Optimized perturbation approach with a Legendre transformation to a dissipative system: Correlation functions of a Morse oscillator

Yoko Suzuki and Yoshitaka Tanimura

Institute for Molecular Science, Myodaiji, Okazaki 444-8585, Japan

(Received 27 April 1998; revised manuscript received 18 September 1998)

We apply the optimized perturbation theory (OPT) to study the dynamics of a dimer molecule system in condensed phases described by a Morse potential system coupled to a heat bath. The OPT combines the techniques based on the variational principle and the perturbative expansion. The first-order approximation of the OPT agrees with Feynman’s variational theory developed for the polaron problem [Statistical Mechanics: A Set of Lectures (Benjamin, London, 1972)]. The OPT makes it possible to deal with an anharmonic potential system in a nonperturbative way. Combined with the inversion method, which is a technique to carry out the Legendre transformation, we take into account the asymmetry of the potential effectively. We then calculate the absorption spectrum of the molecule system, which relates to a two-time correlation function of a nuclear coordinate. [S1063-651X(99)04702-9]

PACS number(s): 05.70.Ln, 11.10.–z, 33.20.–t

I. INTRODUCTION

Since the work by Leggett and co-workers [1,2], the dynamical roles of a quantum system in a dissipative environment has been considered in a large number of problems, e.g., chemical reactions [3], electron transfer [4], and nonlinear spectroscopy [5]. The system in a condensed phase can be modeled by a main system and a surrounding environment (a bath system). The interaction between the system and the bath causes dissipation on the main system. In many realistic cases, the fluctuation induced by the environment follows the central limit theorem. A harmonic oscillator bath gives a Gaussian distribution for the density matrix [6]. Therefore, the harmonic oscillator bath can be a good model of the environment [7]. The main system is described by a particle moving in a potential. If the potential is harmonic, this model agrees with the quantum Brownian oscillator system and the dynamical variables such as the two- and three-time correlation functions of the coordinate can be calculated analytically using path-integral techniques [8,9]. For general potential systems, where most of the important quantum dynamics such as tunneling takes place, however, one cannot calculate the dynamical variables analytically. In order to deal with such problems, one has to use the equations of motion for the reduced density matrix. Such an equation is obtained by tracing out the bath degrees of freedom through the projection operator method or the path integral method. The dynamical variables can be calculated using a direct integration of these equations of motion. Examples of such an equation involve the quantum master equation [6], the Redfield equation [10,11], and the quantum Fokker-Planck equation [12,13]. The quantum master equation and the Redfield equation are the equations of motion for the reduced density in the energy state representation. They can be derived by assuming the linear-linear or the rotating wave form of the system-bath interaction with the white noise approximation. For the linear-linear interaction, it has been assumed that the spectral distribution of the bath is Ohmic and the bath temperature is high (the white noise approximation). Thus one cannot use this equation of motion to study a low temperature system where quantum dynamics plays a role. For the rotating wave interaction case, one does not have the temperature limitation. However, the rotating wave approximation may differ from the dynamics that is originally described by the linear-linear system-bath interaction. In addition to this circumstance, these two equations of motion cannot treat the continuous energy states that are involved in the Morse potential system as the dissociation states. For such dissociative systems, the quantum Fokker-Planck equation is easy to apply. The quantum Fokker-Planck equation is the equation of motion for the reduced density matrix in the coordinate space or the Wigner representation. This equation in principle describes the same dynamics as the former two equations if the system-bath interaction is linear-linear; thus it inherits the same high-temperature limitation. This limitation can be partially relaxed by assuming a Gaussian-Markovian noise bath instead of a Gaussian white noise bath [14,15]. This quantum Fokker-Planck equation for a Gaussian-Markovian bath has the capability of dealing with any shape potential surfaces at relatively low temperatures. However, solving such equations of motion for various physical conditions is computationally very expensive. The spectral distribution of the bath is also limited to the case of Ohmic dissipation with a Lorentzian cutoff. In addition, it does not offer much insight into the underlying dynamics from the numerical results. Thus handy analytical solutions that have wider applicability and can supplement the numerical results are called for.

In this paper we employ optimized perturbation theory (OPT) to calculate analytically the dynamical variable of the Morse potential [16] system in a dissipative environment. The Morse potential system is anharmonic and has dissociation states at higher energy levels. It has been used as a model of many molecular systems, especially for dimer molecules. The Morse potential system without coupling to the bath can be studied analytically by solving the Schrödinger equation [17–19] or by performing the path integration [20–24]. These approaches are performed in the coordinate representation [17,20,21,23] or the coherent state representation.
The latter representation is associated with the reducible representation of Lie groups [25]. We are interested in studying the dynamics of molecules in the condensed phase since many important chemical processes play a role in liquids. To include the effects of surrounding molecules, we attached the Morse potential system to the bath. However, if the system is coupled to the bath, one cannot solve the problem exactly. Here we have adapted the path-integral formalism to make approximations. We used the double time path formalism [26–34] to deal with the two-time correlation functions of coordinates, which are the physical observables of various experiments including femtosecond nonlinear spectroscopy. All heat-bath effects were taken into account by the Feynman-Vernon influence functional [28]. In path-integral formalism, we can classify the two types of approaches depending on the method of approximation. The first one is perturbative. We can deal with the anharmonic part of the Hamiltonian or Lagrangian as a perturbation. However, this approach is limited to the case where the anharmonicity is weak and one has to obtain the n-th-order correlation functions for anharmonic potentials analytically [35,36]. The other approach is nonperturbative. An example of this approach involves the resummation of the infinite number of perturbative terms, which introduces the nonperturbative ground state, e.g., the state written as the coherent sum of the modes excited above the old states [37–40]. In this paper we apply the OPT, which was developed to calculate the energy eigenvalues or the wave functions [41–43]. The OPT introduces an artificial parameter δ that does not appear in the original problem. One defines an action $S_δ$, which interpolates between the theory we hope to solve, with an action $S$, and another action $S_δ(µ)$, which must be solvable and is chosen to reflect the physical properties of the original action $S$ with the use of adjustable parameters $µ$. We then perturbatively expand the Green’s function for $S$ by $δ(S−S_δ)$ in powers of $δ$ and truncate at a given order. By assuming that the expanded and truncated Green’s function can be evaluated by specifying $µ$ to optimize the trial action, we evaluate the Green’s function as a sum of expanded and fitted Green’s functions. The first-order OPT agrees with Feynman’s variational theory, which has been used to solve the polaron problem [44]. The second-order OPT gives the correction of it. Thus the OPT can be regarded as the generalization of Feynman’s variational theory. In this paper we apply the OPT to calculate the two-time correlation functions of the Morse potential system in the dissipative environment.

In addition to the simple OPT analysis, we also tested the OPT with the Legendre transformation in the framework of the field theory in order to make the OPT more efficient, even in the lowest order. We use the inversion method in performing the Legendre transformation. The Legendre transformation converts the generating functional $W[J]$, which is the functional of the auxiliary source $J$, to the another functional $Γ[φ]$, where $φ = δW[J]/δJ$. In general cases, $W[J]$ is perturbatively obtained within the finite-order calculation. On the other hand, $Γ[φ]$ is obtained by making a resummation of the diagrams of $W[J]$. The mathematical structure of the converted $Γ[φ]$ is quite different from original $W[J]$. Thus we can approximate $W[J]$ in a different manner by approximating $Γ[φ]$ instead of $W[J]$ itself and by reconverting it to $W[J]$ through the relation between $W[J]$ and $Γ[φ]$. The inversion method is a systematic way to evaluate $W[J]$ through $Γ[φ]$ for a system with some perturbation. Both $Γ[φ]$ and $W[J]$ can be expanded perturbatively. The inversion method gives simple relations between the n-th-order term of $Γ[φ]$ and the first n terms of $W[J]$ by regarding $φ$ as a order of unity. We apply this technique for the $δ$ expansion of the OPT.

In Sec. II we introduce the nonequilibrium generating functional [45]. The two nonperturbative methods, i.e., the OPT and the method of Legendre transformation, are reviewed in Secs. III and IV, respectively. We then apply the OPT and the OPT with the inversion method in Sec. V. The numerical results for these two approaches are shown in Sec. VI. Section VII is devoted to a conclusion and some remarks. A result of the inversion method that is a technique to carry out the Legendre transformation is reviewed in Appendix A. The relation between the results of [8] and a propagator is given in Appendix B. The calculation of the free energy at zero temperature is written in Appendix C.

II. NONEQUILIBRIUM GENERATING FUNCTIONALS

Consider a system described by the Hamiltonian operator $H$. We are interested in calculating the expectation value of $\hat{Ω}^i$ defined by

$$\langle \hat{Ω}^i \rangle = \text{Tr} [\hat{ρ}_t \hat{U}^\dagger(t, t_f) \hat{Ω}^i \hat{U}(t, t_f)]$$

(2.1)

$$\hat{U}(t_1, t_f) = T \exp \left( -\frac{i}{\hbar} \int_{t_1}^{t_f} ds \hat{H}(s) \right)$$

(2.2)

where the symbol $T$ implies the time ordering operation and $\hat{A}^\dagger$ denotes the adjoint of an operator $\hat{A}$. The matrix $\hat{ρ}_t$ is a density operator at the initial time $t_1$. To obtain such an expectation value, it is convenient to introduce a time-dependent external force $J^i(t)$ that couples to $\hat{Ω}^i$. Here and in what follows, the indices $i$ represent the set of indices of the field components. $J^i(t)$ is an auxiliary source to be set to zero at the end of the calculation. The total Hamiltonian therefore depends on time and is expressed as

$$\hat{H}_J(t) = \hat{H} - \sum_i J^i(t) \hat{Ω}^i$$

(2.3)

Let us introduce a generating functional as an extension of the Gibbs free energy. Assuming an equilibrium initial distribution, i.e., $\hat{ρ}_t = \exp(-β\hat{H})$, we introduce the imaginary time $τ$, which is defined as $t = t_f - iτ$. We consider the generating functional $W[J_1, J_2, J_3]$ with three kinds of sources $J^i_1$, $J^i_2$, and $J^i_3$;

$$\exp \left( \frac{i}{\hbar} W[J] \right) = \text{Tr} [\hat{ρ}_t \hat{U}^\dagger_{J_1}(t_f, t_1) \hat{U}_{J_2}(t_f, t_1) \hat{U}_{J_3}(t_f, t_1)]$$

(2.4)

$$\hat{U}_{J_1} = T \exp \left( -\frac{i}{\hbar} \int_{t_1}^{t_f} dt \left( \hat{H} - \sum_i J^i_1(t) \hat{Ω}^i \right) \right)$$

$$= T \exp \left( -\frac{i}{\hbar} \int_{t_1}^{t_f} dt (\hat{H}_{J_1}(t)) \right)$$

(2.5)
For later convenience, we introduce the contour path ordering operator defined by

\[ a \to \exp \left( - \int_0^\beta \tau \frac{\partial}{\partial \tau} \hat{H}_J(\tau) \right) \exp \left( - \int_0^\beta \tau \frac{\partial}{\partial \tau} \hat{H}_J(\tau) \right) \]  

The final time \( t_F \) is taken to be sufficiently large and \( t_I < t_i < t_F \). The symbol \( T_\tau \) stands for \( \tau \) ordering. The real time path and the imaginary one are represented by suffixes \( \alpha = 1,2 \) and \( \alpha = 3 \), respectively. This enables one to study the connection with the equilibrium free energy.

Here we introduce the notion of the complex contour for time integration in order to write various formulas in a compact way [29, 33, 34]. The contour time integral \( \int_C dt \) extends over the contour \( C \), which runs from \( C_1 \) to \( C_2 \) to \( C_3 \) (see Fig. 1). Each path is defined to be \( C_1 : t_i \to t_F \) and \( C_2 : t_F \to t_i \) (return path) and \( C_3 : t_F \to t_i - i \beta \hbar \) (imaginary time path). The contour time ordering operator \( T_C \) orders the time sequence according to the location of the operator on the contour. Furthermore, we use the notation

\[ J(t) = J_\alpha(t) \quad \text{if} \quad t \quad \text{is on} \quad C_\alpha \quad (\alpha = 1,2,3) \]  

Assuming the equilibrium initial distribution, we can then write

\[ \exp \left( \frac{i}{\hbar} W[J_1, J_2, J_3] \right) = \exp \left( \frac{i}{\hbar} W[J] \right) \]

\[ = \text{Tr} T_C \exp \left( - \frac{i}{\hbar} \int_C dt \hat{H}_J(t) \right) \]

\[ \hat{H}_J(t) = \hat{H}_J(t) = \hat{H} - \sum \delta J_\alpha(t) \hat{O}^i \quad (\alpha = 1,2,3) \]  

For later convenience, we introduce the contour \( \delta \) function, the contour \( \theta \) function, and the contour functional differentiation defined by

\[ \int_C dt \delta_C(t-t') f(t) = f(t') \]  

\[ \theta_C(t-t') = \int_C dt^\alpha \delta_C(t^\alpha - t') \]  

\[ \frac{\delta f(t)}{\delta f(t')} = \delta_C(t-t') \]

respectively.

In the path-integral representation, Eq. (2.9) is described by

\[ \exp \left( \frac{i}{\hbar} W[J] \right) = \mathcal{N} \int \mathcal{D}Q \exp \left( \frac{i}{\hbar} \int_C dt \hat{H}(t) \right) \]

\[ \times \left( S_C[Q] + \sum_i \int_C dt J_i(t) \hat{O}(t) \right) \]  

where \( \mathcal{N} \) is the normalization constant and \( S_C \) is the action with the contour path time integration of the Lagrangian \( L \) derived from \( \hat{H} : S_C = \int_C dt L = \int_C dt L + \int_C dt \hat{L} 

+ \int_C dt \hat{L} \).

Using the generating functional, Eq. (2.1) can be expressed as

\[ \langle \hat{O}(t) \rangle = \frac{\delta W[J_1, J_2, J_3]}{\delta J_1(i)} \bigg|_{J_1 = J_2 = J_3 = 0} \]

\[ = - \frac{\delta W[J_1, J_2, J_3]}{\delta J_2(i)} \bigg|_{J_1 = J_2 = J_3 = 0} \]

\[ = \frac{i}{\hbar} \frac{\delta W[J_1, J_2, J_3]}{\delta J_3(t)} \bigg|_{J_1 = J_2 = J_3 = 0} \]  

The functional \( W[J_1, J_2, J_3] \) itself is not a physical quantity. It is introduced just for mathematical convenience to calculate expectation values for nonequilibrium processes. All the physical quantities (as far as they are related to the expectation values that we are probing by introducing the source term) can be extracted from it. For example, the two-time correlation function \( \langle \hat{O}(t) \hat{O}(t') \rangle \) is derived by taking the second derivative of \( W[J_1, J_2, J_3] \) with respect to \( J(t) \). Note that we use three paths [29, 33, 34], an extension of the double path formalism [26, 27, 30] by including the imaginary time path, to take into account the effects of anharmonicity in the initial equilibrium state.

### III. Optimized Perturbation Theory

In this section we briefly explain the OPT for a system with an action \( S \). The OPT employs a modified action defined by

\[ S_\delta = (1 - \delta) S_0(\mu) + \delta S = S_0(\mu) + \delta(S - S_0(\mu)) \]

where \( S_0(\mu) \) is the action for a solvable model and includes the arbitrary (variational) parameters \( \mu \). For \( \delta = 1 \), the modified action agrees with the original one, whereas for \( \delta = 0 \), the solvable one. We are interested in the time evolution of a density matrix with the initial inverse temperature \( \beta = 1/k_B T \).

The generating functional (2.14) for the action is defined by
where \( X(t) \) means that \( X_1(t), X_2(t), \) and \( X_3(t) \) are \((\hbar/i)X(t)\) for \( t \in C_1, \ t \in C_2, \) and \( t \in C_3, \) respectively. The symbol \( \langle \hat{A} \rangle_{\mu, \delta} \) in Eq. (3.3) is regarded as the expectation value of the operator \( \hat{A} \) for the action \( S_{C, \delta} + \Sigma \int d\tau J(t)O(t). \) By treating the term \( \delta(S_C - S_{C_0}) \) as a perturbation, \( W^{(n)}_{\delta}(t_1, \ldots, t_n) \) is expanded in the powers of \( \delta, \)

\[
W^{(n)}_{\delta}(t_1, \ldots, t_n) = \sum_{k=0}^{\infty} \frac{\delta^k W^{(n)}_{\delta k}(t_1, \ldots, t_n)}{k!}.
\]

(3.4)

Differentiation of \( W^{(n)}_{\delta} \) with respect to \( \mu \) gives

\[
\frac{\partial}{\partial \mu} W^{(n)}_{\delta}(t_1, \ldots, t_n) = (1 - \delta) \left( \frac{\partial \delta S_0(\mu)}{\partial \mu} \hat{O}(t_1) \cdots \hat{O}(t_n) \right)_{\delta, \mu}.
\]

(3.5)

where \( \delta S_0(\mu) \) is the action in the operator form. If we set \( \delta \) to unity, then we obtain the following relation for all \( \mu: \)

\[
\frac{\partial}{\partial \mu} W^{(n)}_{\delta=1}(t_1, \ldots, t_n) = \sum_{k=0}^{\infty} \frac{\delta^k W^{(n)}_{\delta=1[k]}(t_1, \ldots, t_n)}{k!} \neq 0.
\]

(3.6)

In practice, the perturbative expansion in powers of \( \delta \) will be truncated at some order. In such a case, \( W^{(n)}_{\delta=1[k]}(t_1, \ldots, t_n) \) can have a residual dependence on the parameter \( \mu: \)

\[
\frac{\partial}{\partial \mu} W^{(n)}_{\delta=1[k]}(t_1, \ldots, t_n) = \sum_{k=0}^{\infty} \frac{\delta^k W^{(n)}_{\delta=1[k]}(t_1, \ldots, t_n)}{k!} \neq 0.
\]

(3.7)

Then we consider different criteria to fix \( \mu. \) One of them is the principle of minimal sensitivity, which is a way of optimizing the theory in which \( W^{(n)}_{\delta[k]} \) is to be evaluated at the point where \( W^{(n)}_{\delta[k]}(\mu) / \partial \mu = 0. \) If there is no value \( \mu \) satisfying this condition, one seeks the point at which \( \partial W^{(n)}_{\delta[k]}(\mu) / \partial \mu \) has the minimal sensitivity to a variation of \( \mu. \) With this procedure \( \mu \) can be regarded as an adjustable parameter to fit the solvable model to the original one.

If one sets \( n = 0, \) Eq. (3.2) becomes

\[
\frac{i}{\hbar} W^{(n)}_{\delta}(J) = \ln \int D\xi \exp \left[ \frac{i}{\hbar} \left( S_{C, \delta}[\xi] \right) \right] + \sum_i \int_C \left[ \delta(t) O(t) \right].
\]

(3.2)

The \( n \)-point Green’s function is then expressed as

\[
W^{(n)}_{\delta}(t_1, \ldots, t_n) = \frac{\delta^k W^{(n)}_{\delta}[J]}{\delta C(t_1) \cdots \delta C(t_n)}
\]

\[
= \left( \frac{i}{\hbar} \right)^{(n-1)} \langle \hat{T}_C \hat{O}(t_1) \cdots \hat{O}(t_n) \rangle_{\delta, \mu}
\]

\[ (n = 0, 1, \ldots) \]

(3.3)

where \( X(t) \) means that \( X_1(t), X_2(t), \) and \( X_3(t) \) are \((\hbar/i)X(t)\) for \( t \in C_1, \ t \in C_2, \) and \( t \in C_3, \) respectively. The symbol \( \langle \hat{A} \rangle_{\mu, \delta} \) in Eq. (3.3) is regarded as the expectation value of the operator \( \hat{A} \) for the action \( S_{C, \delta} + \Sigma \int d\tau J(t)O(t). \) By treating the term \( \delta(S_C - S_{C_0}) \) as a perturbation, \( W^{(n)}_{\delta}(t_1, \ldots, t_n) \) is expanded in the powers of \( \delta, \)

\[
W^{(n)}_{\delta}(t_1, \ldots, t_n) = \sum_{k=0}^{\infty} \frac{\delta^k W^{(n)}_{\delta k}(t_1, \ldots, t_n)}{k!}.
\]

(3.4)

IV. LEGENDRE TRANSFORMATION OF A GENERATING FUNCTIONAL

Let us consider the Legendre transformation defined in the contour time path by

\[
\Gamma[\phi] = \Gamma[\phi_1, \phi_2, \phi_3] = W[J] - \sum_i \int_C \left[ \phi_i J_i(t) \phi_i^*(t) \right],
\]

(4.1)

where

\[
\phi_i^*(t) = \frac{\delta W[J]}{\delta J_i(t)}.
\]

(4.2)

The inverted relation of Eq. (4.2) is therefore

\[
J_i(t) = -\frac{\delta \Gamma[\phi]}{\delta \phi_i^*(t)}.
\]

(4.3)

Substituting \( J_i(t) = 0 \) into Eq. (4.3), we obtain

\[
0 = \frac{\delta \Gamma[\phi]}{\delta \phi_i^*(t)}.
\]

(4.4)

The solution of Eq. (4.4) is written as \( \phi_i^{(0)}(t) \) below. The function \( \phi_i^{(0)}(t) \) is the solution of Eq. (4.4) at \( J_i(t) = 0, \) which corresponds to the solution for the original action \( S_0. \) At the point \( \phi_i(t) = \phi_i^{(0)}, \) it is known that

\[
\frac{i}{\hbar} W[J = 0] = \frac{i}{\hbar} \Gamma[\phi^{(0)} = \phi[J = 0]] = -\beta F.
\]

(4.5)
where \( F \) is the free energy. In the solution of Eq. (4.4), \( \phi^{(0)} \) is not unique and \( W[J=0] \) is a multivalued function. We adapt the notation below, for example,

\[
W^{(2)}_{\alpha_1 \alpha_2}(t_1, t_2) = \frac{\delta^2 W}{\delta J^{(1)}_{\alpha_1}(t_1) \delta J^{(2)}_{\alpha_2}(t_2)}.
\]

(4.6)

For \( J_1 = J_2 = J_3 \), we introduce a special notation defined by the superscript \( J \):

\[
W^{(2)}_{\alpha_1 \alpha_2}(t_1, t_2) = \left[ W^{(2)}_{\alpha_1 \alpha_2}(t_1, t_2) \right]_{J_1(t_1) = J_2(t_2) = J_3(t_3) = J(t)}.
\]

(4.7)

We also use the superscript \( J \) for \( \Gamma \), i.e., \( \Gamma^{(2)}_{\alpha_1 \alpha_2} \), but it implies that it is evaluated at the value of \( \phi(t) \) satisfying Eq. (4.2). The superscript 0 then implies the stationary value of \( \phi(t) \) corresponding to \( J_1 = J_2 = J_3 = 0 \). For example,

\[
\Gamma^{(2)}_{\alpha_1 \alpha_2}(t_1, t_2) = \left[ \Gamma^{(2)}_{\alpha_1 \alpha_2}(t_1, t_2) \right]_{J_1(t_1) = \phi_0(t_1) = \phi_0(t_2) = \phi_0(t), \phi_0(t) = 0},
\]

(4.8)

where we used the notation of Eq. (4.6) for \( \Gamma \). Higher degrees of differentiation of \( W \) or \( \Gamma \) are also expressed in this notation. In such a case, \( F \) is estimated on the smallest minimal point of \( (i \hbar/\beta) [\Gamma^{(0)}[\phi]] \). Several important relations involving \( W[J] \) and \( \Gamma[\phi] \) in the double path formalism are summarized in Appendix B of [45]. The relations in the three-time path can be derived by using the same procedure of [45] and we can get the same equations as in Appendix B of [45] even for the three-time path. The physical quantity calculated through \( W[J] \) is evaluated on the perturbative ground state. In the OPT this ground state is obtained from the trial action \( S_0 \). Therefore, if \( S_0 \) does not have a property found in the original action, the result derived from \( W[J] \) lacks information of this property. For instance, the original action for the Morse potential is asymmetric under the transformation \( Q \rightarrow -Q \); however, the harmonic trial action that we will use in Sec. V is symmetric and the results obtained from this action may not show asymmetric physical properties in the lowest-order OPT. Using the Legendre transformation, however, we can evaluate the physical quantities on \( \phi^{(0)} \), which involves an infinite number of perturbative expansion terms not on the perturbative ground state. Since this procedure corresponds to a resummation of \( W[J] \), we can recover the properties of the original action that are not included in the form \( W[J] \).

The generating functional \( W[J] \) is evaluated by using Eq. (2.4). Physical quantities, for example \( \langle \hat{O} \rangle_J \), can be calculated from \( \Gamma[\phi] \) through \( W[J] \) using the relation between \( \Gamma[\phi] \) and \( W[J] \) (see [45]).

Up to now there are three ways of performing the Legendre transformation to obtain \( \Gamma[\phi] \). The first is the functional method where the auxiliary field is introduced by a Hubbard-Stratonivich transformation [46–48]. The second is the method relying on the resummation of graphs [49,50]. These two methods can be applied only to the limited case in which the operator \( \hat{O} \) is coupled to the source \( J \). The third method is the inversion method [51]. The inversion method consists of perturbative calculations and an inversion of \( \phi = \delta[J] \) to \( J[\phi] \) using the Legendre transformation. This type of manipulation can readily be generalized from the equilibrium case to the nonequilibrium case by introducing contour time integration. The result of the inversion method in the contour time path is presented in Appendix A. After \( \Gamma[\phi] \) is evaluated using the inversion method, \( W^{(n)}[J] \) is obtained from \( \Gamma^{(n)}[\phi] \) through a relation that is given in Appendix B of [45]. In the following we show how one can apply the inversion method to calculate the correlation function of the Morse potential system.

V. APPLICATION TO THE MORSE POTENTIAL SYSTEM

We now apply the OPT to a molecular system with the mass \( M \), the coordinate \( \hat{Q} \), and the momentum \( \hat{P} \) coupled to a heat bath. The system Hamiltonian is given by

\[
\hat{H}_S = \frac{\hat{P}^2}{2M} + U_S(\hat{Q}),
\]

(5.1)

where \( U_S(\hat{Q}) \) is the molecular potential. We assume that the heat bath consists of a set of harmonic oscillators with the coordinate \( \hat{q}_i \) and momenta \( \hat{p}_i \). The interaction between the system and the \( i \)th oscillator is assumed to be linear with a coupling strength \( c_i \). The heat bath Hamiltonian is then given by

\[
\hat{H}_B + \hat{H}_{SB} = \sum_i \left\{ \frac{\hat{p}_i^2}{2m_i} + \frac{m_i \omega_i^2}{2} \left( \hat{q}_i - \frac{c_i \hat{Q}}{m_i \omega_i^2} \right)^2 \right\}.
\]

(5.2)

The summation over \( i \) goes to infinity in order to describe the dissipation on the molecular system. The term \( \sum_i \left( \frac{c_i^2 \hat{Q}^2_i m_i \omega_i^2}{2} \right) \) on the right-hand side is the counterterm that cancels the unphysical divergence from the coupling to the bath degrees of freedom. The total Hamiltonian is then expressed as \( \hat{H} = \hat{H}_S + \hat{H}_B + \hat{H}_{SB} \). We add the source term to the Hamiltonian as

\[
\hat{J} = \hat{H} - \int_c dt J(t) \hat{Q}.
\]

(5.3)

By integrating over the bath coordinate \( q_i \), the generating functional in the path-integral representation \( W[J] \) is given by

\[
\exp \left( \frac{i}{\hbar} W[J] \right) = \int DQ \exp \left\{ \frac{i}{\hbar} \left[ S^{(S+B)}_C[Q] + \int_c dt J(t) Q(t) \right] \right\},
\]

(5.4)

where \( S^{(S+B)}_C[Q] \) is the influence functional

\[
S^{(S+B)}_C[Q] = \int_c dt \left[ \frac{M}{2} \hat{Q}(t)^2 - U_S(Q) - \frac{1}{2} \sum_i \left( \frac{c_i^2}{m_i \omega_i^2} \hat{Q}(t)^2 \right) \right]
\]

\[
+ \frac{1}{2} \int_c dt dt' \hat{Q}(t) Q(t') \sum_i c_i^2 G^{(m_i \omega_i)}_C(t, t')
\]

(5.5)

and \( G^{(m \omega)}_C(t, t') \) is the propagator of the harmonic oscillator system and is given by
where \( m \) is the variational parameter corresponding to the square of the frequency (\( \mu = \Omega^2 \)). By substituting Eq. (5.7) into Eq. (3.8), \( W_{\delta[0]}[J] \) is calculated as

\[
W_{\delta[0]}[J] = \frac{h}{i} \ln \int C \mathcal{D}Q \exp \left( i \frac{h}{\hbar} S_{C0}^{(S+B)}[Q] \right)
\]

\[
= \frac{h}{i} \ln \int C \mathcal{D}Q \exp \left( i \frac{h}{\hbar} S_{C0}^{(S+B)}[Q] \right) + \frac{1}{2} \int_C ds ds' J(s) K_c(s,s') J(s'),
\]

and so forth. Hence \( K_c(s,s') \) is the propagator defined by the differential equation

\[
\int_C dt' \left( \frac{M}{2} \frac{d^2}{dt^2} + M \mu + \sum_i \frac{c_i^2}{m_i \omega_i} \right) \delta_c(t-t') - \sum_i c_i^2 G_{C}^{(m_i,\omega_i)}(t,t') \right) K_c(t',t'') = \delta_c(t-t'').
\]

The Euler-Lagrange equation derived from the action \( S_{C}^{(S+B)}[Q] \) is the generalized Langevin equation

\[
M \frac{d^2 Q(t)}{dt^2} + \frac{dU_c[Q(t)]}{dQ(t)} + M \int_{t_1}^t dt' \gamma(t-t') \frac{dQ(t')}{dt'} = J(t),
\]

where the damping kernel \( \gamma(t-t') \) is given by

\[
\gamma(t-t') = \sum_i \frac{c_i^2}{M m_i \omega_i} \cos \omega_i(t-t')
\]

\[
= \frac{2}{M} \int_0^\infty \frac{d\omega}{\pi} I(\omega) \cos(\omega(t-t'))
\]

and \( I(\omega) \) is the spectral distribution function defined by

\[
I(\omega) = \pi \sum_i \frac{c_i^2}{2 m_i \omega_i} \delta(\omega - \omega_i).
\]

The character of the heat bath is described by \( I(\omega) \). In the following we consider Ohmic dissipation

\[
I(\omega) = M \gamma \omega.
\]

The friction term of Eq. (5.11) is \( M \gamma \dot{Q} \) in this case. That is, the constant \( \gamma \) corresponds to the strength of the damping. If the dissipation is Ohmic, the propagator \( K_c(t,t') \) is derived from Eqs. (5.10), (5.13), and (5.14). The result was given in [8]. We show the relation between \( K_c(t,t') \) and the result of [8] in Appendix B.

The system potential is chosen in the Morse potential form

\[
U(Q) = E_x(e^{-2aQ} - 2e^{-aQ}),
\]

where \( E_x \) and \( a \) are the dissociation energy and the curvature of the potential, respectively. We consider the case in which \( A \) and \( a \) are not small and the anharmonicity plays a major role. The difference between \( S_{C}^{(S+B)} \) and \( S_{C0}^{(S+B)} \) is now given by

\[
S_{C}^{(S+B)}[Q] - S_{C0}^{(S+B)}[Q] = -\int_C dt \{ E_x(e^{-2aQ(t)} - 2e^{-aQ(t)}) - \frac{1}{2} M \mu Q^2(t) \}.
\]

Then Eq. (5.9) reduces to

\[
W_{\delta[1]}[J] = -E_x \int_C ds \left( \exp \left( \frac{\hbar}{i} 2a^2 K_c(s,s) \right) \right.
\]

\[
\times \exp \left( -2a \int_C dt K_c(s,t) J(t) \right)
\]

\[
-2 \exp \left( \frac{\hbar}{i} \frac{1}{2} a^2 K_s(s,s) \right) \times \exp \left( -a \int_C dt K_c(s,t) J(t) \right)
\]

\[
+ \frac{1}{2} M \mu \int_C ds \left( \frac{\hbar}{i} K_c(s,s) \right)
\]

\[
+ \left[ \int_C dt K_c(s,t) J(t) \right]^2.
\]
The system potential (5.15) is not symmetric under the transformation $\mathbf{Q} \rightarrow - \mathbf{Q}$. This transformation can be achieved in Eq. (5.17) by letting $a \rightarrow -a$. It is clear, however, that Eq. (5.17) cannot involve this asymmetric feature since we will set $J=0$. To overcome this difficulty without increasing the order of the $\delta$ expansion (i.e., fixing $n$ in $W_\delta = \sum_{n=0}^\infty W_\delta^{(n)}$), we perform the Legendre transformation from $W_\delta[J]$ to $\Gamma_\delta[\phi]$. We apply the inversion method presented in [51]. In the present case, $\delta$ corresponds to $g$ in Eq. (A1) and the index $i$ in Eq. (A2) to $t$. From the relation (A10), $h_0[\phi;t]$ is

$$h_0[\phi;t] = \int_C ds \, K^{-1}_c(t,s) \phi(s).$$  (5.18)

By substituting Eqs. (5.8), (5.17), and (5.18) into Eqs. (A7) and (A8), the generating functional $\Gamma_\delta[\phi]$ is calculated as

$$\Gamma_\delta[\phi]=\frac{\hbar}{i} \ln \int_C D\mathbf{Q} \exp \left( i \frac{h}{\hbar} S^{(S+\gamma)}_{\delta=0}[\mathbf{Q};\mu] \right)$$

$$- \frac{1}{2} \int_C ds \, ds' \phi(s) K^{-1}_c(s,s') \phi(s').$$  (5.19)

The source $J(t)$ is obtained by differentiating $\Gamma_\delta[\phi]$ with respect to $\phi(t)$,

$$J(t) = - \frac{\delta \Gamma_\delta[\phi]}{\delta \phi_c(t)}$$

$$= \int_C ds \, K^{-1}_c(t,s) \phi(s) + \int_C dt \exp \left( -2a \phi(t) + \frac{h}{i} a^2 K_c(t,t) \right)$$

$$\times \exp \left( -2a \phi(t) + \frac{h}{i} a^2 K_c(0,0) \right) - 2(-a)$$

$$\times \exp \left( -a \phi(t) + \frac{h}{i} a^2 K_c(0,0) \right) - M \mu \phi(t).$$  (5.21)

In the time-independent case, the static solution $\phi^{(0)}$ is obtained as

$$\phi^{(0)}(t) = \frac{3}{2} \frac{h}{i} a + K_c(0,0),$$  (5.22)

where we set $\delta=1$. Inserting Eq. (5.22) into Eqs. (5.19) and (5.20), we obtain

$$\Gamma_\delta[\phi^{(0)}] = \frac{\hbar}{i} \int C D\mathbf{Q} \exp \left( i \frac{h}{\hbar} S^{(S+\gamma)}_{\delta=0}[\mathbf{Q};\mu] \right)$$

$$+ \frac{\hbar}{i} \beta E_c \exp \left( -a^2 \frac{h}{i} K_c(0,0) \right)$$

$$+ \frac{1}{2} M \mu \frac{h}{i} K_c(0,0).$$  (5.23)

Various nonlinear femtosecond experiments have been carried out for the systems described by the present model of the Morse potential system coupled to the bath. The physical observable in optics is the correlation function of the dipole moment $\mu(Q)$, which is expressed as a function of the nuclear coordinate $Q$. Since one can expand $\mu$ as $\mu_0 + \mu_1 Q + \cdots$, what experiments are measuring is actually the correlation function for the nuclear coordinates, such as $C(t) = i(\hbar \mu(Q(t)), \mu(Q(0)) \rangle \sim i(\langle Q(t), Q(0) \rangle)$. The linear absorption spectrum denoted by $\sigma(\omega)$ is the Fourier transform of $C(t)$. From the above results, this is expressed as

$$\sigma_\delta(\omega) = \text{Im} \left[ W^{(2)}_{\delta,R}(\omega) \right],$$  (5.24)

$$W^{(2)}_{\delta,R}(\omega) = \int_{t_1}^{t_2} dt_1 dt_2 e^{i \omega (t_1 - t_2)} W^{(2)}_{\delta,R}(t_1 - t_2).$$  (5.25)

Here $W^{(2)}_{\delta,R}(t,t')$ is retarded Green’s function defined by

$$W^{(2)}_{R}(t,t') = W^{(2)}_{11}(t,t') + W^{(2)}_{12}(t,t')$$

$$= \frac{1}{\hbar} \left\{ \langle \hat{\mathbf{T}}(t') \hat{\mathbf{O}}(t') \rangle_{\text{cont}} - \langle \hat{\mathbf{O}}(t') \hat{\mathbf{T}}(t') \rangle_{\text{cont}} \right\}$$

$$= \frac{i}{\hbar} \theta(t-t') \left\{ \langle \hat{\mathbf{O}}(t), \hat{\mathbf{T}}(t) \rangle \right\}.$$  (5.26)

For the action $S_\delta(\mu)$, we use the notation $W_\delta$, or $\Gamma_\delta$; instead of $W$ or $\Gamma$ of the equations as shown in Appendix B of [45]. From Eqs. (5.8) and (5.17) the second functional differentiation of $W_\delta$ is

$$W^{(2)}_{\delta}[\phi^{(1)}(t_1,t_2)] = [K_{11}(t_1,t_2) - K_{12}(t_1,t_2)] = K_R(t_1,t_2),$$  (5.27)

$$W^{(2)}_{\delta}[\phi^{(1)}(t_1,t_2)] = \int_{t_1}^{t_2} ds \, K_R(t_1,s) K_R(s,t_2)$$

$$\times \left[ - E_c \left( -2a \right)^2$$

$$\times \exp \left( -2a \int_C ds' K_c(s,s') J(s') + 2a^2 \frac{h}{i} K_c(0,0) \right) - 2(-a)^2$$

$$\times \exp \left( -a \int_C ds' K_c(s,s') J(s') \right)$$

$$+ \frac{1}{2} M \mu \frac{h}{i} K_c(0,0) \right] + M \mu.$$.  (5.28)
In the case of Ohmic dissipation, $K_C(0,0)$ is given by

$$
\frac{\hbar}{i} K_C(0,0) = \frac{\hbar}{4M\xi} \left( \coth \frac{i \beta \hbar \lambda}{2} - \coth \frac{i \beta \hbar \lambda_1}{2} \right) - \Gamma_\Omega(0), 
$$

(5.29)

where

$$
\Gamma_\Omega(t) = \frac{1}{M \beta \hbar} \sum_{n=0}^{\infty} \frac{2 \hbar^4 \gamma \omega_n e^{-\omega_n/\hbar}}{(\omega_n^2 + \hbar^2 \Omega^2)^2 - (\hbar \gamma \omega_n)^2} 
$$

$t \in C$, $st = \mu$),

(5.30)

$$\lambda_{1/2} = \frac{1}{2} \gamma \pm i \xi$,  

(5.31)

Setting $J = 0$, the second response function is derived from Eqs. (B1)–(B6) and (5.27)–(5.29) as

$$
W^{(2)}_{\delta,R}(\omega) = \frac{1}{M \mu - i \omega \gamma - \omega^2 + \frac{1}{M^2} \left( \mu - i \omega \gamma - \omega^2 \right)^2} 
$$

$$
\times - E \left( -2a \right)^2 \exp \left( 2a^2 \frac{\hbar}{i} K_C(0,0) \right) 
$$

$$
- 2(-a)^2 \exp \left( 2a^2 \frac{\hbar}{i} K_C(0,0) \right) + M \mu ].
$$

(5.32)

Within the framework of the OPT explained in Sec. III, the absorption spectra $\sigma(\omega)$ is obtained by evaluating this expression at the point $\mu = \mu_0(\omega)$, where the following condition is satisfied:

$$
\left( \frac{\partial}{\partial \mu} \sigma \delta(\omega) \right)_{\delta = 1} = 0.
$$

(5.33)

Then setting $\delta = 1$ and $\mu = \mu_0$ in Eq. (5.32), i.e., $W^{(2)}_{\delta = 1,R}(\omega; \mu = \mu_0)$, and taking its imaginary part, the absorption spectra is given by

$$
\sigma(\omega) = \text{Im} W^{(2)}_{\delta = 1,R}(\omega; \mu = \mu_0).
$$

(5.34)

As mentioned before, this result dose not contain enough of the asymmetric features of the potential. As a result, the absorption calculated from the above formula will not show the correct temperature dependence as it will be seen in Fig. 3(a) in Sec. VI. To improve the result from Eqs. (5.32) and (5.34), we derive the formula using both the OPT and the Legendre transformation. First, we calculate $\Gamma^{(2)}_{\delta,R}(t_1,t_2)$,

$$
\Gamma^{(2)}_{\delta,R}(t_1,t_2) = \sum_{a=1,2} (-1)^a (K^{-1}_C)_{1,a}(t_1,t_2)
$$

$$
= - K^{-1}_R(t_1,t_2),
$$

(5.35)
This result is the renormalized form of the correlation function $W_{d,R}(t_1, t_2)$ obtained through Legendre transformation. For Ohmic dissipation, the Fourier transformation of Eq. \(\sim 5.42\) is expressed as

\[
W_{d,R}^{(2)}(\omega) = \frac{1}{M} \frac{1}{\mu - i \omega \gamma - \omega^2} + \frac{1}{M^2} \left( \frac{\mu - i \omega \gamma - \omega^2}{\mu - i \omega \gamma} \right)^2 
\times \left[ -2E_c \alpha^2 \exp \left( -a^2 \frac{h}{i} K_C(0,0) \right) + M \mu \right].
\]

(5.43)

Then, following the prescription of the conventional OPT [see Eqs. (5.33) and (5.34)], we obtain the absorption spectra.

**VI. NUMERICAL RESULTS**

We now calculate the free energy and the absorption spectra of the Morse potential system numerically using the expression given in the preceding section. We set $M = 66.4527$ mu, $E_e = 3649.5$ cm$^{-1}$, and $\alpha = 0.6361$ Å as the ground state of the Cs$_2$ molecule. We normalized the parameters by the frequency $\omega_0 = \sqrt{\left[ \frac{\partial^2 U(Q)}{\partial Q^2} \right]_{Q=0}/M}$. In the Morse potential system, this frequency is given by

\[
\omega_0 = \left( \frac{2E_c \alpha^2}{M} \right)^{1/2}.
\]

Using $\omega_0$, the physical quantities are normalized as

\[
\bar{F} = \frac{F}{\hbar \omega_0}, \quad \bar{\omega} = \frac{\omega}{\omega_0},
\]

\[
\bar{\gamma} = \frac{\gamma}{\omega_0}, \quad \bar{\mu} = \frac{\mu}{\omega_0}.
\]

(6.3)

In order to see the validity of the present approach, first we calculate the free energy without the heat bath and compare with the exact solution. In this simple case, the functions to be optimized are then obtained by replacing $K_C$ by $G_C$ in Eqs. (5.8), (5.17), (C1), and (5.23). The numerical calculations were carried out by obtaining the minimal point in the sum of Eqs. (5.8) and (5.17) for the first-order optimization, in the sum of Eqs. (5.8), (5.17), and (C1) for the second-order optimization and in Eq. (5.23) for the first-order optimization with the Legendre transformation, respectively. To solve these problems, we use the bisection method to search for the solution of the equation.

Figures 2 and 3 show the temperature dependence of the free energy from the first-order OPT with the Legendre transformation. (a) The first-order OPT with the Legendre transformation is shown as the solid line. The dashed line and the dotted line have the same meanings as in Fig. 2(a). (b) The difference between the first-order OPT with the Legendre transformation and the exact result. The solid line and the dashed line denote $F_{OPT+Legendre} - F_{exact}$ and $F_{OPT+Legendre} - F_{harmonic}$ respectively.

**Fig. 2.** Temperature dependence of the free energy. (a) The first-order OPT is shown as the solid line. The dashed line and the dotted line are the exact results of the Morse potential and the harmonic potential with the fundamental frequency $\omega_0$, respectively. (b) The difference between the first-order OPT and the exact result. The solid line and the dashed line denote $F_{OPT} - F_{exact}$ and $F_{OPT} - F_{harmonic}$ respectively.

**Fig. 3.** Temperature dependence of the free energy from the first-order OPT with the Legendre transformation. (a) The first-order OPT with the Legendre transformation is shown as the solid line. The dashed line and the dotted line have the same meanings as in Fig. 2(a). (b) The difference between the first-order OPT with the Legendre transformation and the exact result. The solid line and the dashed line denote $F_{OPT+Legendre} - F_{exact}$ and $F_{OPT+Legendre} - F_{harmonic}$ respectively.
we have presented the calculation with the Legendre transformation, and, as a reference, the Morse potential with the frequency \( \omega_0 \). As can be seen from Fig. 2(b), the discrepancy between the exact result and the approximated one becomes large for higher temperatures. The result from the OPT with the Legendre transformation in Fig. 3, however, agrees with the exact one for all temperature. The free energy at the zero temperature \( (\beta = 1/k_B T \to \infty) \) is summarized in Table I. In addition to the cases in Table I, we have presented the result calculated from the second-order optimization theory. Note that the ground state energy \( E \) agrees with the free energy at the zero temperature. As can be seen, the result from the first-order OPT is closer to the harmonic one. This is because we chose the harmonic system as the trial action. The results from OPT improve if we include the second-order perturbation. However, even within the framework of the first-order approximation, we can obtain the same accuracy with use of the Legendre transformation. Since the calculation from the second-order OPT is much harder than the one from the first-order OPT with the Legendre transformation, hereinafter we concentrate our analysis on the first-order OPT and the first-order OPT with the Legendre transformation. Note that in the first-order OPT, there is no point where the condition \( \partial W^{(1)}_0 / \partial \mu = 0 \) is satisfied if the temperature is very high. The reason for this is attributed to the dissociation states of the Morse potential. This situation may be improved if we take into account the higher-order derivatives of \( W^{(1)}_0 \). This will be the next step of the present study.

We include the heat bath. The equations to be optimized are then given by Eqs. (5.8), (5.17), and (5.23). The linear absorption spectrum that is the Fourier transformation of the two-time correlation function of the coordinate can be evaluated by searching for the minimal point of Eq. (5.32) or (5.43). Figure 4 shows the linear absorption spectrum for the different temperatures. Figure 4(a) is calculated from the first-order OPT, whereas Fig. 4(b) is calculated from the first-order OPT with the Legendre transformation. In the Morse potential, the energy between adjacent levels \( E_{n+1} - E_n \), where \( E_n \) is the \( n \)th energy level, decreases with increasing quantum number. Therefore, at higher temperatures, the Morse system shows a smaller resonant frequency, as was observed in Ref. [13]. As can be seen in Fig. 4(a), however, the peak shifts to the blue with increasing temperature. This unphysical result is due to the choice of the trial function. As it was pointed out before, the Morse potential is asymmetric for the transformation \( Q \to -Q \). However, the trial action (5.7) is symmetric. On the other hand, if one performs a Legendre transformation, the asymmetry of the potential can be taken into account through the higher-order perturbations and thus the approximation will be improved dramatically without increasing the order of calculation.

Here we should note the case in which the trial action is chosen as the shifted harmonic potential \( \langle M/2 \rangle \mu (Q - \xi)^2 \), where \( \mu \) and \( \xi \) are the variational parameters instead of the harmonic potential \( M/2 \mu Q^2 \) in Eq. (5.7). In the first-order optimized perturbation, the free energy is closer to the exact one than the result from the trial action (5.7). However, the peak of the absorption spectra shifts the same amount as in Fig. 4(a). This indicates that the introduction of another variational parameter does not always improve the resummation of the terms in the ordinary perturbation expansion.

From the quantum Fokker-Plank equation approach [13], it was shown that the width of the peak becomes larger as the temperature increases. However, the present calculation does not show such a change. The overtone peak, which is the tiny peak caused by the anharmonicity of potential located around twice the fundamental frequency \( 2\omega_0 \), was not observed. This is because the first-order calculation gives only the type of self-energy in Fig. 5. Here we remark that the self-energy \( \Sigma \) is defined by the Schwinger-Dyson equation

\[
G_C(t_1, t_2) = K_C(t_1, t_2) + \int_C ds_1 ds_2 K_C(t_1, s_1) \Sigma_C(s_1, s_2) G_C(s_2, t_2),
\]

(6.4)
where we write the equation in the contour time-path form and the $G_c$ is the full propagator. In order to obtain the overtone poles, we have to include the type of self-energy in Fig. 6, which was missing in the present order of the calculation.

**VII. CONCLUSION AND REMARKS**

In this paper we have developed the optimized perturbation theory for a system coupled to a dissipative environment. The first-order OPT is equivalent to Feynman’s variational theory and the higher order OPT can be regarded as its correction. We have calculated the free energy for a Morse potential system and have shown that the result from the first-order OPT is close to the harmonic one. However, the result from the second-order OPT agrees very well with the exact one. We then found that the result from the first-order OPT with Legendre transformation is as good as the one from the second-order OPT. Since calculations from the second-order OPT are much harder, we used the first-order OPT with the Legendre transformation for the rest of the calculation. We then calculate the linear absorption spectrum, which is the Fourier transformation of the two-time correlation function of the coordinate. It was shown that the temperature dependence of the peak shifts from the first-order OPT since the trial action in the first-order OPT has a different symmetry from the original action. We then discovered that the Legendre transformation based on the inversion method corrects such a problem. Although some features, such as the existence of an overtone peak and the change of peak width, are missing in the present calculation, the OPT gives reasonable results.

In this paper we discussed the Morse potential system only. However, our approach can be applied to systems with any shape of potentials. To study the dynamics of an anharmonic system in a dissipative environment, we have so far three approaches: the perturbative diagrammatic approach [35,36], the quantum Fokker-Planck approach [13], and the present OPT approach. Each approach has advantages and disadvantages. For instance, the diagrammatic approach is straightforward. However, it may not be good for a system with strong anharmonicity. The quantum Fokker-Planck approach is a powerful approach for studying the time evolution of a system with an arbitrary potential. Still, it can be applied only for the high-temperature Gaussian white noise or Gaussian-Markovian noise cases. The present approach is complementary to the other approaches and has special advantages in the study of a system with strong anharmonicity at low temperature, where the other approaches fail. Such problems involving tunneling processes in a double well system are left for future studies.

**ACKNOWLEDGMENTS**

This work has been supported by the Grant-in-Aid on Priority Area of ‘‘Chemical Reaction Dynamics in Condensed Phases’’ and the Shimazu Science Foundation.

**APPENDIX A: INVERSION METHOD**

The general procedure of the inversion method is explained in this appendix. Suppose that the Hamiltonian $\hat{H}$ is divided into two parts, the free part and the interaction part

$$\hat{H} = \hat{H}_0 + g\hat{H}_I,$$

(1)

where $g$ is the coupling constant. We add the source term to $\hat{H}$ as

$$\hat{H}_J = \hat{H} - \sum_i J^i \hat{O}^i$$

(2)

to investigate the set of the nonperturbative states. The source term is chosen so as to give a nonzero perturbation series of $\phi' = \langle \hat{O}^i \rangle$, where the term in angular brackets can be the expectation value including the static or the time-dependent one. Notice here that it is not necessary for the source term to have the form $\Sigma_i J^i \hat{O}^i$. Then we can regard our method as an extension of ordinary Legendre transformation formalism. In order to recover to the original Hamiltonian, the source is set to be zero at the end of the calculation.

Let us review the result of the inversion method below. The generating functional $W[J]$ is expanded in the powers of $g$,

$$W[J] = \sum_{n=0}^{\infty} g^n W_{[n]}[J].$$

(3)

The expectation value of $\hat{O}^i$ is obtained by

$$\phi' = \langle \hat{O}^i \rangle = \sum_{n=0}^{\infty} g^n \frac{\partial W_{[n]}[J]}{\partial J^i}.$$  

(4)

By performing the Legendre transformation, the functional $\Gamma[\phi]$ is written in the power series of $g$ as

$$\Gamma[\phi] = W[J] - \sum_i J^i \frac{\partial W_{[n]}[J]}{\partial J^i} = \sum_{n=0}^{\infty} g^n \Gamma_{[n]}[\phi].$$

(5)

According to the identity of the Legendre transformation, we obtain
\[ J' = -\frac{\partial \Gamma[\phi]}{\partial \phi'} = -\sum_{n=0}^{\infty} g^n \frac{\partial \Gamma_{[n]}[\phi]}{\partial \phi'} \]  

Following the procedure of the inversion method, Eqs. (A3)–(A6) lead to

\[ \Gamma_{[0]}[\phi] = W_{[0]}[J = h_0^t] - \sum_t h_0^t \phi', \]

\[ \Gamma_{[1]}[\phi] = W_{[1]}[J = h_0^t], \]

\[ \Gamma_{[2]}[\phi] = W_{[2]}[J = h_0^t] + \frac{1}{2!} \sum_{t,i} W_{[1]}^{ij}[J = h_0^t] \times \frac{\partial^2 \Gamma_{[0]}[\phi]}{\partial \phi' \partial \phi'} W_{[1]}^{ij}[J = h_0^t], \]

and so on. Here \( h_0^t[\phi] \) is defined as

\[ h_0^t[\phi] = (f_0^{-1})[\phi], \]

that is, \( f_0^{ij}[h_0[\phi]] = \phi' \),

\[ h_0^t = -\frac{\delta \Gamma_{[0]}[\phi]}{\delta \phi'}, \quad f_0^i = -\frac{\delta W_{[0]}[J]}{\delta J^i}, \]

and

\[ W_{[1]}^{ij}[J] = \frac{\partial W_{[1]}[J]}{\partial J^i}. \]

The general forms of \( h_n^t \) and \( \Gamma_{[n]} \) are given in [52].

**APPENDIX B: PROPAGATOR WITH A HEAT BATH**

We show the relation between the result of [8] and the propagator \( K_{\zeta}(t,t') \) derived from Eqs. (5.10), (5.13), and (5.14) below:

\[ K_R(t-t') = K_{11}(t,t') - K_{12}(t,t') \]

\[ = K_{21}(t,t') - K_{22}(t,t') \]

\[ = \theta(t-t') \frac{1}{M_k} \exp \left(-\frac{\gamma(t-t')}{2}\right) \sin[\zeta(t-t')] \]

\[ = \int \frac{dz}{2\pi i} \left( -\frac{2}{\hbar} \hat{A}(z) \right) e^{iz(t-t')}, \]

\[ K_A(t-t') = K_{11}(t,t') - K_{21}(t,t') \]

\[ = K_{12}(t,t') - K_{22}(t,t') = K_R(t-t'), \]

\[ K_{13}(t,t') = K_{32}(t,t) = \int_0^\beta d\tau \times \left( -\frac{2}{\hbar} \hat{A}(z) + \frac{2}{\hbar} \hat{A}(-|\omega_n|/\hbar) \right), \]

where \( \omega_n \) is defined by \( \omega_n = 2\pi n/\beta \) and

\[ \zeta = \sqrt{\mu - \gamma^2/4}, \]

\[ \hat{A}(z) = -\frac{\hbar}{2M} \frac{1}{\mu_0 + z^2 + z \gamma}. \]

\[ \hat{S}(z) = \frac{2}{\beta \hbar} \sum_{n=-\infty}^{\infty} \frac{z}{z^2 - (\omega_n/\hbar)^2} \left[ \hat{A}(z) - \hat{A}(-|\omega_n|/\hbar) \right]. \]

The functions \( \hat{A}(z) \) and \( \hat{S}(z) \) are given in [8] under the condition that the quantity \( \omega_n^2 \) in these functions is replaced with \( \mu \) in this paper.

**APPENDIX C: FREE ENERGY AT ZERO TEMPERATURE**

In this appendix we calculate the free energy without a heat bath at zero temperature. The expressions of the zeroth and first orders of the \( \delta \) expansion are given in Sec. V. From Eq. (3.8) the second-order contribution is calculated as
\[
W_{\delta}[J] = \frac{i}{\hbar} \left( \frac{E^2}{2} \int_c ds \int_c ds' \left[ \exp \left( -2a \int_c dt'[K_c(s,t') + K_c(s',t')]J(t') + \frac{h}{i} 2a^2[K_c(s,s) + K_c(s,s')] \right) \right. \right.
\]
\[
\times \left[ \exp \left( \frac{h}{i} 2a^2K_c(s,s') \right) - 1 \right] - 4 \exp \left( -a \int_c dt'[K_c(s,t') + 2K_c(s',t')]J(t') + \frac{h}{i} a^2 \left( \frac{1}{2} K_c(s,s) + 2K_c(s',s') \right) \right) \left. \right).
\]

Substituting \( T = 0 \) into the propagators \( K_c \) of Eqs. (5.8), (5.17), and (C1), the free energy at zero temperature, which is derived from \( F_\delta = -i(\hbar \beta)W_\delta^0 \), is given by
\[
F_\delta = F_{\delta[0]} + F_{\delta[1]} + F_{\delta[2]},
\]
\[F_{\delta[0]} = \frac{1}{2} \hbar \Omega,\]
\[F_{\delta[1]} = E_c \left[ \exp \left( 2a^2 \frac{h}{2 \Omega} \right) - 2 \exp \left( \frac{1}{2} a^2 \frac{h}{2 \Omega} \right) \right] - \frac{1}{4} \hbar \Omega,\]
\[F_{\delta[2]} = \frac{E_c^2}{2h^2} \left( \exp \left( 4a^2 \frac{h}{2 \Omega} \right) L(4a^2) - 4 \exp \left( \frac{5}{2} a^2 \frac{h}{2 \Omega} \right) \right) \times L(2a^2) + 4 \exp \left( a^2 \frac{h}{2 \Omega} \right) L(a^2) \right] \right).
\]
Here we have introduced the function \( L(x) \) defined by
\[
L(x) = \frac{1}{\hbar \Omega} \left[ \left( \frac{\hbar}{2 \Omega} \right)^2 \left( \frac{\hbar}{2 \Omega} \right) \right] \left( \frac{x}{\hbar} \right) - \gamma - \ln \left( \frac{x}{\hbar \Omega} \right).\]
where \( \bar{E}_c(x) \) is the related exponential integral and \( \gamma \) is the Euler constant. After performing the Legendre transformation and using the relation \( F_\delta = -i(\hbar \beta)W_\delta^0 \), we obtain the free energy at zero temperature in the form
\[
F_\delta = F_{\delta[0]} + F_{\delta[1]},
\]
\[= \frac{\hbar \Omega}{2} - E_c \exp \left( -a^2 \frac{h}{2 \Omega} \right) - \frac{1}{2} \Omega^2 \frac{h}{2 \Omega}.
\]

As mentioned in Sec. III, the free energy is calculated from the above equation by obtaining the minimal point \( \mu = \mu_0 \) of Eq. (C2) or (C8). We present the numerical results for \( C_s \) in Table I.


