Quantum Theory of a Two-Dimensional Rotator in a Dissipative Environment: Application to Far-Infrared Spectroscopy

Yoko SUZUKI and Yoshitaka TANIMURA

Institute for Molecular Science Myodaiji, Okazaki 444-8585

(Received January 22, 2001)

Quantum coherence and its destruction by coupling to a dissipative environment play important roles in time-resolved optical response. We study a two-time correlation function of a two-dimensional rotator coupled to a harmonic-oscillator bath. Generating functionals of reduced density matrix elements for the rotator degrees of freedom are calculated by diagonalizing the total Hamiltonian with the use of unitary transformations and then performing path integrals. A closed-form expression of linear absorption spectrum for a dipole rotator, i.e., a Fourier transformation of the dipole two-time correlation function, is derived from the generating functionals characterized by the bath spectral density. Based on the theory, the spectra for a methyl rotation in a toluene are depicted for various damping constants and temperatures. Because of the cyclic boundary condition that is constrained to fit the rotator degree of freedom, the energy states of the rotator in the absence of damping are discrete: the spectra consist of rotational branches, which correspond to change of the angular momentum. Owing to damping, the spectra exhibit a continuous band which is broadened as temperatures increase.

KEYWORDS: two-dimensional rotator, dissipative system, path integral, correlation function

Rotational motion in general plays an important role in many fields such as physics, chemistry, and biology. Optical measurement can reveal information about molecular rotation and optical spectra are obtained from the two-time correlation function of the angle of the rotator \( \theta \) as \([\cos \theta(t), \cos \theta(0)]\).

For free rotators, transitions between their rotational energy levels are observed with spectrographs as a series of closely spaced lines. Such lines are due to the quantization of the rotational degrees of freedom with a cyclic boundary condition and are given by \( E_l = l^2 \hbar^2 / 2\mu \) \((l = 0, \pm 1, \cdots)\), where \( \mu \) is the moment of inertia. This is a purely quantum effect that classical theory cannot explain. In this Letter, we are interested in the effects of a dissipative environment on the dynamics of a quantal rotator. In classical cases, the damped rotator system has been studied in terms of a phenomenological Langevin equation approach with various realistic conditions. In quantal cases, however, one needs a quantum mechanical treatment of the system and dissipative environment. For this purpose, one introduces a model Hamiltonian for the system and an environmental system represented by an ensemble of harmonic oscillators. This problem can be regarded as one of the central issues in statistical physics: similar problems are analytically solved for quantum Brownian motion\(^1\) and for a quantum damped free particle.\(^2\) Here we take the same approach to the two-dimensional rotator and introduce the Hamiltonian,

\[
\hat{H} = \frac{L^2}{2\mu} + \sum_i \left[ \frac{\hat{p}_i^2}{2m_i} + \frac{m_i\omega_i^2}{2} \left( \hat{q}_i - \frac{c_i\theta}{m_i\omega_i^2} \right)^2 \right],
\]

which reduces to the Langevin equation for the rotational motion in the classical limit. Here, \( L \) and \( \theta \) are the angular momentum defined by \( L \equiv (\hbar/\mu)\partial/\partial\theta \) and the angular coordinate, respectively. The bath operators \( \hat{q}_i \) and \( \hat{p}_i \) commute with \( \theta \) and \( L \). Note that the original rotational symmetry of the rotator recovers and the angular coordinate is \(-\pi \leq \theta < \pi \) with \( \theta = -\pi \) and \( \theta = \pi \) identified after tracing out the bath degrees of freedom owing to the properties of the Gaussian integration.

In order to calculate the two-time correlation function, we introduce the generating functional \( Z[J] \) as follows:

\[
Z[J] = \text{Tr} \left( \hat{\rho}_T^{J=0} \hat{U}_J^{\infty}(\infty, t_f) \hat{U}_J(\infty, t_i) \right),
\]

where

\[
\hat{U}_J(\infty, t_f) = T_f \left( e^{-\int_{t_f}^{\infty}d\tau (\hat{H} - J_\alpha(\tau)\theta)} \right)
\]

and

\[
\hat{\rho}_T^{J=0} = T_\tau \left( e^{-\int_{-\hbar}^{0}d\tau (\hat{H} - J_\beta \theta)} \right).
\]

Here, \( \hat{\rho}_T^{J=0} \) gives an equilibrium distribution at the initial time \( t_i \) and \( \tau \) is the imaginary time parameter with \( 0 \leq \tau \leq \beta \hbar \) in which \( \beta \) is the inverse temperature. The symbol \( T_{\tau}(\tau) \) stands for the real (imaginary) time ordering operator. We represent the function in the two real time path by the suffix \( \alpha = 1, 2 \) and the imaginary one by \( \alpha = 3 \).

We consider the optical response of the rigid rotator. The linear absorption spectrum is calculated from the Fourier transformation of the two-time correlation function of the dipole moment. Since the dipole moment is
expressed as \( d \equiv d_0 \cos \theta \), this is written as\(^{3} \)

\[
\sigma(\omega) = \text{Im} \left[ \frac{i}{\hbar} \frac{d^2}{dt^2} \int_0^\infty dt e^{i\omega t} \langle [\cos \theta(t), \cos \theta(0)] \rangle \right].
\] (5)

Note that eq. (5) corresponds to the third-order off-resonant Raman response by the replacement of \( d \) with the polarizability \( \alpha \). The two-time correlation function of \( \cos \theta \) is evaluated from the generating functional as

\[
\langle T_C \cos \theta(t_1) \cos \theta(t_2) \rangle = \sum_{a_1,a_2=\pm 1} \frac{Z[J]}{4Z[J=0]} \bigg|_{J=s=\hbar (a_1 \delta_C(s-t_1)+a_2 \delta_C(s-t_2))}.
\] (6)

Here, the index \( C \) implies the contour path that starts from \( t_1 \) to \( t_2 \) along the real path (\( C_1 \)), returns to \( t_1 \) (\( C_2 \)) and goes to \( t_1 - i\beta \) parallel to the imaginary axis (\( C_3 \)).\(^{4,5} \) The operator \( T_C \) and the function \( \delta_C(t) \) are the time-ordering operator and the \( \delta \)-function on the contour time path, respectively.

In order to evaluate \( Z[J] \), we consider the unitary transformation which was utilized in the study of a free particle coupled to a harmonic-oscillator bath.\(^2 \) We set \( y_i \equiv m \omega_i^2 \hat{q}_i / c_i, p_{pi} \equiv c_i \hat{p}_i / (m \omega_i^2), \mu_i \equiv \hat{c}_i^2 / (m \omega_i^2) \) and \( r_i \equiv \mu_i / \mu ' \) with \( \mu' \equiv \mu + \sum_j \mu_j \). Then the unitary operator is expressed as

\[
\hat{X} = \exp \left( -i \frac{\hbar}{\beta} \sum_i \hat{p}_{pi} \right) \exp \left( i \frac{\hbar}{\beta} \sum_i r_i \hat{L}_i \right).
\] (7)

The model Hamiltonian is transformed as

\[
\hat{H} \equiv \hat{X}^{\dagger} \hat{H} \hat{X} = \hat{H}_S + \hat{H}_B,
\] (8)

where

\[
\hat{H}_S = \frac{1}{2\beta} \hat{L}^2,
\] (9)

and

\[
\hat{H}_B = \frac{1}{2\mu} \left( \sum_i \hat{p}_{pi} \right)^2 + \sum_i \left( \frac{\hat{p}_{pi}^2}{2\mu_i} + \frac{1}{2} \mu \omega_i^2 \hat{y}_i^2 \right).
\] (10)

After the unitary transformation (7), the generating functional is rewritten as

\[
Z[J] = \text{Tr} \left( \hat{\rho}_0^{(1)} \hat{U}_J(\infty, t) \hat{U}_J(\infty, t) \right),
\] (11)

where \( \hat{\rho}_0^{(1)} \) and \( \hat{U}_J(\infty, t) \) are defined by \( \hat{\rho}_0^{(1)} \equiv T_\tau \exp \left( -(i/\hbar) \int_0^\infty dt \hat{H}_J \right) \) and \( \hat{U}_J(\infty, t) \equiv T_t \times \exp \left( -(i/\hbar) \int_\infty^\infty dt \hat{H}_J \right) \), and \( \hat{H}_J \) is the transformed Hamiltonian expressed as \( \hat{H}_J \equiv \hat{H} - J(t)(\theta - \sum_i r_i \hat{y}_i) \) with the aid of \( \hat{X} \equiv e^{i \phi} \hat{X} \). Since the Hamiltonian is divided into the rotator part, \( \hat{H}_S = J(t)\theta \), and the bath coordinate part, \( \hat{H}_B + J(t) \sum_i r_i \hat{y}_i \), the generating functional is factorized as

\[
Z[J] = Z_S[J] Z_B[J],
\] (12)

where \( Z_S[J] \) and \( Z_B[J] \) are defined by eq. (11) for the Hamiltonian \( \hat{H}_S \) and \( \hat{H}_B \), respectively. The calculation of \( Z_B[J] \) is parallel to the Brownian free particle.\(^1 \) It is given by

\[
Z_B[J] = e^{\Xi[J]} e^{-\Upsilon[J]} Z_B[J=0].
\] (13)

Here, \( \Upsilon[J] \) is expressed as

\[
\Upsilon[J] = \frac{i}{2\hbar} \int_0^\infty dt \int_0^\infty dt' J(t) J(t') \left\{ \lim_{\omega \to 0} \left[ \frac{i}{2\mu' \sinh \frac{\omega \hbar}{2}} \times \left( \theta_C(t-t') \cos \omega(t-t' + \frac{i \beta \hbar}{2}) + (t \leftrightarrow t') \right) \right]\right\},
\] (14)

The function \( \theta_C(t) \) in eq. (14) is a step function on the contour time path. To characterize the bath we choose the spectral density defined formally by \( I(\omega) \equiv \pi \sum_i c_i^2 / (2m \omega_i) \delta(\omega - \omega_i) \) as the Ohmic dissipation \( I(\omega) = \mu \omega \gamma \). Here, the constant \( \gamma \) relates to the mass-independent damping kernel, \( \gamma(t) \equiv \int_0^\infty dt' \mu(\omega)/|\mu(\omega)| \), by \( \gamma = 2 \gamma(t) \). In this case, \( \Xi[J] \) is expressed as

\[
\Xi[J] \equiv \Xi^{-+}[J] + \Xi^{--}[J] + \Xi^{-3}[J] + \Xi^{33}[J],
\] (15)

where

\[
\Xi^{-+}[J] = \int_{t_{\tau}}^\infty \int_{t_{\tau}}^\infty dt_1 \int_{t_{\tau}}^\infty dt_2 \left( \frac{1}{\mu \gamma} \right) J_+(t') \left[ \frac{\mu}{\mu \gamma} \right] \left[ \frac{1}{\gamma} \right] \left[ \frac{1}{\mu \gamma} \right] J_-(t'),
\] (16)

\[
\Xi^{--}[J] = -\frac{1}{2\beta \hbar^2} \int_{t_{\tau}}^\infty \int_{t_{\tau}}^\infty dt_1 \int_{t_{\tau}}^\infty dt_2 \left( \frac{2}{\mu \gamma} \right) \left[ \frac{\mu}{\mu \gamma} \right] \left[ \frac{1}{\gamma} \right] \left[ \frac{1}{\mu \gamma} \right] J_-(t'),
\] (17)

\[
\Xi^{-3}[J] = \int_{t_{\tau}}^\infty dt_1 \int_{t_{\tau}}^\infty dt_2 \left( \frac{1}{\mu \gamma} \right) \left[ \frac{\mu}{\mu \gamma} \right] \left[ \frac{1}{\gamma} \right] \left[ \frac{1}{\mu \gamma} \right] J_3(t),
\] (18)

and

\[
\Xi^{33}[J] = \int_{t_{\tau}}^\infty dt_1 \int_{t_{\tau}}^\infty dt_2 \left[ \frac{\mu}{\mu \gamma} \right] \left[ \frac{1}{\gamma} \right] \left[ \frac{1}{\mu \gamma} \right] J_3(t).
\] (19)

Here, \( J_+ \equiv \langle J_1 + J_2 \rangle / 2, J_- \equiv J_1 - J_2 \), and \( \nu_1 \equiv 2\pi l / (\beta \hbar) \). To evaluate the rotator part \( Z_S[J] \), we introduce the...
Here, \{l\} in eq. (20) is a set of eigenstates of \( L \) defined by \( L\l| = \hbar\l| \) for an integer \( l \), and the matrix element of the function \( f(\theta) \) is given by \( \langle \l| f(\theta) |\l' \rangle = \int_\pi^{2\pi} d\theta e^{il\theta} f(\theta) e^{-il'\theta} \). The overlap of the eigenstates is given by \( \langle l|\l' \rangle = \delta_{l,l'} \). We divide the time interval on the contour path \( C \) into \( N+1 \) pieces \( (t_0 = t_1, t_1, \ldots, t_N, \text{ and } t_{N+1} = t_N - i(\beta\hbar) \) and insert the completeness relations (20). The functional \( Z_S[J] \) is then given by

\[
Z_S[J] = \lim_{N \to \infty} \left( \prod_{j=1}^{N+1} \int_{-\pi}^{\pi} d\theta_j \right) \left( \prod_{j=1}^{N+1} \frac{1}{2\pi} \sum_{l_j=-\infty}^{\infty} \right) \times \exp \left\{ \sum_{j=1}^{N+1} \left[ l_j(\theta_j - \theta_{j-1}) - \Delta t_j \left( \frac{\hbar l_j^2}{2 \mu' I} - J(t_j-1)\theta_j \right) \right] \right\}_{\theta_0 = \theta_{N+1}}^{\theta_{N+1} = \theta_0 = \theta_{N+1}},
\]

where \( \Delta t_j = t_j - t_{j-1} \) \((j = 1, \ldots, N + 1) \). The periodic boundary condition \( \theta_0 = \theta_{N+1} \) arises from the "trace" operation involved in defining the generating functional. After integrating over \( \delta_0, \theta_2, \ldots, \) and \( \theta_{N+1} \), we get \( Z_0 = \int_{t_1}^{t_{N+1}} dt J(t)/\hbar \) which allows us to sum up over \( t_1, t_2, \ldots, t_N \). Note that \( \Delta t_j J(t_j-1)/\hbar = \int_{t_j-1}^{t_j} dt J(t)/\hbar \) is 0 or 1 because \( J(t) \) is set as in eq. (6). Rewriting the result with the aid of the relation, \( \sum_{j=1}^{N+1} \exp[i(Ak^2 + Bk)] = \sum_{l} \sqrt{\pi/4A} \exp[-i(B + 2\mu l^2)/(4A)] \), we obtain

\[
Z_S[J] = \frac{1}{\delta(0)} \delta_{0,R_J} e^{\Theta[J]} Z_0 \times \sum_{l} e^{-\frac{\pi l^2}{\beta \hbar}} \left[ -2\pi i \int_{t_1}^{t_N} ds (t_l - i\hbar\hbar s) J(s) + \mu J(2\pi l)^2 \right],
\]

where \( R_J = \int_{t_1}^{t_N} dt J(s)/\hbar \) and \( Z_0 = \int_{-\infty}^{\infty} d\theta \times (\theta \bar{\rho}_I^S dS(\infty,t_1) \bar{\rho}_S(\infty,t_1)) \) in which \( \bar{\rho}_S^S \) and \( \bar{\rho}_S^I \) are defined by \( \bar{\rho}_I^S \equiv T \exp \left[ (-1/\hbar) \int_{t_0}^{t} d\tau H_S \right] \) and \( \bar{\rho}_I^S \equiv T \exp \left[ (-i/\hbar) \int_{t_0}^{t} d\tau H_S \right] \). The condition \( R_J = 0 \) selects transitions induced by radiated pulses, as shown later. From eqs. (12), (13) and (22) we have the generating functional in the form

\[
Z[J] = \frac{1}{\delta(0)} Z_0 \delta_{0,R_J} e^{\Xi[J]} \sum_{l} e^{-\frac{\pi l^2}{\beta \hbar}} \left[ -2\pi i \int_{t_1}^{t_N} ds (t_l - i\hbar\hbar s) J(s) + \mu J(2\pi l)^2 \right].
\]

In consequence of eqs. (6) and (23), we arrive at an expression for a two-body correlation function

\[
\langle [\cos(\theta(t_1), \cos(\theta(t_2))] \rangle
\]

\[
= \frac{\sum_{l} e^{-\frac{\pi l^2}{\beta \hbar}} \cosh \left( 2eI(\beta l - \beta \hbar) / \beta \hbar \right)}{\sum_{l} e^{-\frac{\pi l^2}{\beta \hbar}} \cosh \left( 2eI(\beta l - \beta \hbar) / \beta \hbar \right)} \times \int_{t_1}^{t_2} d\tau \delta_{0}(t_1 - t_2) \sin \left( -\frac{\hbar(1 - e^{-\gamma(t_1 - t_2)})}{2\mu} \right),
\]

where

\[
\delta_{0}(t_1 - t_2) = \frac{1}{\beta} \sum_{l=1}^{\infty} \frac{2\gamma(e^{-\gamma(t_1 - t_2)} - 1)}{\mu \gamma(\gamma^2 - \mu^2)} - \frac{\beta \hbar e^{-\gamma(t_1 - t_2)} - 1}{2\mu \gamma} \cot \frac{\gamma \beta \hbar}{2} - t_1 - t_2 \mu \gamma.
\]
In this Letter, we derived an analytical expression of
the generating functional for a rotator system that is
linearly coupled to a harmonic bath with the use of a
unitary transformation and path integral method. The
generating functional leads to the two-time correlation
function which is related to the response functions of
the dielectric relaxation, the infrared absorption, and
the Raman scattering process spectrum. To demonstrate our
result, we employed the parameter from the rotational
motion of a methyl group and plotted absorption spectra
for different temperatures and damping constants. In the
absence of damping, the spectrum consists of the discrete
lines corresponding to the rotational branches. On the
other hand, a broad band peak appeared for the damped
case due to the continuous energy band induced by the
Ohmic dissipation.

In this study we assumed continuous Ohmic distri-
bution for the spectral distribution of the heat bath.
If we employ the discrete spectra distribution, such as
$I(\omega) \propto \delta(\omega - \omega_B)$, then an absorption spectrum is no
longer continuous and consists of the discrete energy
levels. The effects of spectral distribution of the bath
upon the absorption spectra and the detailed derivation
of the present results will be presented in a separate pa-
der. Generalization of the present study to the three-
and four-time correlation functions aiming at the two-
dimensional Raman and infrared spectroscopy
is under investigation.

In this study, we limited our analysis to the free rota-
tor case. In many realistic problems, however, the rota-
tors are confined by a potential. For instance, internal
rotation of a molecule has rotational barriers which are
expressed by a periodic potential $\sum_n V_n \{1 - \cos(n\theta)\}/2$, where $V_n$ is a parameter of the barrier height. For small
barriers, we can take into account such effects perturba-
tively by expanding the source terms of the generating
functional. For large barriers where the perturbative the-
ory breaks down, we can employ a variety of variational
approaches, such as the optimized perturbation method
using the generating functional. We will leave them
for future studies.

The present investigations were supported by a Grant-
in-Aid on the Priority Area of Chemical Reaction Dy-
namics in Condensed Phases (10206210), a Grant-in-Aid
for Scientific Research (B)(12440171), and the Shimazu
Science Foundation.

3) S. Mukamel: Principle of Nonlinear Optical Spectroscopy
(1992) 3559.
5) R. Fukuda, M. Komachiya, Y. Yokojima, Y. Suzuki, K. Oku-
mura and T. Inagaki: Novel Use of Legendre Transformation
in Field Theory and Many Particle Systems—On-shell Ex-