the nonadiabatic and adiabatic reaction rate constants. Later, numerous workers generalized Zusman's theory, although the essential aspect of those results are virtually identical. The overall electron transfer rate is given by the standard formula³

$$1/k = 1/k_a + 1/k_{na},$$
 (1)

where k_a and k_{na} are the adiabatic and nonadiabatic reaction rates, respectively. The nonadiabatic reaction rate is proportional to the square of the electron exchange matrix element, whereas the adiabatic rate is not and instead depends on the relaxation rate (survival time) as $1/\tau$. One can understand this crossover behavior as following. Suppose that the initial state is in thermal equilibrium with the electron donor state. The fluctuation of the bath degrees of freedom can create the nuclear wave packet at the curve crossing region, where the potential energy surfaces are constructed by the solvent nuclear degrees of freedom. The second-order action of the coupling potential can induce the transition from the donor to the acceptor electronic states. If the solvation dynamics on the acceptor state is sufficiently fast, that is, the survival time of the reactive state around the transition state region is very short, the rate is mainly determined by the second-order process, that is, the nonadiabatic reaction rate.⁷ On the other hand, if the solvation is very slow (long survival time), the recrossing of the wave packet back to the donor state, where this recrossing process is associated with the higher-order terms with respect to Δ , becomes possible so that the rate determining process is now the solvation dynamics. Consequently, the adiabatic reaction rate is solvent controlled. Sparpaglione and Mukamel⁵ presented a formal derivation of the generalized rate equation by using the projection operator techniques. Expanding the generalized rate kernel perturbatively and invoking static approximation, they were able to exactly perform the resummation of the perturbatively expanded rate kernel. This is identical to the resummation of the expansion of the rate kernel by considering the first two terms, which are the second-order and the fourth-order rate kernels, and using the [1,0]-Padé approximant,⁵

$$k = k^{(2)} + k^{(4)} + \dots \cong \frac{k^{(2)}}{1 - k^{(4)}/k^{(2)}}.$$
(2)

When the zero-frequency component is considered to be the *rate constant* and the characteristic solvent timescale is properly considered, Zusman's result can be obtained from their result.

The second resummation method is to utilize the Landau–Zener theory.¹⁶⁻¹⁹ In this case the rate is expressed by the exponential functional form. Since it is not our goal to compare the two procedures, we shall not discuss the detailed aspect of the Landau–Zener-type resummation scheme studied by Frauenfelder and Wolynes.²⁰

In this paper we shall reconsider the first scheme, the resummation of the perturbatively expanded rate kernel, by using Schwinger's stationary variational principle in Liouville space. Defining the perturbation operator *symmetrically* and using the Cini–Fubini-type trial function in Liouville space, the stationary rate kernel, which is an approximated rate kernel, is determined variationally. In Sec. II derivations of the generalized master equation with properly defined rate kernels are summarized by closely following Sparpaglione and Mukamel. Schwinger's stationary variation principle is applied to the calculation of the electron transfer rate kernel in Sec. III. Discussions on the noninteracting blip approximation and nonadiabatic approximations are given in the context of the Padé approximants in Sec. IV. The results are summarized in Sec. V.

II. GENERALIZED RATE EQUATION AND FREQUENCY-DEPENDENT RATE KERNEL

We consider a two-state electron transfer system dissolved in a condensed medium. Instead of considering a specific bath model, by using the Liouville space projection operator used by Mukamel and co-workers,^{5,12} we summarize the generalized rate equation where the rate is determined by the time-dependent rate kernels.

The electron donor and acceptor states are denoted by $|d\rangle$ and $|a\rangle$, respectively. The two states are coupled via a

nonadiabatic coupling Δ , the electron exchange matrix element. For the sake of simplicity, we assume that the electron exchange matrix element is not affected by the dynamical aspect of the bath, that is to say, Δ does not depend on the bath degrees of freedom. This is similar in spirit to the classical Condon approximation in the optical transition process, where the electric dipole matrix element does not depend on the nuclear degrees of freedom. The solvent Hamiltonians, when the electron transfer systems are in states $|d\rangle$ and $|a\rangle$, are denoted by $h_d(Q)$ and $h_a(Q)$, respectively. Here Q represents the nuclear degrees of freedom of the bath that are coupled to the electron transfer process. Note that the intramolecular nuclear degrees of freedom are not explicitly included in this paper. However, it is a straightforward procedure to include the intramolecular vibrational modes. Throughout this paper we will ignore the effect of the solvent electronic degrees of freedom, since they are extremely fast in comparison to the timescale of the nuclear degrees of freedom so that they quickly adjust themselves to the charge distribution of the electron transfer system. Perhaps, the energetics of the two-state system could be changed when the polarizability of the solvent molecules is included in the calculation.

The total Hamiltonian for the electron transfer system is then

$$H = H_0 + H_1,$$
 (3)

where the zeroth-order Hamiltonian is

1

$$H_0 = |d\rangle \{E_d + h_d(Q)\} \langle d| + |a\rangle \{E_a + h_a(Q)\} \langle a|$$

$$\tag{4}$$

and the interaction Hamiltonian is

$$H_1 = |d\rangle \Delta \langle a| + |a\rangle \Delta^* \langle d|. \tag{5}$$

 E_d (E_a) is the energy of the isolated donor (acceptor) state. Δ is the electron exchange matrix element. Throughout this paper, \hbar will be assumed to be a unity. By specifying the solvent Hamiltonians, one can study the dynamical effect of the solvent on the electron transfer reaction. We instead consider an arbitrary bath in this paper.

Before we present the formal derivation of the rate equation, it is useful to discuss the initial condition of the electron transfer reaction. Usually the initial state is assumed to be a thermal equilibrium state on the donor state. However, this is not likely the case if the initial state is created by an ultrafast laser pulse, a photoinduced electron transfer. A small portion of the electronic ground state population is photoexcited to create the initial state on the electron donor (electronic excited state) surface, which has to be a nonequilibrium state on the potential energy surface of the donor state. Then this nonequilibrium state relaxes to the quasi-equilibrium state on the donor surface as time progresses. During the relaxation process, the continuous leakage of the donor population to the acceptor state progresses. Therefore, a complete description of the photoinduced electron transfer should include this nonequilibrium nature of the initial preparation.²¹ This was presented by the authors in Ref. 22. Although it is rather straightforward to include the nonequilibrium effect discussed above in this paper, for the sake of simplicity we shall focus on the conventional case that the initial state is the thermal equilibrium state on the electron donor potential surface.

The rate equations can be obtained by solving the Liouville equation

$$\frac{d\rho(t)}{dt} = -iL\rho(t),\tag{6}$$

where the Liouville operators are defined as commutators

$$LA = (L_0 + L_I)A \equiv [H_0 + H_I, A] = [H_0, A] + [H_I, A].$$
(7)

For the sake of simplicity we shall denote the Liouville space vector by $|\cdots\rangle\rangle$, and the scalar product of two Hilbert space operators is denoted as

$$\langle\langle A|B\rangle\rangle = \operatorname{Tr}[A^{+}B].$$
 (8)

Here the trace is over the complete Hilbert space including the system and the solvent. By following Sparpaglione and Mukamel⁵ closely, the Liouville space projection operator \hat{P} is defined as

$$\hat{P} \equiv |\hat{D}\rho_d\rangle\rangle\langle\langle\hat{D}| + |\hat{A}\rho_a\rangle\rangle\langle\langle\hat{A}|, \qquad (9)$$

where the donor and acceptor operators in the Hilbert space are denoted by $\hat{D} \equiv |d\rangle \langle d|$ and $\hat{A} \equiv |a\rangle \langle a|$, respectively, and the two density operators associated with the donor and the acceptor, ρ_d and ρ_a , are, respectively

$$\rho_{d} = \frac{\exp(-H_{d}/k_{B}T)}{\operatorname{Tr}[\exp(-H_{d}/k_{B}T)]},$$

$$\rho_{a} = \frac{\exp(-H_{a}/k_{B}T)}{\operatorname{Tr}[\exp(-H_{a}/k_{B}T)]}.$$
(10)

The complimentary operator \hat{Q} is

$$\hat{Q} = 1 - \hat{P}.\tag{11}$$

By using the standard projection operator techniques, the reduced equation of motion for the populations can be obtained,

$$\frac{dp_{d}}{dt} = -\int_{0}^{t} d\tau [k_{da}(t-\tau)p_{d}(r) - k_{ad}(t-\tau)p_{a}(\tau)],$$

$$\frac{dp_{a}}{dt} = \int_{0}^{t} d\tau [k_{da}(t-\tau)p_{d}(\tau) - k_{ad}(t-\tau)p_{a}(r)],$$
(12)

where the populations of the donor and the acceptor are

$$p_{d}(t) = \operatorname{Tr}[\hat{D}\rho(t)]$$

$$p_{a}(t) = \operatorname{Tr}[\hat{A}\rho(t)].$$
(13)

The time-dependent rate kernel $k_{da}(t)$ [$k_{ad}(t)$] describes the transition rate from donor (acceptor) to acceptor (donor) and is given as

$$k_{da}(t) \equiv \langle \langle \hat{D} | L \exp(-i\hat{Q}Lt)\hat{Q}L | \hat{D}\rho_d \rangle \rangle,$$

$$k_{ad}(t) \equiv \langle \langle \hat{A} | L \exp(-i\hat{Q}Lt)\hat{Q}L | \hat{A}\rho_a \rangle \rangle.$$
(14)

Equation (12) with the time-dependent rate kernels, Eq. (14), is formally exact, since the full Liouville operator L instead of L_0 was used in Eq. (14).

It turns out that the Fourier-Laplace transform of the generalized rate equation is useful in the following derivation of the resummed rate kernel. By denoting the Fourier-Laplace transform of an arbitrary time-dependent function f(t) as $F(\omega)$

$$F(\omega) = \int_0^\infty dt \, \exp(i\omega t) f(t) \tag{15}$$

with its inverse transform

$$f(t) = (2\pi)^{-1} \int_{-\infty}^{\infty} d\omega \, \exp(-i\omega t) F(\omega), \qquad (16)$$

the generalized rate equations, Eqs. (12), can be written as

$$i\omega \begin{bmatrix} P_{d}(\omega) \\ P_{a}(\omega) \end{bmatrix} + \begin{bmatrix} p_{d}(t=0) \\ p_{a}(t=0) \end{bmatrix} = \begin{bmatrix} K_{da}(\omega) & -K_{ad}(\omega) \\ -K_{da}(\omega) & K_{ad}(\omega) \end{bmatrix} \times \begin{bmatrix} P_{d}(\omega) \\ P_{a}(\omega) \end{bmatrix}, \quad (17)$$

where $P(\omega)$ and $K(\omega)$ correspond to the Fourier-Laplace transforms of p(t) and k(t), respectively. Likewise we define the Liouville space advanced Green functions as

$$G(\omega) = -i \int_0^\infty dt \, \exp(i\,\omega t) \exp(-iLt) = \frac{1}{\omega - L}$$
(18)

and

$$G_0(\omega) = -i \int_0^\infty dt \, \exp(i\,\omega t) \exp(-iL_0 t) = \frac{1}{\omega - L_0}.$$
 (19)

Thus, the Fourier–Laplace transform of the rate kernel, for example, $K_{da}(\omega)$, is given by

$$K_{da}(\omega) = i \langle \langle \hat{D} | L_I \frac{1}{\omega - \hat{Q}L} \hat{Q} L_I | \hat{D} \rho_d \rangle \rangle.$$
⁽²⁰⁾

From now on we shall focus on $K_{da}(\omega)$ only, since the calculation of $K_{ad}(\omega)$ is precisely identical to that of $K_{da}(\omega)$. Using the formal relation

$$\hat{Q}L = L_0 + \hat{Q}L_1 \tag{21}$$

and the identity²³

$$\frac{1}{\omega - \hat{Q}L} = \frac{1}{\omega - \hat{Q}L_0} \left(I + \frac{\hat{Q}L_I}{\omega - \hat{Q}L} \right)$$
$$= \frac{1}{\omega - \hat{Q}L_0} \sum_{n=0}^{\infty} \left[\hat{Q}L_I \frac{1}{\omega - \hat{Q}L_0} \right]^n, \quad (22)$$

one can obtain the formally exact perturbative expansion of the rate kernel

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$$K_{da}(\omega) = \sum_{n=1}^{\infty} K_{da}^{(2n)}(\omega), \qquad (23)$$

where the 2nth-order contribution to the rate kernel in Fourier–Laplace space is

$$K_{da}^{(2n)}(\omega) = i \langle \langle \hat{D} | [L_I G_0(\omega) L_I G_0(\omega) \hat{Q}]^{(n-1)} \\ \times L_I G_0(\omega) L_I | \hat{D} \rho_d \rangle \rangle.$$
(24)

Note that the terms including the odd number of actions of the L_I operator vanish since the diagonal matrix elements are taken, and the contribution, $K_{da}^{(2n)}(\omega)$, is order 2n in the nonadiabatic coupling Δ . For example, the usual second-order Fermi golden rule expression is the first term in Eq. (23), that is,

$$K_{da}^{(2)}(\omega) = i \langle \langle \hat{D} | L_I G_0(\omega) L_I | \hat{D} \rho_d \rangle \rangle, \qquad (25)$$

which is called the *nonadiabatic rate kernel* throughout this paper.

The calculation of the time-dependent population evolution is now reduced to that of the rate kernel in Fourier-Laplace space. There are numerous cases where the secondorder expression for the rate kernel is quantitatively accurate enough to predict the rate. However, as briefly discussed in Sec. I, there are two important cases where the nonadiabatic rate does not correctly represent the reaction rate. The first obvious case is when the electron exchange matrix element is sufficiently large so that one cannot ignore the higherorder terms in the perturbative expansion of the rate kernel in Eq. (23). The second is when the bath correlation time is very slow. In this case the solvation of the wave packet created in the product state, e.g., $L_I G_0(\omega) L_I |\hat{D} \rho_d \rangle$, becomes the predominant factor in the electron transfer process, and consequently the reaction rate does not depend on the electron exchange matrix element. It is our goal in this paper to present a systematic method to calculate the generalized rate kernel given in Eq. (23) by using Schwinger's stationary variational principle.24

III. VARIATIONAL PRINCIPLE AND PADE APPROXIMATION

The generalized rate kernel was expanded in terms of the even-order perturbation terms. We now discuss the resummation of Eq. (23) based on the stationary variational principle.²⁴ From now on, we shall only focus on the rate kernel $K_{da}(\omega)$ and omit the subscript "da."

In order to rewrite the perturbational expansion of the rate kernel, it is useful to define the zeroth-order state $|\phi_0(\omega)\rangle\rangle$ and the new perturbation operator $v(\omega)$ in Liouville space as

$$|\phi_0(\omega)\rangle\rangle \equiv G_0^{1/2}(\omega)L_I |\hat{D}\rho_d^{1/2}\rangle\rangle, \qquad (26)$$

$$v(\omega) = \frac{G_0^{1/2}(\omega)L_I G_0(\omega)\hat{Q}L_I G_0^{1/2}(\omega)}{|\Delta|^2}.$$
 (27)

The rate kernel in Eq. (23) can be rewritten in terms of $|\phi_0(\omega)\rangle$ and $v(\omega)$ as

$$K(\omega) = i \langle \langle \phi_0 | \chi(\omega) \rangle \rangle, \tag{28}$$

where

$$|\chi(\omega)\rangle\rangle \equiv \sum_{n=0}^{\infty} \left[|\Delta|^2 v(\omega) \right]^n |\phi_0(\omega)\rangle\rangle$$
$$= \sum_{n=0}^{\infty} |\Delta|^{2n} |\phi_n(\omega)\rangle\rangle.$$
(29)

Here the *n*th-order state vector is naturally defined as above, that is, $|\phi_n(\omega)\rangle\rangle \equiv [v(\omega)]^n |\phi_0(\omega)\rangle\rangle$. The physical meaning of Eq. (29) is that the Liouville state vector $|\chi(\omega)\rangle\rangle$ is given by a linear combination of $|\phi_n(\omega)\rangle\rangle$'s, where the expansion coefficient of the *n*th term is given by $|\Delta|^{2n}$. Therefore, a set of $\{|\phi_n(\omega)\rangle\rangle$ is a complete basis set in this case, and the Liouville space is completely spanned by this basis set.

From the definition of $|\chi(\omega)\rangle$, one can find the relation,

$$\chi(\omega)\rangle\rangle = |\phi_0(\omega)\rangle\rangle + |\Delta|^2 v(\omega)|\chi(\omega)\rangle\rangle$$
(30)

which corresponds to the Lippman–Schwinger-type equation extended to *Liouville space*. We next apply Schwinger's variational principle to find the variational functional $K^{S}(\omega)$,

$$K^{S}(\omega) = i \langle \langle \phi_{0}(\omega) | \chi^{T}(\omega) \rangle \rangle + i \langle \langle \chi^{T}(\omega) | \phi_{0}(\omega) \rangle \rangle$$
$$- i \langle \langle \chi^{T}(\omega) | 1 - \Delta^{2} v(\omega) | \chi^{T}(\omega) \rangle \rangle, \qquad (31)$$

which is assumed to be *stationary* for small variations of the trial state $|\chi^{T}(\omega)\rangle\rangle$ about $|\chi(\omega)\rangle\rangle$, which means that *the stationary value of* $K^{S}(\omega)$ *is* $K(\omega)$. This is proved in the Appendix. There exist several attempts using the variational approaches to calculate the rate constant. Most of them concern the energy of the transition state or the position of the dividing surface and utilize the minimum-energy variational principle. Unlike those approaches, here the rate kernel itself is the objective of the variational procedure, instead of the energy. Therefore, we found this approach is perhaps a more direct way to calculate the rate kernel in general.

We now introduce a trial state vector, $|\chi^T(\omega)\rangle$, as

$$|\chi^{T}(\omega)\rangle\rangle = \sum_{n=0}^{N-1} c_{n} |\phi_{n}(\omega)\rangle\rangle, \qquad (32)$$

where c_n are the variational parameters. Note that the trial state is expressed as a linear combination of $|\phi_n(\omega)\rangle\rangle$ (for n=0 to N-1), that is, the trial state $|\chi^T(\omega)\rangle\rangle$ is expanded in a subspace constructed by $|\phi_n(\omega)\rangle\rangle$ (for n=0 to N-1). This type of trial state vector is known as the Cini–Fubini trial function,²⁵ where the trial function is given by a linear combination of a finite set of $|\phi_n(\omega)\rangle\rangle$'s instead of infinite basis functions. One can prove that the stationary variational functional $K^S(\omega)$ becomes identical to the true rate kernel $K(\omega)$ when the trial vector $|\chi^T(\omega)\rangle\rangle$ equals the correct one $|\chi(\omega)\rangle\rangle$ by inserting Eq. (30) into (31) and using the expanded form of $|\chi(\omega)\rangle\rangle$ in Eq. (29).

For the sake of notational simplicity, we now define the inner product in Liouville space constructed by $|\phi_n(\omega)\rangle\rangle$'s as

$$b_i(\omega) = \langle \langle \phi_0(\omega) | \phi_i(\omega) \rangle \rangle.$$
(33)

It should be noted that the second-order Fermi golden rule formula, Eq. (25), is identical to $ib_0(\omega)$, which is proportional to $|\Delta|^2$, and $i|\Delta|^{2n}b_n(\omega)$ represents the (2n+2)-order (with respect to the electron exchange matrix element Δ) contributions to the rate kernel, $K^{(2n+2)}(\omega)$. Inserting Eq. (32) into the variational functional, Eq. (31), gives

$$-iK^{S}(N,\omega) = -\sum_{i,j=0}^{N-1} c_{i}c_{j}\{b_{i+j} - |\Delta|^{2}b_{i+j+1}\} + 2\sum_{i=0}^{N-1} c_{i}b_{i}$$
$$= -\mathbf{c}^{T}\mathbf{M}\mathbf{c} + 2\mathbf{c}^{T}\mathbf{b},$$
(34)

where **c** and **b** are the column vectors whose elements are $\{c_i\}$ and $\{b_i\}$, respectively, and

$$[\mathbf{M}]_{ij} = b_{i+j} - |\Delta|^2 b_{i+j+1}.$$
(35)

Note that the stationary variational functional, $K^{S}(N,\omega)$, is determined by the *N* perturbative expansion terms. In order to determine the variational parameters, $\{c_i\}$, we solve the linear equation,

$$[N,M] = \frac{\begin{vmatrix} T_{M-N+1} & T_{M-N+2} & \cdots & T_{M+1} \\ \vdots & \vdots & & \vdots \\ T_M & T_{M+1} & \cdots & T_{M+N} \\ \Sigma_{j=N}^M T_{j-N} \lambda^j & \Sigma_{j=N-1}^M T_{j-N+1} \lambda^j & \cdots & \Sigma_{j=0}^M T_j \lambda^j \end{vmatrix}}{\begin{vmatrix} T_{M-N+1} & T_{M-N+2} & \cdots & T_{M+1} \\ \vdots & \vdots & & \vdots \\ T_M & T_{M+1} & \cdots & T_{M+N} \\ \lambda^N & \lambda^{N-1} & \cdots & 1 \end{vmatrix}}$$

where *T*-matrix elements are equal to those of **b**, and λ equals to $|\Delta|^2$ in our case. Here $T_j=0$ if j<0. Equations (37) with (33) and (35) are the main results in this section and will be discussed for some limiting cases.

IV. RESULTS AND DISCUSSION

It was found that the stationary value $K^{S}(N,\omega)$ is approximately equal to the generalized rate kernel based on Schwinger's stationary variational principle. The variationally determined rate kernel was shown to be equal to the [N,N-1]-Padé approximants, which is completely determined by N matrix elements $b_n(\omega)$ (for n=0,1,..,N-1) in the subspace constructed by the N perturbatively expanded states.

A. One-dimensional case (N=1): [1,0]–Padé approximant

First consider the simplest case of all, that is the case when N=1. The trial function is given by

$$|\chi^{T}(\omega)\rangle\rangle = c_{0}|\phi_{0}(\omega)\rangle\rangle,$$

where c_0 is the only variational parameter determined from the stationary variational principle. In this case, the Cini–

$$\frac{\partial K^{s}(N,\omega)}{\partial c_{i}} = 0 \quad \text{for all } i$$

and find that

$$\mathbf{c} = \mathbf{M}^{-1} \mathbf{b}. \tag{36}$$

Finally, the stationary value $K^{S}(N,\omega)$ is found to be

$$K^{S}(N,\omega) = i\mathbf{b}^{T}\mathbf{M}^{-1}\mathbf{b}.$$
(37)

The functional form of Eq. (37) was found to be equal to the [N,N-1]-Padé approximants and the Nuttall's identity can be used to obtain a more compact formula.²⁶ The general [N,M]-Padé approximant can be written by the ratio of the two determinants as

Fubini subspace is constructed by $|\phi_0(\omega)\rangle$. Then one finds that the variationally determined trial function becomes

$$|\chi^{T}(\omega)\rangle\rangle = \frac{b_{0}(\omega)}{b_{0}(\omega) - |\Delta|^{2}b_{1}(\omega)} |\phi_{0}(\omega)\rangle\rangle.$$
(38)

Note that the variational parameter thus determined is frequency dependent. Here, from the definitions, $ib_0(\omega)$ and $i|\Delta|^2b_1(\omega)$ are identical to the second- and fourth-order contributions to the rate kernel, which are $K^{(2)}(\omega)$ and $K^{(4)}(\omega)$, respectively. Therefore, the stationary value for the rate kernel is

$$K^{S}(N=1,\omega) = \frac{[K^{(2)}(\omega)]^{2}}{K^{(2)}(\omega) - K^{(4)}(\omega)}.$$
(39)

Now, if we take the zero-frequency components of the perturbative rate kernels that are the corresponding rate constants, we recover Eq. (2) from Sec. I. Since the frequency dependence of the rate kernels in Eq. (39) is fully retained, Eq. (39) should be considered as an improved version of Eq. (2).

Equation (39) can be rewritten in terms of a geometric series,

$$K^{S}(N=1,\omega) = K^{(2)}(\omega) - |K^{(4)}(\omega)| + \frac{[K^{(4)}(\omega)]^{2}}{K^{(2)}(\omega)} + \dots,$$
(40)

where we emphasized that the magnitude of $K^{(4)}(\omega)$ is negative once it is evaluated with Eq. (24).⁵ Thus, the approximated rate kernel in Eq. (39) is exact up to the fourth-order contribution to the rate kernel, but deviated from the exact result after the sixth-order terms.

1. Frequency-dependent transmission coefficient

One can reinterprete the result, Eq. (39), as

$$K^{S}(N=1,\omega) = \chi^{(1)}(\omega) K_{na}(\omega), \qquad (41)$$

where $K_{na}^{(2)}(\omega)$ is the nonadiabatic rate kernel equal to the second-order Fermi golden rule expression, Eq. (25), and $\chi^{(1)}(\omega)$ denotes the frequency-dependent transmission coefficient calculated in the one-dimensional subspace and is defined as

$$\chi^{(1)}(\omega) = \frac{1}{1 + K_{na}(\omega)\tau(\omega)}$$
(42)

with

$$\tau(\omega) = |K^{(4)}(\omega)| / [K_{na}(\omega)]^2.$$
(43)

Here $\tau(\omega)$ is the frequency-dependent survival time and is related, *not identical*, to the bath correlation time. Note that the transmission coefficient $\chi^{(1)}(\omega) < 1$ for all frequencies. It is also possible to interpret that the factor $\chi^{(1)}(\omega)$ describes the renormalization effect on the coupling matrix element Δ induced by the higher-order rate contribution and the bath fluctuation. The product $K_{na}(\omega)\tau(\omega)$ in Eq. (41) is often interpreted as the frequency-dependent *adiabaticity parameter* since, if $K_{na}(\omega)\tau(\omega) \ll 1$ for all frequencies, the rate is completely determined by the second-order rate process (nonadiabatic limit), whereas if $K_{na}(\omega)\tau(\omega) \gg 1$ for all frequencies the reaction is governed by the (survival) time $\tau(\omega)$ and does not depend on the electron exchange matrix element, that is,

$$K^{S}(N=1,\omega)=\tau^{-1}(\omega)$$

This is the case of the adiabatic limit and is realized when the solvent bath correlation time is very slow so that the probability of the recrossing, more precisely multiple actions of the transition operator $v(\omega)$, become large.

2. Time-dependent transmission coefficient and rate kernel

As can be seen in Eq. (41), the generalized frequencydependent rate kernel is given by a product of the frequencydependent transmission coefficient and the second-order rate kernel. Thus, the time-dependent rate kernel is given by a convolution, such as

$$k_{da}^{S}(t) = \int_{-\infty}^{\infty} d\tau \kappa^{(1)}(t-\tau) k_{na}(\tau), \qquad (44)$$

where $\kappa^{(1)}(t)$ and $k_{na}(t)$ are the inverse Fourier transforms of $\kappa(\omega)$ and $K_{na}(\omega)$, respectively. The rate kernel thus obtained

is determined by that of the cross correlation between the time-dependent transmission coefficient and second-order rate kernel. If the timescale of the second-order rate kernel is fast compared to that of the transmission coefficient, i.e., $k_{na}(\tau) \approx k_{na}\delta(\tau)$, the time dependence of the rate kernel is determined by that of the transmission coefficient so that $k^{S}(t) \approx \kappa^{(1)}(t)k_{na}$. On the other hand, if the timescale of the second-order rate kernel, i.e., $\kappa^{(1)}(t-r) \approx \kappa_{0}^{(1)}\delta(t-\tau)$, the rate kernel, i.e., $\kappa^{(1)}(t-r) \approx \kappa_{0}^{(1)}\delta(t-\tau)$, the rate kernel becomes $k^{S}(t) = \kappa_{0}^{(1)}k_{na}(t)$.

3. Nonadiabatic limit, $\kappa^{(1)}(\omega) \approx 1$

Next we consider the nonadiabatic limit more in detail. This limit is the case when the transmission coefficient $\kappa^{(1)}(\omega)$ is approximately equal to a unity. The nonadiabatic condition, $K_{na}(\omega)\tau(\omega) \ll 1$, can be met when the electron exchange matrix element is very small regardless of the characteristic solvent timescale. Usually the nonadiabatic limit has been assumed by such a limit. However, there is another possibility satisfying this inequality, that is, when the survival timescale, $\tau(\omega)$, is much faster than the inverse of the second-order rate kernel. This limit is in spirit identical to the celebrated noninteracting blip approximation, where there is no correlation between the two consecutive off-diagonal density matrix evolutions (blips) separated by the diagonal density matrix evolutions (sojourns). This approximation is applicable when the bath correlation time is fast, that is to say, the memory of the bath fluctuation does not last long time.²⁷ These two cases, (i) small Δ and (ii) short bath memory (short bath correlation time), are apparently independent of each other because the former depends on the intrinsic properties of the electron donor and acceptor states whereas the latter is determined by the dynamical aspect of the bath. However, if either the (i) or (ii) condition is satisfied, the rate kernel is determined by the second-order expression, $K_{na}(\omega)$. Finally, we find it interesting to note that, based on Schwinger's stationary variational principle, the first-order approximation to the rate kernel equals Eq. (39), not $K_{na}(\omega)$.

B. Two-dimensional case (*N*=2): [2,1]–Padé approximant

We now consider the next higher-order approximation, that is the [2,1]–Padé approximant for the stationary rate kernel. In this case the trial function is given by a linear combination of two basis vectors, $|\phi_0(\omega)\rangle\rangle$ and $|\phi_1(\omega)\rangle\rangle$, as

$$|\chi^{T}(\omega)\rangle\rangle = c_{0}(\omega)|\phi_{0}(\omega)\rangle\rangle + c_{1}(\omega)|\phi_{1}(\omega)\rangle\rangle,$$

where $c_0(\omega)$ and $c_1(\omega)$ are the variational parameters. Using the stationary variational principle and from Eq. (36), they are

$$c_0(\omega) = \frac{1 - |\Delta|^2 x(\omega)}{1 - |\Delta|^2 x(\omega) + |\Delta|^4 y(\omega)},$$
$$c_1(\omega) = \frac{|\Delta|^2}{1 - |\Delta|^2 x(\omega) + |\Delta|^4 y(\omega)},$$

where

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$$x(\omega) \equiv \frac{b_0 b_3 - b_1 b_2}{b_0 b_2 - b_1^2},$$
$$y(\omega) \equiv \frac{b_1 b_3 - b_2^2}{b_0 b_2 - b_1^2}.$$

Then the approximated rate kernel in the two-dimensional subspace constructed by $|\phi_0(\omega)\rangle$ and $|\phi_1(\omega)\rangle$ is

$$K^{S}(N=2,\omega) = i \frac{b_{0} - |\Delta|^{2} z(\omega)}{1 - |\Delta|^{2} x(\omega) + |\Delta|^{4} y(\omega)},$$
(45)

where

$$z(\omega) = \frac{b_0^2 b_3 - 2b_0 b_1 b_2 + b_1^3}{b_0 b_2 - b_1^2}$$

Equation (45) can be recast in the form, like Eq. (41),

$$K^{S}(N=2,\omega) = \kappa^{(2)}(\omega) K_{na}(\omega),$$

where the transmission coefficient in this case is

$$\kappa^{(2)}(\omega) = \frac{1 - |\Delta|^2 z(\omega) / b_0(\omega)}{1 - |\Delta|^2 x(\omega) + |\Delta|^4 y(\omega)}$$

Unfortunately, in this two-dimensional case, there does not appear any simple physical picture provided in the onedimensional case above. Expanding Eq. (45) in terms of a geometric series, we find

$$K_{da}^{S}(N=2,\omega) = K_{da}^{(2)}(\omega) + K_{da}^{(4)}(\omega) + K_{da}^{(6)}(\omega) + K_{da}^{(8)}(\omega) + O(|\Delta|^{10}).$$

Note that the approximated expression for the rate kernel given in Eq. (45) is exact up to the eighth-order (with respect to Δ) contribution to the rate kernel. Therefore, one can expect that Eq. (45) would provide more accurate result in comparison to the [1,0] Padé approximant. However, one has to pay the price that the higher-order perturbative terms—often they are much involved in comparison to the second-or fourth-order contributions to the rate kernel—should be calculated. Therefore, it is desirable to use simpler trial functions instead of $|\phi_n(\omega)\rangle$'s in Eq. (31).

V. SUMMARY

In this paper we considered the generalized rate kernel describing the transition process between two electronic states in the condensed phases. Using the well-known projection operator method, the generalized rate kernel was expanded in terms of the perturbative contributions in Fourier–Laplace space. The resummation of the rate kernel was carried out by using Schwinger's stationary variational principle in Liouville space. The Cini–Fubini-type trial function was used to variationally determine the generalized rate kernel. For the one-dimensional subspace constructed by a single vector defined as $|\phi_0(\omega)\rangle\rangle$ in Eq. (26), we recover the standard formula for the rate kernel, Eq. (39), where the corresponding survival time $\tau(\omega)$ is frequency dependent. It is interesting to note that the second-order golden rule expression is not the first-order approximation satisfying the

variational principle, so that one has to be careful when the golden rule is used to describe the transition rate for the reactions in condensed phases. The nonadiabatic limit was found to be realized either when the coupling matrix element is very small or when the frequency-dependent survival time $\tau(\omega)$ defined in Eq. (43) is very short. The latter case is identical in spirit to the noninteracting blip approximation, although this was invoked in the theoretical studies on the tunneling process in the quantum dissipative media by using the path-integral method. If the Cini-Fubini-type trial function constructed in the two-dimensional subspace is used, the variationally determined rate kernel is given by Eq. (45), where the result is exact up to the eighth-order contribution to the rate kernel. Thus, we found that Schwinger's stationary variation principle can be used to systematically calculate the rate kernel.

It will be interesting to numerically test the result presented in this paper by using a simple bath model such as spin-boson Hamiltonian or even simpler one. For instance, the frequency-dependent expression for the rate kernel $K_{na}(N=1, \omega)$ in the one-dimensional subspace could show the nonexponential decaying pattern if the frequencydependent survival time is significantly deviated from a constant, that is, its time-dependent analog cannot be approximated as a delta function. In other words, one may be able to find the case satisfying neither condition $K_{na}(\omega)\tau(\omega) \ll 1$ nor $K_{na}(\omega)\tau(\omega) \ge 1$ for all frequencies ω . Perhaps the activationless process is likely to be the case because the timescale separation between the reaction rate and the characteristic solvent time is not always acceptable and therefore the frequency-dependent rate kernel instead of the zerofrequency rate constant has to be taken into account. Next, the higher-order approximation to the rate kernel based on the variational principle was found to be equal to the [2,1]-Padé approximant. By calculating this two-dimensional result, the [2,1]-Padé approximant, for a given bath, one could show the validity of the one-dimensional result, the [1,0]-Padé approximant to the rate kernel. Finally, it will be interesting to find some simple trial function that can be applied to the variational principle discussed in this paper. These are all under investigation and will be presented in the future.

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APPENDIX

In this Appendix we prove that Schwinger's variational functional $K_{da}^{S}(\omega)$ in Eq. (31) is stationary for small variations of $|\chi^{T}(\omega)\rangle\rangle$ about $|\chi(\omega)\rangle\rangle$. First let's replace the trial state $|\chi^{T}(\omega)\rangle\rangle$ with $|\chi(\omega)\rangle+|\delta\chi(\omega)\rangle\rangle$ in the variational functional and collect terms which are first-order with respect to $|\delta\chi(\omega)\rangle\rangle$,

$$\begin{split} \delta K^{S}_{da}(\omega) &= i \langle \langle \phi_{0}(\omega) | \delta \chi(\omega) \rangle \rangle + i \langle \langle \delta \chi(\omega) | \phi_{0}(\omega) \rangle \rangle \\ &- i \langle \langle \delta \chi(\omega) | 1 - |\Delta|^{2} v(\omega) | \chi(\omega) \rangle \rangle - i \langle \langle \chi(\omega) | 1 \\ &- |\Delta|^{2} v(\omega) | \delta \chi(\omega) \rangle \rangle \\ &= i \{ \langle \langle \phi_{0}(\omega) | - \langle \langle \chi(\omega) | + \langle \langle \chi(\omega) | v(\omega) | \Delta |^{2} \} \\ &\times | \delta \chi(\omega) \rangle \rangle + i \langle \langle \delta \chi(\omega) | \{ | \phi_{0}(\omega) \rangle \rangle - | \chi(\omega) \rangle \rangle \\ &+ |\Delta|^{2} v(\omega) | \chi(\omega) \rangle \}. \end{split}$$
(A1)

By inserting Eq. (28) into the above equation (A1), we find that the above equation is indeed zero. Consequently, the stationary value of $K_{da}^{S}(\omega)$ is $K_{da}(\omega)$.

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