JOURNAL OF CHEMICAL PHYSICS VOLUME 115, NUMBER 12 22 SEPTEMBER 2001

Linear and nonlinear response functions of the Morse oscillator: Classical divergence and the uncertainty principle

Jianlan Wu and Jianshu Cao[a)]
Department of Chemistry, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139

(Received 8 May 2001; accepted 14 June 2001)

The algebraic structure of the quantum Morse oscillator is explored to formulate the coherent state, the phase-space representations of the annihilation and creation operators, and their classical limits. The formulation allows us to calculate the linear and nonlinear quantum response functions for microcanonical Morse systems and to demonstrate the linear divergence in the corresponding classical response function. On the basis of the uncertainty principle, the classical divergence is removed by phase-space averaging around the microcanonical energy surface. For the Morse oscillator, the classical response function averaged over quantized phase space agrees exactly with the quantum response function for a given eigenstate. Thus, phase-space averaging and quantization provide a useful way to establish the classical-quantum correspondence of anharmonic systems. © *2001 American Institute of Physics.* [DOI: 10.1063/1.1389840]

I. INTRODUCTION

Linear and nonlinear spectroscopy measurements can be formulated generally as the response of the polarization to the incident electric fields.[1,2] The response function is well-defined in terms of quantum transitions in eigenstate space and is often expressed as a summation of oscillations or damped oscillations. The classical limit of the quantum response function is usually obtained by replacing commutation relations with Poisson brackets and neglecting terms in higher order of the Planck constant. However, the classical response function thus defined diverges for a given initial condition in phase space. As pointed out by van Kampen, even a weak perturbation leads to the failure of the classical nonequilibrium perturbation theory at sufficiently long times; therefore, the divergence poses a fundamental limitation to classical response theory.[3] This argument does not lead to practical difficulties in applying linear response theory because the phase-space averaging over the Boltzmann distribution cancels the divergence at long times. The same line of reasoning also applies to the nonlinear response function associated with multidimensional spectroscopy.[4–7] However, different from linear response, the classical nonlinear response function involves the stability matrix, which characterizes the chaotic behavior of classical dynamics. Based on this observation, Mukamel and co-workers have suggested that the nonlinear response function can be a sensitive probe of classical chaos and that femtosecond pulse sequences can be designed to measure the stability matrix.[8] Although the Boltzmann averaging leads to finite response functions for thermal equilibrium systems, the classical divergence remains a conceptual challenge. Since physical systems are intrinsically quantum mechanical, we speculate that the classical divergence can be removed by a careful construction of the classical-quantum correspondence. Further, since Bohr's semiclassical quantization is exact for the Morse oscillator, the classical and quantum response functions should be the same for the leading order of the Planck constant.

We will address these questions with a detailed study of the Morse oscillator. The simple analytical solution for the harmonic oscillator often provides the basis for understanding solid-state structures, molecular vibrations, and dissipative Gaussian bath dynamics. These concepts become inconvenient for describing large-amplitude anharmonic lattice dynamics, high overtone vibration, intramolecular energy distribution, and structure transitions, because the anharmonicity effect is so dominant that it has to be included in the zeroth order representation. For these processes, the eigensolution of the Morse oscillator serves as a better starting point. In fact, the harmonic oscillator and the Morse oscillator represent two limiting cases of a unified algebraic description of molecular vibrations. Generally known as vibron models, the algebraic method employs Lie algebraic techniques, widely used in particle and nuclear physics.[9] The unitary group in two dimensions, $U(2)$, simultaneously describes the harmonic oscillator as the subalgebra $U(1)$ of $U(2)$ and the Morse oscillator as the subalgebra $O(2)$ of $U(2)$. Consequently, similar to the harmonic oscillator, quantum mechanics of Morse systems can be formulated with the annihilation and creation operators but with a different commutation relation (cf. Appendix A). As reviewed by Iachello and Levine,[9] much progress has been made in calculating eigenspectra of Morse systems with the algebraic method. The focus of our study is the dynamic response of the Morse oscillator to the external field and the classical-quantum correspondence of its nonlinear dynamics.

The clarification of the classical-quantum correspondence of anharmonic dynamics has several interesting implications. For example, Field and his co-workers have developed an effective Hamiltonian for the bending spectrum of acetylene at high excitation energy from high-resolution

---

[a)] Electronic mail: jianshu@mit.edu

spectroscopy. They found that classical motions associated with the bending dynamics exhibit a transition from normal modes to local modes as the excitation energy increases.[10,11] Similar transitions have been explored in the broader context of intramolecular vibrational relaxation, isomerization, and energy localization by Heller *et al.*[12–19] A question in these studies is the manifestation of classical chaos in quantum dynamics and possible spectroscopic measurements.[20,21] Wilkie and Brumer recently developed a quantum-classical correspondence via Liouville dynamics for both integrable and chaotic systems.[22,23] Recent progress in two-dimensional spectroscopy has stimulated calculations of the response function of anharmonic systems. Okumura and Tanimura have developed a Feynman diagram expansion for calculating the nonlinear response function of anharmonic modes.[24] Since the perturbation theory uses a harmonic basis set, the anharmonic frequencies and couplings are evaluated approximately through the renormalization of infinite expansion terms. Due to the difficulty of exact quantum calculations, it is useful to develop classical or semiclassical methods and to examine the nature of the classical approximation for the response function.[25] Other relevant topics include the correspondence between the anharmonicity of a molecular system and the phase coherence of optical excitation,[26–31] and the relaxation process of a vibrational excited molecule coupled to a thermal bath.[32–38] As a special case of integrable systems, our study of the Morse oscillator does not address all these issues, but will shed light on the classical-quantum correspondence of the nonlinear dynamics of anharmonic systems.

II. CLASSICAL AND QUANTUM MORSE OSCILLATOR

The derivation of the algebraic solution for the Morse oscillator follows the review by Levine and Iachello.[9] The eigenstructure of the Morse oscillator can be constructed from the two-dimensional harmonic oscillator, described by $U(2)$ algebraic operators, which satisfy the following commutation relationships:[9,39–43]

$$[\hat{v},b]=-b, \quad [\hat{v},b^+]=b^+, \quad [b,b^+]=1-\frac{2\hat{v}}{N}. \tag{1}$$

The Hamiltonian of the Morse oscillator can be expressed as

$$\begin{aligned}\hat{H}&=-\frac{\hbar^2}{2\mu}\frac{d^2}{dq^2}+D(1-e^{-\beta q})^2\\ &=\frac{\hbar\omega_0 N}{2(N+1)}(b^+b+bb^+)+\frac{\hbar\omega_0}{4(N+1)},\end{aligned} \tag{2}$$

where μ is the mass of the Morse oscillator, D is the dissociation energy, β is the anharmonic parameter, $\omega_0=\sqrt{2D\beta^2/\mu}$, and $N=\sqrt{8D\mu/\hbar^2\beta^2}-1$. The Morse Hamiltonian is diagonal in the $|[N],v\rangle$ basis, and the corresponding eigenenergy E_v is

$$E_v=\hbar\omega_0\left[(v+1/2)-\frac{(v+1/2)^2}{N+1}\right], \tag{3}$$

where $v=0,1,...,[N/2]$. As shown in Appendix A, the operators b and b^+ can be expressed explicitly in phase space as

$$\begin{aligned}b+b^+=&\frac{\cos 2\theta}{\sqrt{N}}\left[\hat{N}+1-(N+1)e^{-\beta q}+\frac{4}{(N+1)\beta^2}e^{\beta q/2}\right.\\ &\left.\times\frac{\partial}{\partial q}e^{\beta q/2}\frac{\partial}{\partial q}\right]-i\frac{\sin 2\theta e^{\beta q}}{\sqrt{N}(N+1)}\left(\frac{2}{\beta}\frac{\partial}{\partial q}+1\right)(\hat{N}-2\hat{v}),\end{aligned} \tag{4}$$

where θ is the angle in the polar coordinate representation.

In classical mechanics, the action-angle variables I and ϕ are used to describe the one-dimensional Morse oscillator.[44] Here, the action is defined as $2\pi I=\oint p\,dq$, which differs from the standard notation by a factor of 2π. The action-angle variables are related to the coordinate-momentum variables via the transformation[20]

$$\begin{aligned}q&=\beta^{-1}\ln\left[\frac{1-(1-\lambda^2)^{1/2}\cos\phi}{\lambda^2}\right],\\ p&=\frac{\mu\omega_0}{\beta}\left[\frac{(1-\lambda^2)^{1/2}\sin\phi}{1-(1-\lambda^2)^{1/2}\cos\phi}\right],\end{aligned} \tag{5}$$

where $\lambda=1-I/I_b$ and $I_b=\sqrt{2\mu D/\beta^2}=(N+1)\hbar/2$. The classical Hamiltonian becomes

$$H=\frac{p^2}{2\mu}+D(1-e^{-\beta q})^2=D(1-\lambda^2)=\frac{\omega_0}{2}\left(2I-\frac{I^2}{I_b}\right), \tag{6}$$

where the action I is a conserved quantity for one-dimensional anharmonic systems. The time evolution of the angular variable $\phi(t)$ follows[44]

$$\frac{d\phi(t)}{dt}=\frac{\partial E}{\partial I}=\omega_0\lambda, \tag{7}$$

which yields $\phi(t)=\phi(0)+\omega_0\lambda t$. It is further shown in Appendix A that the classical correspondence of $b+b^+$ is

$$\begin{aligned}b+b^+&\leftrightarrow\frac{N+1}{\sqrt{N}}\left[1-e^{-\beta q}-\frac{4e^{\beta q}p^2}{\beta^2(N+1)^2}\right]\\ &=\frac{N+1}{\sqrt{N}}[-(1-\lambda^2)^{1/2}\cos\phi],\end{aligned} \tag{8}$$

which provides a bridge between the classical and quantum response functions.

III. CLASSICAL AND QUANTUM RESPONSE FUNCTIONS

A generalized quantum response function can be written as[2,8]

$$\begin{aligned}&R_Q^{(2n+1)}(t_n,\ldots,t_0)\\ &\quad=\left(\frac{i}{\hbar}\right)^n\langle[\alpha(t_n),[\alpha(t_{n-1}),\ldots,[\alpha(t_1),\alpha(t_0)]\ldots]]\rangle,\end{aligned} \tag{9}$$

where $\alpha(t)$ is the time-dependent polarization operator. The correspondence between the quantum commutator and the classical Poisson bracket

$$\frac{1}{i\hbar}[A,B]\leftrightarrow\{A,B\},\tag{10}$$

allows us to write the generalized classical response function as

$$R_C^{(2n+1)}(t_n,\ldots,t_0) = (-1)^n\langle\{\alpha(t_n),\{\alpha(t_{n-1}),\ldots,\{\alpha(t_1),\alpha(t_0)\}\ldots\}\}\rangle.\tag{11}$$

In this paper, we focus on the two lowest order response functions $R^{(3)}(t)$ and $R^{(5)}(t_1,t_2)$

$$R_Q^{(3)}(t)=\frac{i}{\hbar}\langle[\alpha(t),\alpha(0)]\rangle,\tag{12a}$$

$$R_C^{(3)}(t)=-\langle\{\alpha(t),\alpha(0)\}\rangle,\tag{12b}$$

and

$$R_Q^{(5)}(t_1,t_2)=-\frac{1}{\hbar^2}\langle[\alpha(t_1+t_2),[\alpha(t_1),\alpha(0)]]\rangle,\tag{13a}$$

$$R_C^{(5)}(t_1,t_2)=\langle\{\alpha(t_1+t_2),\{\alpha(t_1),\alpha(0)\}\}\rangle.\tag{13b}$$

These formulas, especially the classical formulas, are not easy to use in numerical calculations and are simplified in Appendix C. Since the Hamiltonian H depends on the action I, the third-order response function reduces to

$$\begin{aligned}R_C^{(3)}(t)&=-\mathrm{Tr}\left[\alpha(t)\dot{\alpha}(0)\frac{\partial\rho(I)}{\partial H}\right]\\&=-\frac{1}{2\pi}\oint dI\,d\phi\,\alpha(t)\dot{\alpha}(0)\frac{\partial I}{\partial E}\frac{\partial\rho(I)}{\partial I},\end{aligned}\tag{14}$$

where $\rho(I)$ is the normalized distribution function of the action I. Two functional forms of $\rho(I)$ are examined in this paper. The first one corresponds to the microcanonical distribution, $\rho(I)=\delta(I-I_0)$, where I_0 is the action of a given energy. With this distribution, $R_C^{(3)}(t)$ is simplified to

$$R_C^{(3)}(t)=-\frac{1}{2\pi I_b}\partial_\lambda\left[\oint d\phi\,\alpha(t)\frac{\partial\alpha(0)}{\partial\phi}\right]\Bigg|_{I=I_0},\tag{15}$$

where $\lambda=1-I/I_b$. The second one is a distribution with a width Δ around I_0

$$\overline{\rho}(I)=\begin{cases}1/\Delta, & \text{if } I_0-\Delta/2<I<I_0+\Delta/2\\0, & \text{otherwise}\end{cases}.\tag{16}$$

Substituting Eq. (16) into Eq. (14), we obtain

$$\overline{R}_C^{(3)}(t)=\frac{1}{2\pi\Delta}\left[\oint d\phi\,\alpha(t)\frac{\partial\alpha(0)}{\partial\phi}\Bigg|_{I=I_0+\Delta/2}-\oint d\phi\,\alpha(t)\frac{\partial\alpha(0)}{\partial\phi}\Bigg|_{I=I_0-\Delta/2}\right].\tag{17}$$

As shown in Appendix C, the nonlinear response function $R^{(5)}(t_1,t_2)$ can be simplified in two ways. In this paper, we adopt the first formula

$$R_C^{(5)}(t_1,t_2)=\frac{1}{2\pi}\oint dI\,d\phi\{\alpha(t_2),\alpha(t_1)\}\dot{\alpha}(0)\frac{\partial I}{\partial E}\frac{\partial\rho}{\partial I},\tag{18}$$

so that the response function corresponding to $\rho(I)=\delta(I-I_0)$ is

$$R_C^{(5)}(\tau_1,\tau_2)=\frac{1}{2\pi I_b}\partial_\lambda\left[\oint d\phi\{\alpha(t_2),\alpha(t_1)\}\frac{\partial\alpha(0)}{\partial\phi}\right]\Bigg|_{I=I_0},\tag{19}$$

where $\tau_1=t_1$ and $\tau_2=t_2-t_1$, and the response function corresponding to $\overline{\rho}(I)$ is

$$\overline{R}_C^{(5)}(\tau_1,\tau_2)=-\frac{1}{2\pi\Delta}\left[\oint d\phi\{\alpha(t_2),\alpha(t_1)\}\frac{\partial\alpha(0)}{\partial\phi}\Bigg|_{I=I_0+\Delta/2}-\oint d\phi\{\alpha(t_2),\alpha(t_1)\}\frac{\partial\alpha(0)}{\partial\phi}\Bigg|_{I=I_0-\Delta/2}\right].\tag{20}$$

IV. THIRD-ORDER RESPONSE FUNCTION

With the introduction of the quantum and classical Morse oscillators, we now explicitly calculate the response functions and examine their relationships. Although the polarization operator α is usually the function of the coordinate q, the operator solution for the Morse oscillator suggests that the simplest form of α is a function of the lowering and raising operators. Therefore, our first choice is the linear polarization operator

$$\alpha(t)=\frac{\sqrt{N}}{N+1}[b(t)+b^+(t)],\tag{21}$$

whose classical correspondence is

$$\alpha(I,\phi)=-(1-\lambda^2)^{1/2}\cos\phi.\tag{22}$$

This choice of α is not directly motivated by physical systems but serves the purpose of demonstrating the classical-quantum correspondence as $b+b^+$ corresponds to a single quantum transition. For a specific eigenstate $|[N],v\rangle$, we have $\rho=|v\rangle\langle v|$, so that the quantum response function is

$$\begin{aligned}R_Q^{(3)}(t)&=\frac{i}{\hbar}\langle[\alpha(t),\alpha(0)]\rangle\\&=\frac{i}{\hbar}\langle v|[\alpha(t),\alpha(0)]|v\rangle\\&=\frac{2}{(N+1)\hbar}\left\{(v+1)\left(1-\frac{v+1}{N+1}\right)\right.\\&\quad\times\sin\left[\left(1-\frac{2(v+1)}{N+1}\right)\omega_0t\right]-v\left(1-\frac{v}{N+1}\right)\\&\quad\left.\times\sin\left[\left(1-\frac{2v}{N+1}\right)\omega_0t\right]\right\},\end{aligned}\tag{23}$$

where Eq. (B4) is used.

We calculate the classical response function $R_C^{(3)}(t)$ under the same condition. The action I_v for the eigenstate $|[N],v\rangle$ is $I_v=(v+1/2)\hbar$. Substituting Eq. (22) and $I_0=I_v$ into Eq. (15), we have

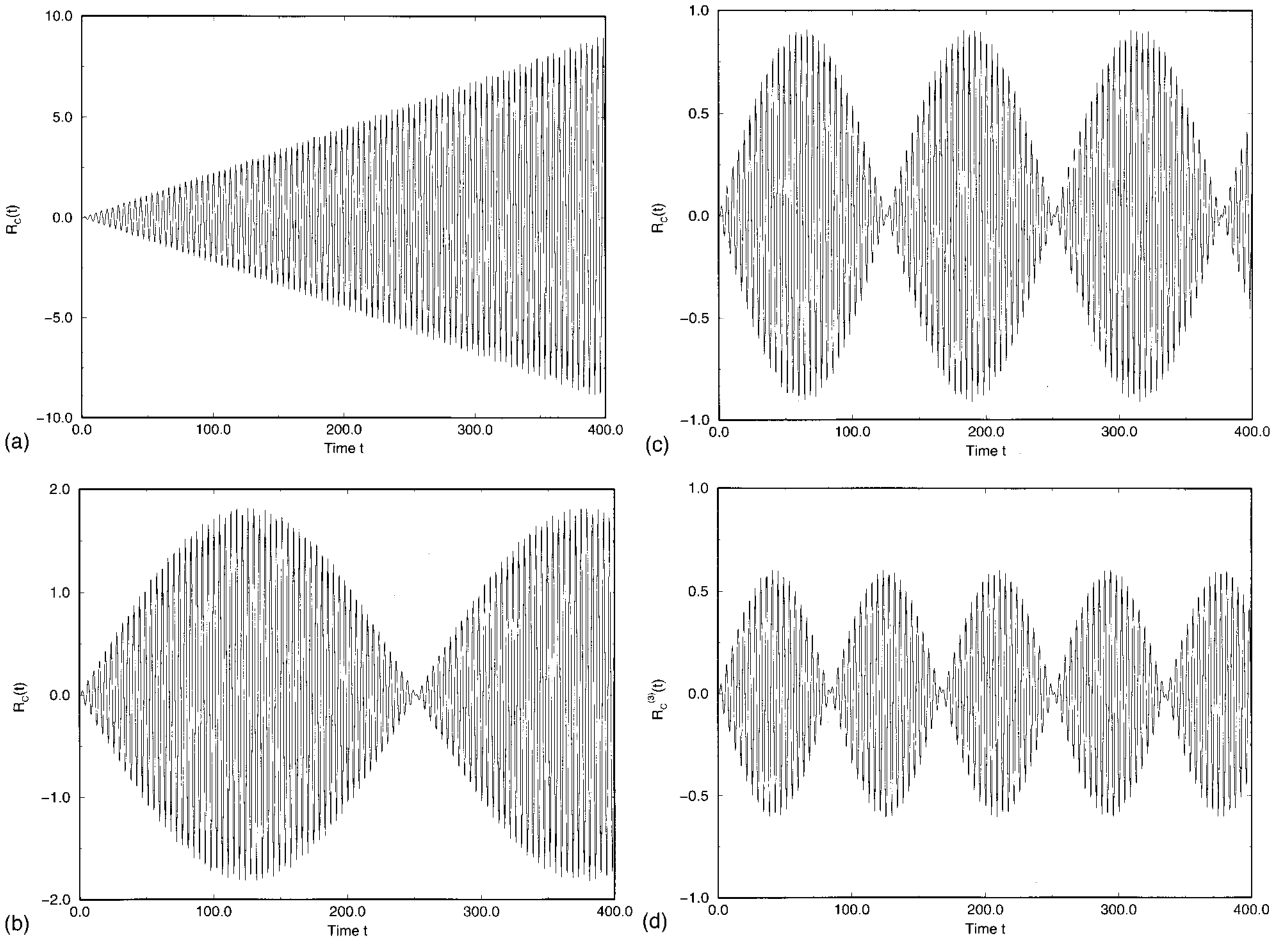

FIG. 1. The third-order classical response function of the Morse oscillator [$\omega_0=5.0$, $N=199$, $v=70$, and the linear polarization $\alpha=-(1-\lambda^2)^{1/2}\cos\phi$]: (a) with the microcanonical condition; (b) with the uncertainty width $\Delta=0.5\hbar$; (c) with the uncertainty width $\Delta=\hbar$; (d) with the uncertainty width $\Delta=1.5\hbar$.

$$R_C^{(3)}(t)=-\frac{1}{2I_b}\partial_\lambda[(1-\lambda^2)\sin\omega_0\lambda t]|_{\lambda=\lambda_v}$$
$$=\frac{1}{2I_b}[2\lambda_v\sin\omega_0\lambda_v t-(1-\lambda_v^2)\omega_0 t\cos\omega_0\lambda_v t], \tag{24}$$

where $\lambda_v=1-I_v/I_b$. As predicted by van Kampan and Mukamel, the amplitude of the linear response function increases linearly with time t and diverges when t approaches to infinity.[3,8] Therefore, under the microcanonical condition, the classical response function differs dramatically from the quantum response function, and classical simulations for microcanonical systems become unstable at long times.

On the other hand, one can argue from the uncertainty principle that it is unphysical to measure the energy and the response of a system at the same time. Thus, instead of the microcanonical distribution function, we consider a distribution with an uncertain width Δ in the phase space around the action I_v, i.e., $\rho(I)\rightarrow\overline{\rho(I)}$. Substituting Eq. (22) into Eq. (17), the modified response function $\overline{R_C^{(3)}}(t)$ becomes

$$\overline{R}_C^{(3)}(t)=\frac{1}{2\Delta}[(1-\lambda_1^2)\sin\omega_0\lambda_1 t-(1-\lambda_2^2)\sin\omega_0\lambda_2 t], \tag{25}$$

where $\lambda_1=1-(I_v+\Delta/2)/I_b$ and $\lambda_2=1-(I_v-\Delta/2)/I_b$. The behavior of the modified classical response function depends strongly on the width Δ. As shown in Fig. 1, the response function $\overline{R}_C^{(3)}(\Delta,t)$ converges faster as Δ increases, and recovers the exact quantum result when Δ equals $\hbar$. With the linear polarization operator, the contribution to the response function is the transition between $|[N],v\rangle$ and $|[N],v-1\rangle$ and the transition between $|[N],v\rangle$ and $|[N],v+1\rangle$. Since the linear response involves either the upper transition or the lower transition, classical dynamics can reproduce this effect by setting $\Delta=\hbar$. In fact, with $\Delta=\hbar$, Eq. (25) becomes

$$\overline{R}_C^{(3)}(t)=\frac{1}{I_b}\left\{(v+1)\left(1-\frac{v+1}{N+1}\right)\sin\left[\left(1-\frac{2v+2}{N+1}\right)\omega_0 t\right]-v\left(1-\frac{v}{N+1}\right)\sin\left[\left(1-\frac{2v}{N+1}\right)\omega_0 t\right]\right\}, \tag{26}$$

which is exactly the same as the quantum result in Eq. (23). The concept of configurational averaging has been invoked in several classical or semiclassical approximations of quantum dynamics, including wave-packet dynamics, nonadiabatic dynamics, and centroid dynamics.[45–50] Surprisingly, the phase-space averaging employed here reproduces the exact quantum dynamics of an anharmonic system.

Next, we examine the quadratic polarization operator

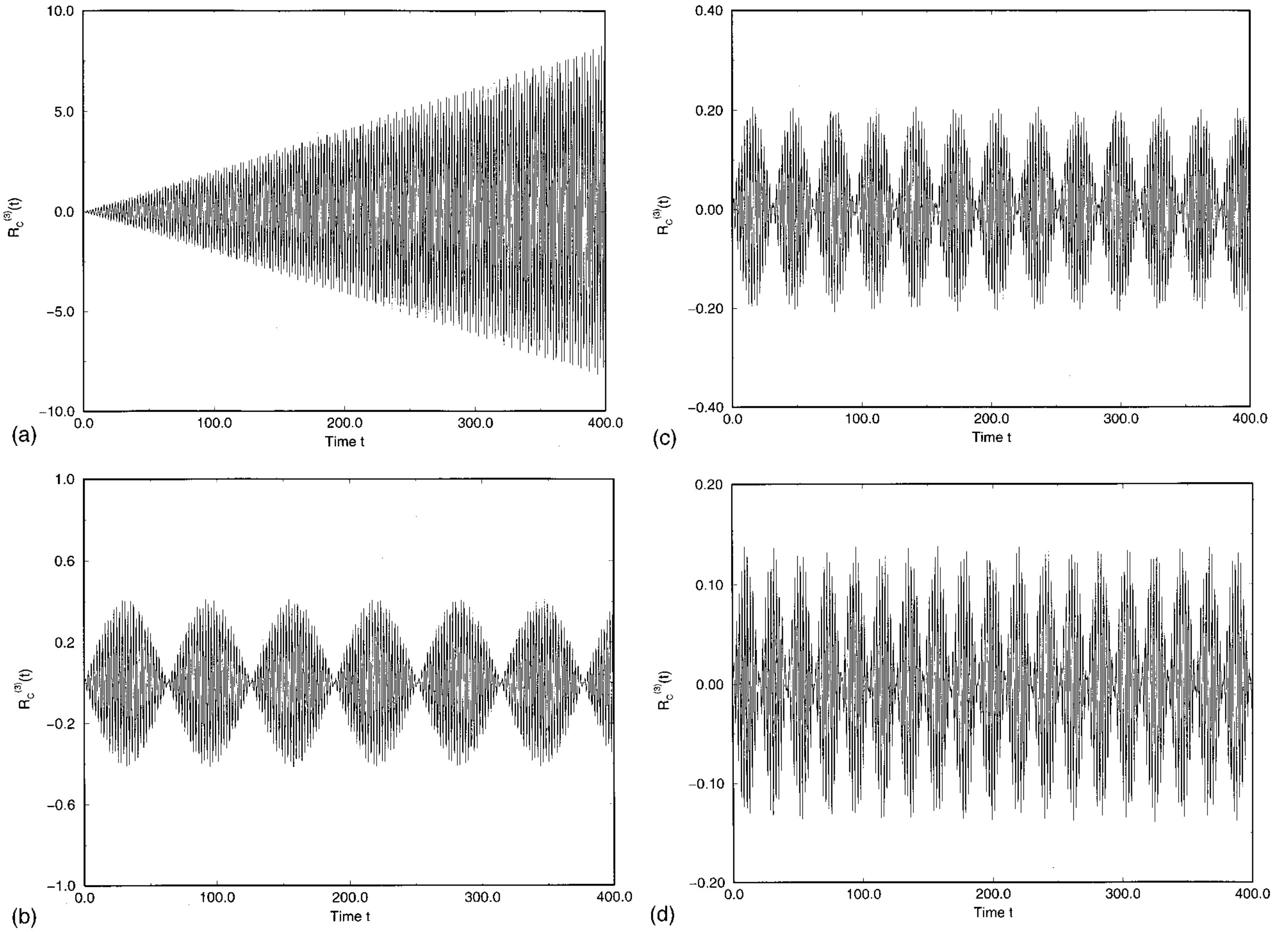

FIG. 2. The third-order classical response function of the Morse oscillator [$\omega_0=5.0$, $N=199$, $v=70$, and the quadratic polarization $\alpha=(1-\lambda^2)\cos^2\phi$]: (a) with the microcanonical condition; (b) with the uncertainty width $\Delta=\hbar$; (c) with the uncertainty width $\Delta=2\hbar$; (d) with the uncertainty width $\Delta=3\hbar$.

$$\alpha(t)=\left(\frac{\sqrt{N}}{N+1}\right)^2[b(t)+b^+(t)]^2, \tag{27}$$

with the classical correspondence

$$\alpha(I,\phi)=[-(1-\lambda^2)^{1/2}\cos\phi]^2. \tag{28}$$

The quantum response function $R_Q^{(3)}(t)$ is

$$\begin{aligned}R_Q^{(3)}(t)=\frac{2}{(N+1)^2\hbar}\bigg\{&(v+1)(v+2)\left(1-\frac{v+1}{N+1}\right)\\&\times\left(1-\frac{v+2}{N+1}\right)\sin\left[2\omega_0\left(1-\frac{2v+3}{N+1}\right)t\right]\\&-v(v-1)\left(1-\frac{v}{N+1}\right)\left(1-\frac{v-1}{N+1}\right)\\&\times\sin\left[2\omega_0\left(1-\frac{2v-1}{N+1}\right)t\right]\bigg\}.\end{aligned} \tag{29}$$

The classical response function $R_C^{(3)}(t)$ under the same condition is

$$\begin{aligned}R_C^{(3)}(t)&=-\frac{1}{4I_b}\partial_\lambda[(1-\lambda^2)^2\sin 2\omega_0\lambda t]|_{\lambda=\lambda_v}bf\\&=\frac{1}{2I_b}[2\lambda_v(1-\lambda_v^2)\sin 2\omega_0\lambda_v t\\&\quad-(1-\lambda_v^2)^2\omega_0 t\cos 2\omega_0\lambda_v t],\end{aligned} \tag{30}$$

which diverges at long times. It is then necessary to introduce the uncertainty width Δ into the phase-space integration. However, for the quadratic polarization function, the contribution to the response function is the transition between $|[N],v\rangle$ and $|[N],v-2\rangle$ and the transition between $|[N],v\rangle$ and $|[N],v+2\rangle$. Comparing with the linear polarization operator, we increase Δ to $2\hbar$ in Eq. (30), so that the modified classical response function becomes

$$\begin{aligned}\overline{R}_C^{(3)}(t)=\frac{2}{(N+1)^2\hbar}\bigg\{&\left(v+\frac{3}{2}\right)^2\left(1-\frac{v+3/2}{N+1}\right)^2\\&\times\sin\left[2\omega_0\left(1-\frac{2v+3}{N+1}\right)t\right]\\&-\left(v-\frac{1}{2}\right)^2\left(1-\frac{v-1/2}{N+1}\right)^2\\&\times\sin\left[2\omega_0\left(1-\frac{2v-1}{N+1}\right)t\right]\bigg\},\end{aligned} \tag{31}$$

which has exactly the same time dependence as the quantum result in Eq. (29). Figure 2 shows the classical response function with difference widths and the convergence to the quantum result at $\hbar=2.0$.

The slight disagreement in the prefactors arises from the intrinsic difference between quantum and classical dynamics. The quantum transition from $|[N],v\rangle$ to $|[N],v+2\rangle$ consists

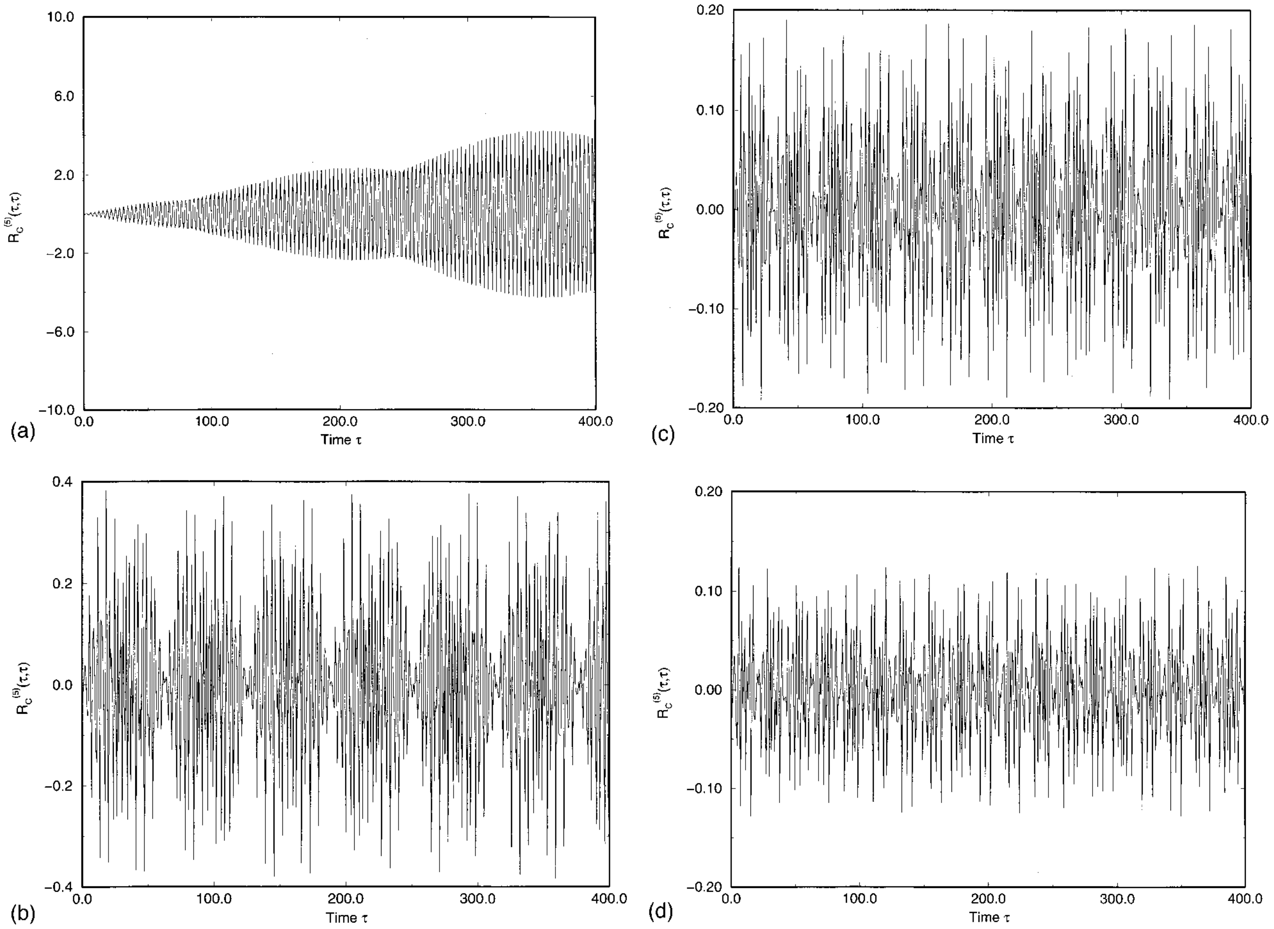

FIG. 3. The diagonal element of the fifth-order classical response function of the Morse oscillator $[\omega_0=5.0,\ N=199,\ v=70$ and the quadratic polarization $\alpha=(1-\lambda^2)\cos^2\phi]$: (a) with the microcanonical condition; (b) with the uncertainty width $\Delta=\hbar$; (c) with the uncertainty width $\Delta=2\hbar$; (d) with the uncertainty width $\Delta=3\hbar$.

of two steps $(v\rightarrow v+1\rightarrow v+2)$, whereas classical dynamics corresponds to the average of these transitions. Hence, the classical correspondence of these two steps is the average result, $(v+1/2\rightarrow v+3/2)^2$. Comparing these two results, $(v+1)$ and $(v+2)$ in the first term of Eq. (29) correspond to $(v+3/2)$ in the first term of Eq. (31). For the same reason, (v) and $(v-1)$ in Eq. (29) correspond to $(v-1/2)$ in Eq. (31). The difference is negligible in the large v limit, where the classical-quantum correspondence becomes more accurate. So, in the dissociation limit, Eq. (29) and Eq. (31) become exactly the same. On the other hand, for $v=0$ and $v=1$, the second part of the classical modified result has to be removed, since the lower quantum transition is prohibited by the lower bound at the ground state.

V. FIFTH-ORDER RESPONSE FUNCTION

The fifth-order response function $R^{(5)}(\tau_1,\tau_2)$ contains more detailed dynamical information that cannot be obtained from the third-order response function. Since $R^{(5)}(\tau_1,\tau_2)$ vanishes for the linear polarization operator, it is necessary to use the quadratic polarization operator to calculate $R^{(5)}(\tau_1,\tau_2)$. For a specific eigenstate $|[N],v\rangle$, substituting Eq. (27) and Eq. (B4) into Eq. (13b), we have

$$\begin{aligned}R^{(5)}(\tau_1,\tau_2)=&-\frac{N^3}{(N+1)^6\hbar^2}\langle v|[[(b(t_2)+b^+(t_2))^2,(b(t_1)+b^+(t_1))^2],(b+b^+)^2]|v\rangle\\ =&-\frac{16}{(N+1)^3\hbar^2}\Bigg\{(v+1)(v+2)\left(1-\frac{v+1}{N+1}\right)\left(1-\frac{v+2}{N+1}\right)\left(1-\frac{2v+3}{N+1}\right)\sin\left[\omega_0\left(1-\frac{2v+3}{N+1}\right)\tau_2\right]\\ &\times\sin\left[\omega_0\left(1-\frac{2v+3}{N+1}\right)(2\tau_1+\tau_2)\right]-v(v-1)\left(1-\frac{v}{N+1}\right)\left(1-\frac{v-1}{N+1}\right)\left(1-\frac{2v-1}{N+1}\right)\\ &\times\sin\left[\omega_0\left(1-\frac{2v-1}{N+1}\right)\tau_2\right]\sin\left[\omega_0\left(1-\frac{2v-1}{N+1}\right)(2\tau_1+\tau_2)\right]\Bigg\}.\end{aligned}\tag{32}$$

The fifth-order classical response function under the microcanonical condition is given in Eq. (19), which requires the explicit calculation of $\{\alpha(t_2),\alpha(t_1)\}$. With the Poisson bracket expressed in the action-angle variables and the polarization given as $\alpha=(1-\lambda^2)\cos^2\phi$, we have

$$\begin{aligned}\{\alpha(t),\alpha(0)\}&=-\frac{1}{I_b}\left[\frac{\partial\alpha(t)}{\partial\lambda}\frac{\partial\alpha(0)}{\partial\phi}-\frac{\partial\alpha(t)}{\partial\phi}\frac{\partial\alpha(0)}{\partial\lambda}\right]\\ &=\frac{1}{I_b}[\lambda(1-\lambda^2)(\sin 2\phi(t)-\sin 2\phi(0))\\ &\quad+\lambda(1-\lambda^2)\sin 2\omega_0\lambda t\\ &\quad-(1-\lambda^2)^2\omega_0 t\sin 2\phi(t)\sin 2\phi(0)],\end{aligned}\tag{33}$$

which can be easily generalized to $\{\alpha(t_2),\alpha(t_1)\}$. Substituting Eq. (33) into Eq. (19), $R_C^{(5)}(\tau_1,\tau_2)$ is given as

$$\begin{aligned}R_C^{(5)}(\tau_1,\tau_2)=\frac{1}{I_b^2}&[(1-\lambda^2)(1-5\lambda^2)\sin\omega_0\lambda\tau_2\\ &\times\sin\omega_0\lambda(2\tau_1+\tau_2)+\omega_0\lambda\tau_2(1-\lambda^2)^2\\ &\times\sin 2\omega_0\lambda(\tau_1+\tau_2)+2\omega_0\lambda\tau_1(1-\lambda^2)^2\\ &\times\sin\omega_0\lambda\tau_2\cos\omega_0\lambda(2\tau_1+\tau_2)],\end{aligned}\tag{34}$$

which diverges along both the τ_1 and τ_2 axis. Again, we use $\overline{\rho}(I)$ instead of $\rho(I)$ to remove the classical divergence, and choose $2\hbar$ as the uncertainty width Δ following the argument for the quadratic polarization operator. Then, from Eq. (20), we have the modified fifth-order response function

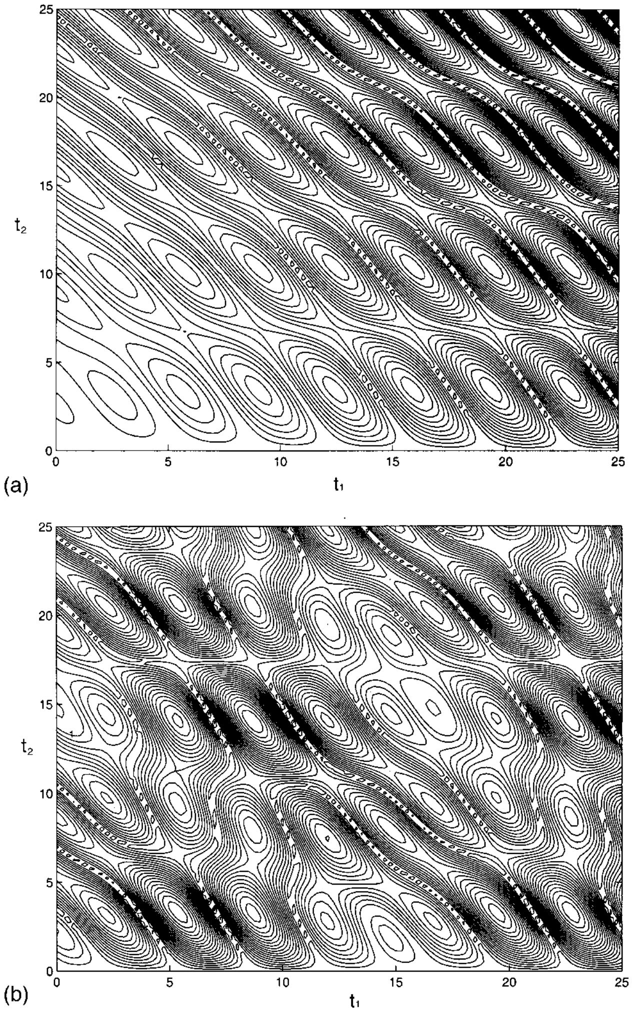

FIG. 4. Two-dimensional contour of the fifth-order classical response function of the Morse oscillator [$\omega_0=5.0$, $N=19$, $v=5$ and the quadratic polarization $\alpha=(1-\lambda^2)\cos^2\phi$]: (a) with the microcanonical condition; (b) with the uncertainty width $\Delta=2\hbar$.

$$\begin{aligned}\overline{R}_C^{(5)}(\tau_1,\tau_2)=-\frac{16}{(N+1)^3\hbar^2}\Bigg\{&\left(v+\frac{3}{2}\right)^2\left(1-\frac{v+3/2}{N+1}\right)^2\left(1-\frac{2v+3}{N+1}\right)\sin\left[\omega_0\left(1-\frac{2v+3}{N+1}\right)\tau_2\right]\sin\left[\omega_0\left(1-\frac{2v+3}{N+1}\right)(2\tau_1+\tau_2)\right]\\ &-\left(v-\frac{1}{2}\right)^2\left(1-\frac{v-1/2}{N+1}\right)^2\left(1-\frac{2v-1}{N+1}\right)\sin\left[\omega_0\left(1-\frac{2v-1}{N+1}\right)\tau_2\right]\sin\left[\omega_0\left(1-\frac{2v-1}{N+1}\right)(2\tau_1+\tau_2)\right]\Bigg\},\end{aligned}\tag{35}$$

which reproduces the similar time dependence as the quantum response function. Comparing Eq. (32) and Eq. (35), the slight discrepancy is the same as that appeared in the third-order response function for the quadratic polarizability. Therefore, from the discussion in Sec. IV, $(v+1)$ and $(v+2)$ in Eq. (32) correspond to $(v+3/2)$ in Eq. (35), and (v) and $(v-1)$ in Eq. (32) correspond to $(v-1/2)$ in Eq. (35). Figure 3 plots the diagonal value of the response function and demonstrates the convergence with the increasing uncertainly width. Figure 4 compares the two-dimensional contours of the response functions with the microcanonical condition and with the uncertainly width $\Delta=2\hbar$. Evidently, the response function with the microcanonical condition increases with time along both axes, whereas the response function averaged over the uncertainty width $\Delta=2\hbar$ shows an echo along the diagonal cross section.

VI. CONCLUSION

To summarize, the unique algebraic structure of the quantum Morse oscillator allows us to define the creation and annihilation operators, their explicit phase-space expressions, and the Morse coherence state. These relations are then used to calculate and compare the linear and nonlinear response functions for microcanonical Morse oscillators. The divergence in the classical response function can be removed by taking a phase-space average resulting from the uncertainly principle. Further, the nearly exact classical-quantum correspondence can be established by quantizing the phase-space averaging: $\hbar$ for the linear polarizability operator and $2\hbar$ for the quadratic polarizability operator. It is reasonable to speculate that the approach applies to a polarization operator with any combination of the annihilation and creation operators. For future studies, we will explore nonintegrable systems, including coupled anharmonic oscillators and dissipative anharmonic oscillators. For these systems, it remains a challenge to formulate their linear and nonlinear response functions and to establish their classical-quantum correspondence. These studies are useful in the context of the current effort in developing two-dimensional optical spectroscopy.

ACKNOWLEDGMENTS

This work is supported by the Solomon Buchsbaum AT&T Research Fund Award, the Petroleum Research Fund administrated by the American Chemical Society, and the National Science Foundation (No. Che-0093210). The authors thank Professor Bob Field for introducing the interesting topic of anharmonic molecular dynamics.

APPENDIX A: ALGEBRAIC SOLUTION AND PHASE-SPACE REPRESENTATIONS

In this Appendix, we use the algebraic method to construct the quantum mechanics of the one-dimensional Morse oscillator and derive an explicit expression connecting the algebra operators and their phase-space representation. Our derivation and notation follow the extensive work of Levine, Iachello, Frank, and others.[9,39,41,42] To describe the two-dimensional harmonic oscillator, we introduce two pairs of boson creation and annihilation operators (τ,τ^+) and (σ,σ^+), which satisfy the following relations:

$$[a_i,a_j]=0,\ [a_i^+,a_j^+]=0,\ [a_i,a_j^+]=\delta_{ij}, \tag{A1}$$

where $a_i=\tau,\sigma$. These operators are represented by the differential operators acting on two coordinates x and y,

$$\begin{aligned}\tau&=\frac{1}{\sqrt{2}}\left(x+\frac{\partial}{\partial x}\right),\quad \tau^+=\frac{1}{\sqrt{2}}\left(x-\frac{\partial}{\partial x}\right),\\ \sigma&=\frac{1}{\sqrt{2}}\left(y+\frac{\partial}{\partial y}\right),\quad \sigma^+=\frac{1}{\sqrt{2}}\left(y-\frac{\partial}{\partial y}\right).\end{aligned} \tag{A2}$$

The operators for a $U(2)$ group can be constructed as

$$\begin{aligned}J_x&=\tfrac{1}{2}(\sigma^+\sigma-\tau^+\tau),\quad J_y=\tfrac{1}{2}(\tau^+\sigma+\sigma^+\tau),\\ J_z&=\frac{i}{2}(\tau^+\sigma-\sigma^+\tau),\quad \hat{N}=(\tau^+\tau+\sigma^+\sigma),\end{aligned} \tag{A3}$$

which are also the angular momentum operators with the invariant operator $J=\hat{N}/2$.

Replacing the coordinates x and y by the polar coordinates r and θ,

$$x=r\cos\theta,\quad y=r\sin\theta,\quad 0<r<\infty,\quad -\pi<\theta<\pi, \tag{A4}$$

the phase-space expressions of the operators $\hat{N}$, J_z, J_x, and J_y are

$$\hat{N}=\frac{1}{2}\left[r^2-\frac{1}{r}\frac{\partial}{\partial r}\left(r\frac{\partial}{\partial r}\right)-\frac{1}{r^2}\frac{\partial^2}{\partial\theta^2}\right]-1, \tag{A5}$$

$$J_z=\frac{i}{2}\frac{\partial}{\partial\theta}, \tag{A6}$$

$$\begin{aligned}J_x=&\frac{\cos 2\theta}{4}\left(-r^2+\frac{\partial^2}{\partial r^2}-\frac{1}{r}\frac{\partial}{\partial r}-\frac{1}{r^2}\frac{\partial^2}{\partial\theta^2}\right)\\ &-\frac{\sin 2\theta}{2}\left(\frac{1}{r}\frac{\partial^2}{\partial r\partial\theta}-\frac{1}{r^2}\frac{\partial}{\partial\theta}\right),\end{aligned} \tag{A7}$$

$$\begin{aligned}J_y=&-\frac{\sin 2\theta}{4}\left(-r^2+\frac{\partial^2}{\partial r^2}-\frac{1}{r}\frac{\partial}{\partial r}-\frac{1}{r^2}\frac{\partial^2}{\partial\theta^2}\right)\\ &-\frac{\cos 2\theta}{2}\left(\frac{1}{r}\frac{\partial^2}{\partial r\partial\theta}-\frac{1}{r^2}\frac{\partial}{\partial\theta}\right).\end{aligned} \tag{A8}$$

Next, the operators $\hat{N}$ and J_z are diagonal in the eigenstate $|N,m\rangle$,

$$\hat{N}|N,m\rangle=N|N,m\rangle,\quad J_z|N,m\rangle=m|N,m\rangle, \tag{A9}$$

where $\hat{N}$ denotes the operator and N denotes the eigenvalue. To solve the eigenequations, $|N,m\rangle$ is factorized into the radial part and the angular part, $|N,m\rangle=R_{N,m}(r)e^{-2im\theta}$, where the radial part $R_{N,m}(r)$ satisfies

$$\frac{1}{2}\left[r^2-\frac{1}{r}\frac{\partial}{\partial r}\left(r\frac{\partial}{\partial r}\right)-\frac{1}{r^2}\frac{\partial^2}{\partial\theta^2}\right]R_{N,m}(r)=(N+1)R_{N,m}(r). \tag{A10}$$

With $r^2=(N+1)e^{-\beta q}$, the radial part is rewritten as

$$\begin{aligned}&\left[-\frac{\hbar^2}{2\mu}\frac{d^2}{dq^2}+\frac{\hbar^2\beta^2}{8\mu}(N+1)^2(e^{-2\beta q}-e^{-\beta q})\right]R_{N,m}(r)\\ &\quad=-\frac{\hbar^2\beta^2}{2\mu}m^2R_{N,m}(r),\end{aligned} \tag{A11}$$

which is exactly the Schrödinger equation of the one-dimensional Morse oscillator. Consequently, $R_{N,m}(r)$ is the eigenstate of the one-dimensional Morse oscillator, the dissociation energy of the Morse oscillator D, is related to N by $N+1=\sqrt{8\mu D/\hbar^2\beta^2}$, and the mth eigenenergy of the one-dimensional Morse oscillator in Eq. (2) is

$$E_m=\frac{\hbar^2\beta^2}{8\mu}(N+1)^2-\frac{\hbar^2\beta^2}{2\mu}m^2. \tag{A12}$$

With $\theta=0$, the eigenstate $|N,m\rangle$ of the two-dimensional harmonic oscillator is reduced to $R_{N,m}(r)$, which is the eigenstate of the one-dimensional Morse oscillator. Therefore, the one-dimensional Morse oscillator can be regarded as the one-dimensional projection of the two-dimensional harmonic oscillator.

To further explore the algebraic method, J_x and J_y are combined to define the raising and lowering operators

$$J_+=J_x+iJ_y,\quad J_-=J_x-iJ_y, \tag{A13}$$

which satisfy

$$J_+|N,m\rangle=\sqrt{J(J+1)-m(m+1)}|N,m+1\rangle,$$
$$J_-|N,m\rangle=\sqrt{J(J+1)-m(m-1)}|N,m-1\rangle, \tag{A14}$$

with $J=N/2$. We now introduce three new operators,

$$b=\frac{J_+}{\sqrt{N}},\quad b^+=\frac{J_-}{\sqrt{N}},\quad \hat{v}=\frac{\hat{N}}{2}-J_z, \tag{A15}$$

which act on the eigenstate $|N,m\rangle$ as

$$b|N,m\rangle=\frac{J_+}{\sqrt{N}}|N,m+1\rangle=\sqrt{v\left(1-\frac{v-1}{N}\right)}|N,v-1\rangle, \tag{A16}$$

$$b^+|N,m-1\rangle=\frac{J_-}{\sqrt{N}}|N,m\rangle=\sqrt{(v+1)\left(1-\frac{v}{N}\right)}|N,v+1\rangle, \tag{A17}$$

$$\hat{v}|N,m\rangle=\left(\frac{\hat{N}}{2}-J_z\right)|N,m\rangle=v|N,v\rangle, \tag{A18}$$

with $v=N/2-m$. These relations are similar to those for the one-dimensional harmonic oscillator. The eigenenergy E_v corresponding to the eigenstate $|N,v\rangle$ is rewritten as

$$E_v=\hbar\omega_0\left[\left(v+\frac{1}{2}\right)-\frac{(v+1/2)^2}{N+1}\right], \tag{A19}$$

so that the Hamiltonian becomes

$$H=\frac{N\hbar\omega_0}{2(N+1)}(bb^++b^+b)+\frac{\hbar\omega_0}{4(N+1)}. \tag{A20}$$

Furthermore, we use Eq. (A8) to derive the differential formulas of operators b and b^+,

$$b=\frac{e^{-2i\theta}}{2\sqrt{N}}\left[\hat{N}+1-r^2+\frac{\partial^2}{\partial r^2}-2\left(\frac{1}{r}\frac{\partial}{\partial r}-\frac{1}{r^2}\right)J_z\right], \tag{A21}$$

$$b^+=\frac{e^{2i\theta}}{2\sqrt{N}}\left[\hat{N}+1-r^2+\frac{\partial^2}{\partial r^2}+2\left(\frac{1}{r}\frac{\partial}{\partial r}-\frac{1}{r^2}\right)J_z\right], \tag{A22}$$

so that

$$b+b^+=\frac{\cos 2\theta}{\sqrt{N}}\left(\hat{N}+1-r^2+\frac{\partial^2}{\partial r^2}\right)+i\frac{2\sin 2\theta}{\sqrt{N}}\left(\frac{1}{r}\frac{\partial}{\partial r}-\frac{1}{r^2}\right)J_z. \tag{A23}$$

However, we cannot set $\theta=0$ in Eq. (A23) before applying operators on the wave function, because these operators do not commute with each other. The right way to use the operators is first to apply them on the two-dimensional system and then set $\theta=0$.

Finally, we derive the classical correspondence of $b+b^+$ by rewriting Eq. (A23) as

$$b+b^+=\frac{\cos 2\theta}{\sqrt{N}}\left[\hat{N}+1-(N+1)e^{-\beta q}+\frac{4}{(N+1)\beta^2}e^{\beta q/2}\frac{\partial}{\partial q}e^{\beta q/2}\frac{\partial}{\partial q}\right]-i\frac{\sin 2\theta e^{\beta q}}{\sqrt{N}(N+1)}\left(\frac{2}{\beta}\frac{\partial}{\partial q}+1\right)(\hat{N}-2\hat{v}). \tag{A24}$$

Since in classical mechanics all variables commute, we set $\theta=0$ so that the imaginary part in Eq. (A24) is removed. Then, replacing the operators by the corresponding variables and using the classical-quantum correspondence

$$\frac{\hbar}{i}\frac{\partial}{\partial q}\leftrightarrow p, \tag{A25}$$

we obtain the classical correspondence of $b+b^+$ as

$$b+b^+\leftrightarrow\frac{N+1}{\sqrt{N}}\left(1-e^{-\beta q}-\frac{e^{\beta q}p^2}{\beta^2 I_b^2}\right)$$
$$=\frac{N+1}{\sqrt{N}}[-(1-\lambda^2)^{1/2}\cos\phi]. \tag{A26}$$

Thus, we have derived the explicit expressions for b and b^+ and established their classical correspondence.

APPENDIX B: COHERENT STATE OF THE MORSE OSCILLATOR

The fact that the harmonic oscillator and the Morse oscillator are two exactly solvable cases of the $U(2)$ algebra suggests that a formal solution for a driven Morse oscillator can be formulated in a similar fashion as the coherent state for a driven harmonic oscillator.[51] In this Appendix, we derive the time evolution of b and b^+ and construct the coherent state of the Morse oscillator. The time-dependent operators, defined in the Heisenberg picture,

$$b(t)=e^{iH_0t/\hbar}be^{-iH_0t/\hbar},\quad b^+(t)=e^{iH_0t/\hbar}b^+e^{-iH_0t/\hbar}, \tag{B1}$$

obey the equations of motion,

$$\frac{db(t)}{dt}=\frac{1}{i\hbar}[b(t),H],\quad \frac{db^+(t)}{dt}=\frac{1}{i\hbar}[b^+(t),H]. \tag{B2}$$

Using the commutation relations, Eq. (B2) is rewritten as

$$\frac{db(t)}{dt}=-i\omega_0 b(t)+i\frac{2\omega_0}{N+1}b(t)\hat{v},$$
$$\frac{db^+(t)}{dt}=i\omega_0 b^+(t)-i\frac{2\omega_0}{N+1}\hat{v}b^+(t), \tag{B3}$$

which can be solved explicitly to give

$$b(t)=e^{-i\omega_0 t}be^{i[2\omega_0/(N+1)]\hat{v}t},$$
$$b^+(t)=e^{i\omega_0 t}e^{-i[2\omega_0/(N+1)]\hat{v}t}b^+. \tag{B4}$$

Next, we calculate the quantum mechanics of the Morse oscillator driven by an external electric field. A simple and effective approximation of the interaction is

$$V(t) = -[b(t)f(t) + b^+(t)f^*(t)], \tag{B5}$$

where $f(t)$ represents the time-dependent external field. In the interaction picture, the time evolution of the system with an external interaction $V_I(t)$ is formally given as

$$|\Psi(t)\rangle_I = \exp\left[\frac{i}{\hbar}\int_{t_0}^{t} V_I(t)\,dt\right]|\Psi(t_0)\rangle_I. \tag{B6}$$

From Eq. (B4), $V_I(t)$ for the Morse oscillator is given as

$$\begin{aligned} V_I(t) = &-[e^{-i\omega_0 t} b e^{i[2\omega_0/(N+1)]\hat{v}t} f(t) \\ &+ e^{i\omega_0 t} e^{-i[2\omega_0/(N+1)]\hat{v}t} b^+ f^*(t)]. \end{aligned} \tag{B7}$$

Substituting Eq. (B7) into Eq. (B6), we obtain

$$\begin{aligned} |\Psi(t)\rangle_I = \exp\Bigg\{ &\frac{i}{\hbar}\int_{t_0}^{t} [e^{-i\omega_0 t} b e^{i[2\omega_0/(N+1)]\hat{v}t} f(t) \\ &+ e^{i\omega_0 t} e^{-i[2\omega_0/(N+1)]\hat{v}t} b^+ f^*(t)]\Bigg\} |\Psi(t_0)\rangle_I. \end{aligned} \tag{B8}$$

Therefore, in principle, given the functional form of $f(t)$ and the initial state of the system, we can determine the wave function at a later time. As a specific case, we determine the asymptotic limit with $t_0 = -\infty$ and $t = \infty$. With $|[N],0\rangle$ as the initial state. Eq. (B8) becomes

$$\begin{aligned} |\Psi(\infty)\rangle_I &= e^{G(\omega,\hat{v})b^+ - bG^+(\omega,\hat{v})}|\Psi(-\infty)\rangle_I \\ &= e^{G(\omega,\hat{v})b^+ - bG^+(\omega,\hat{v})}|N,0\rangle, \end{aligned} \tag{B9}$$

where

$$G(\omega_0,\hat{v}) = \frac{i}{\hbar}\int_{-\infty}^{+\infty} e^{-i[2\omega_0/(N+1)]\hat{v}t} f^* e^{i\omega_0 t}\,dt. \tag{B10}$$

Equation (B10) is similar to the coherent state of a harmonic oscillator interacting with an external field. This similarity arises from the fact that both the Morse oscillator and the harmonic oscillator belong to the $U(2)$ group. However, for the Morse oscillator, G and G^+ are operators, and the frequency is a function of v, dramatically increasing the difficulty of evaluating the coherent state. Nevertheless, the formal solution of the Morse oscillator coherent state is revealing and useful.

APPENDIX C: SIMPLIFICATION OF CLASSICAL RESPONSE FUNCTIONS

In this Appendix, we simplify the third-order and fifth-order classical response functions. Substituting the two identities

$$\mathrm{Tr}[\{A,B\}C] = \mathrm{Tr}[A\{B,C\}], \tag{C1}$$

and

$$\{A,\rho\} = \{A,H\}\frac{\partial\rho}{\partial H} = \frac{dA}{dt}\frac{\partial\rho}{\partial H}, \tag{C2}$$

into Eq. (12b), the general expression of $R_C^{(3)}(t)$ reduces to

$$\begin{aligned} R_C^{(3)}(t) &= -\mathrm{Tr}\left[\alpha(t)\dot{\alpha}(0)\frac{\partial\rho}{\partial H}\right] \\ &= -\frac{\oint dI\,d\phi\,\alpha(t)\dot{\alpha}(0)(\partial\rho/\partial H)}{\oint dI\,d\phi\,\rho}. \end{aligned} \tag{C3}$$

For the Morse oscillator, H is independent of ϕ, so that Eq. (C3) is rewritten as

$$R_C^{(3)}(t) = -\frac{1}{2\pi}\oint dI\,d\phi\,\alpha(t)\dot{\alpha}(0)\frac{\partial I}{\partial E}\frac{\partial\rho}{\partial I}, \tag{C4}$$

where $\rho(I)$ is the normalized distribution function of I. Generally, ρ is a function of H, but, for integrable systems, H depends only on I so that $\rho(H)$ is equivalent to $\rho(I)$.

Next, we simplify the fifth-order classical response function $R_C^{(5)}(t_1,t_2)$. The general form of $R_C^{(5)}(t_1,t_2)$ is given in Eq. (13b). Two possible approaches can be applied. The first approach is to substitute Eq. (C1) and Eq. (C2) into Eq. (13b), so that $R_C^{(5)}(t_1,t_2)$ is given as

$$\begin{aligned} R_C^{(5)}(t_1,t_2) &= \mathrm{Tr}[\{\alpha(t_2),\alpha(t_1)\}\{\alpha(0),\rho\}] \\ &= \mathrm{Tr}\left[\{\alpha(t_2),\alpha(t_1)\}\dot{\alpha}(0)\frac{\partial\rho}{\partial E}\right] \\ &= \frac{1}{2\pi}\oint dI\,d\phi\{\alpha(t_2),\alpha(t_1)\}\dot{\alpha}(0)\frac{\partial I}{\partial E}\frac{\partial\rho}{\partial I}. \end{aligned} \tag{C5}$$

The second approach starts from Eq. (C5) and then applies Eq. (C1) to the integrand. With the help of the chain rule, Eq. (C5) is written as

$$\begin{aligned} R_C^{(5)}(t_1,t_2) &= \mathrm{Tr}\left[\{\alpha(t_2),\alpha(t_1)\}\dot{\alpha}(0)\frac{\partial\rho}{\partial E}\right] \\ &= \mathrm{Tr}\left[\alpha(t_2)\left\{\alpha(t_1),\dot{\alpha}(0)\frac{\partial\rho}{\partial E}\right\}\right] \\ &= \mathrm{Tr}\left[\alpha(t_2)\dot{\alpha}(t_1)\dot{\alpha}(0)\frac{\partial^2\rho}{\partial E^2}\right] \\ &\quad + \mathrm{Tr}\left[\alpha(t_2)\{\alpha(t_1),\dot{\alpha}(0)\}\frac{\partial\rho}{\partial E}\right] \\ &= \frac{1}{2\pi}\left[\oint dI\,d\phi\,\alpha(t_2)\dot{\alpha}(t_1)\dot{\alpha}(0)\frac{\partial^2\rho}{\partial E^2}\right. \\ &\quad \left. + \oint dI\,d\phi\,\alpha(t_2)\{\alpha(t_1),\dot{\alpha}(0)\}\frac{\partial\rho}{\partial E}\right]. \end{aligned} \tag{C6}$$

In comparison, the first expression in Eq. (C5) is easy to calculate and is adopted in the paper.

[1] R. Kubo, N. Toda, and N. Hashitsume, *Statistical Physics II* (Springer, Berlin, 1985).
[2] S. Mukamel, *The Principles of Nonlinear Optical Spectroscopy* (Oxford, London, 1995).
[3] N. van Kampen, Phys. Norv. **5**, 271 (1971).
[4] Y. Tanimura and S. Mukamel, J. Chem. Phys. **99**, 9496 (1993).
[5] C. J. Brennan and K. A. Nelson, J. Chem. Phys. **107**, 9691 (1997).
[6] A. Tokmakoff, M. J. Lang, D. S. Larsen, G. R. Fleming, V. Chernyak, and S. Mukamel, Phys. Rev. Lett. **79**, 2702 (1997).
[7] D. A. Blank, G. R. Fleming, M. Cho, and A. Tokmakoff, in *Ultrafast*

Infrared and Raman Spectrosopy, edited by M. D. Fayer, 1999.
[8] S. Mukamel, V. Khidekel, and V. Chernyak, Phys. Rev. E **53**, R1 (1996).
[9] F. Iachello and R. Levine, *Algebraic Theory of Molecules* (Oxford University Press, New York, 1995).
[10] M. P. Jacobson, R. J. Silbey, and R. W. Field, J. Chem. Phys. **110**, 845 (1999).
[11] M. P. Jacobson, C. Jung, H. S. Taylor, and R. W. Field, J. Chem. Phys. **111**, 600 (1999).
[12] E. J. Heller and S. Tomsovic, Phys. Today **46**, 38 (1993).
[13] E. J. Heller, J. Chem. Phys. **99**, 2625 (1995).
[14] S. A. Schofield and P. G. Wolynes, *Picturing Quantized Intramolecular Vibrational Energy Flow: Action Diffusion, Localization, and Scaling* (Dekker, New York, 1996).
[15] D. M. Leitner and P. G. Wolynes, Chem. Phys. Lett. **280**, 411 (1997).
[16] H. Tang, S. Jang, M. Zhou, and S. A. Rice, J. Chem. Phys. **101**, 8737 (1994).
[17] M. Zhou and S. A. Rice, Int. J. Quantum Chem. **58**, 593 (1996).
[18] A. A. Stuchebrukhov and R. A. Marcus, J. Chem. Phys. **98**, 8443 (1993).
[19] R. A. Marcus, J. Chem. Phys. **105**, 5446 (1996).
[20] C. Jaffe and P. Brumer, J. Chem. Phys. **73**, 5646 (1980).
[21] E. L. Sibert, W. P. Reinhardt, and J. T. Hynes, J. Chem. Phys. **77**, 3583 (1982).
[22] J. Wilkie and P. Brumer, Phys. Rev. A **55**, 27 (1997).
[23] J. Wilkie and P. Brumer, Phys. Rev. A **55**, 27 (1997).
[24] K. Okumura and Y. Tanimura, J. Chem. Phys. **105**, 7294 (1996).
[25] S. Mukamel, A. Piryatinski, and V. Chernyak, J. Chem. Phys. **110**, 1711 (1999).
[26] D. J. Tannor and S. A. Rice, J. Chem. Phys. **83**, 5013 (1985).
[27] N. F. Scherer, R. J. Carson, A. Matro, M. Du, A. J. Ruggiero, V. Romero-Rochin, J. A. Cina, G. R. Fleming, and S. A. Rice, J. Chem. Phys. **95**, 1487 (1991).
[28] M. Shapiro and P. Brumer, Acc. Chem. Res. **22**, 407 (1989).
[29] S. Chelkowski, A. D. Bandrauk, and P. B. Corkum, Phys. Rev. Lett. **65**, 2355 (1990).
[30] R. J. Gordon and S. A. Rice, Annu. Rev. Phys. Chem. **48**, 595 (1997).
[31] J. Cao, C. J. Bardeen, and K. R. Wilson, Phys. Rev. Lett. **80**, 1406 (1998).
[32] H. Metiu, D. W. Oxtoby, and K. F. Freed, Phys. Rev. A **15**, 361 (1977).
[33] D. W. Oxtoby, Adv. Chem. Phys. **47**, 487 (1981).
[34] B. J. Berne, M. E. Tuckerman, J. E. Straub, and A. L. R. Bug, J. Chem. Phys. **93**, 5084 (1990).
[35] M. Tuckerman and B. J. Berne, J. Chem. Phys. **98**, 7301 (1993).
[36] J. S. Bader, B. J. Berne, E. Pollak, and P. Hanggi, J. Chem. Phys. **104**, 1111 (1996).
[37] S. A. Egorov and J. L. Skinner, Chem. Phys. **105**, 7047 (1996).
[38] R. B. Williams and R. F. Loring, J. Chem. Phys. **110**, 10899 (1999).
[39] Y. Alhassid, F. Gursey, and F. Iachello, Ann. Phys. (Leipzig) **148**, 346 (1983).
[40] F. Iachello and P. Truini, Ann. Phys. (Leipzig) **276**, 120 (1999).
[41] A. Frank, R. Lemus, M. Cravajal, C. Jung, and E. Ziemniak, Chem. Phys. Lett. **308**, 91 (1999).
[42] R. Lemus and A. Frank, Chem. Phys. **242**, 25 (1999).
[43] A. Frank, R. Lemus, R. Bijker, F. Perez-Bernal, and J. M. Arias, Ann. Phys. (Leipzig) **252**, 211 (1999).
[44] H. Goldstein, *Classical Mechanics* (Addison-Wesley, Reading, MA, 1950).
[45] E. J. Heller, J. Chem. Phys. **62**, 1544 (1975).
[46] M. Ben-Nun and R. D. Levine, J. Chem. Phys. **101**, 8768 (1994).
[47] J. C. Tully, J. Chem. Phys. **93**, 1061 (1990).
[48] D. F. Coker, in *Computer Simulation in Chemical Physics*, edited by M. P. Allen and D. J. Tildesley (Kluwer Academic, Dordrecht, The Netherlands, 1993).
[49] B. J. Schwartz, E. R. Bittner, O. V. Prezhdo, and P. J. Rossky, J. Chem. Phys. **104**, 5942 (1996).
[50] J. Cao and G. A. Voth, J. Chem. Phys. **100**, 5106 (1994).
[51] L. Scarfone, Chem. Phys. **2333**, 217 (1998).