

# Anharmonic molecular spectra-self-consistent mode coupling, nonlinear maps, and quantum chaos

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An exact reduced equation of motion which allows the calculation of zero temperature correlation functions in nonlinear (anharmonic) *quantum* systems is derived. A self-consistent procedure is subsequently developed which enables us to solve for the correlation functions by mapping the anharmonic problem into a harmonic problem with higher dimensionality. Our nonlinear map is of the type commonly used in *classical* nonlinear dynamics and may exhibit critical dependence on the anharmonic potential. Our procedure is particularly adequate for comparing quantum and classical spectra and may lead to a new definition of "quantum chaos" and its relevance to molecular vibrational spectroscopy.

## I. INTRODUCTION

The calculation of spectra of nonlinearly coupled oscillators is a fundamental problem in statistical mechanics which has important implications on many branches of physics and chemistry (e.g., energy transfer and spectra of polyatomic molecules).<sup>1,2</sup> Substantial progress has been made for classical systems. It is well established that classical trajectories of nonlinear systems may be classified as "quasi-periodic" or "stochastic" (chaotic) depending on the nonlinear coupling and the initial conditions.<sup>3-5</sup> In addition, nonlinear maps<sup>6-10</sup> which are intimately related to a discretized version of the classical equations of motion have been thoroughly investigated, leading to considerable insight on the universality properties of chaotic behavior (e.g., the Feigenbaum doubling)<sup>7</sup> and its relation to the theory of critical phenomena.<sup>11</sup> The quantum mechanical significance of these concepts is, however, not at all clear and is the subject of numerous current studies.<sup>12-22</sup> Many attempts have been made to define "quantum chaos" and to suggest criteria for the classification of quantum systems into regular and chaotic. Some examples are: semiclassical quantization,<sup>2,12,13</sup> the regularity of the wave function,<sup>14</sup> time evolution of wave packets,<sup>2,16</sup> the Kolmogorov entropy.<sup>23,24</sup> There is obviously a need to develop a theoretical framework which will allow us to study classical and quantum systems along similar lines and to compare their behavior in detail. The behavior of correlation functions<sup>25</sup> of dynamical variables and their Fourier transforms (spectra) is clearly an important feature which is directly related to experimental observables such as the infrared and the optical spectra of polyatomic molecules. Correlation functions provide a natural level for comparing classical and quantum calculations.<sup>26</sup> A procedure was developed recently towards the calculation of correlation functions of quantum nonlinearly coupled (anharmonic) oscillators.<sup>27</sup> The basic goal is to construct an algorithm towards the direct calculation of correlation functions which are the quantities of interest, without going into the details of individual eigenstates in the quantum case. We define a quasi-probability function  $P(\mathbf{q}, t; \mathbf{q}')$  which plays the role of a joint probability for the coordinates to assume the value  $\mathbf{q}$  at time  $t$ , given a value  $\mathbf{q}'$  at  $t = 0$ .  $P$  is a complex quantity so that it is

not a joint probability in a strict sense. Nevertheless, it enables us to calculate any correlation function of dynamical variables which depend on the coordinates  $\mathbf{q}$ . A non-Markovian reduced equation of motion (REM) may then be derived for  $P$  and the resulting spectra may be conveniently calculated. In this paper we further develop this formalism. We focus on nonlinear oscillator systems initially at zero temperature. This is done since: (i) The most detailed molecular spectra currently available are those obtained for ultracold molecules in supersonic beams.<sup>28</sup> Only under these conditions are the spectra free of inhomogeneous broadening and provide a meaningful dynamical information. (ii) The calculation is greatly simplified in this case. The general REM is an integral equation with a time dependent (non-Markovian) kernel.<sup>29-31</sup> We show in this paper that at zero temperature the *exact* REM becomes a simple time-independent Fokker-Planck type equation regardless of the anharmonicities. The input to the REM in this case is the ground state probability density (wave function square) which may be obtained with a reasonable accuracy without a major difficulty. The solution of the REM in the harmonic case is a multivariable complex Gaussian distribution.<sup>27</sup> For anharmonic systems, however, we cannot find a general analytical solution. We therefore develop a self-consistent procedure towards the solution of the REM. This is based on mapping the anharmonic problem onto an effective linear (harmonic) system with higher dimensionality, which has the same correlation functions. We then obtain self-consistent equations for the spectra which assume the well-known bilinear form commonly used in mode coupling problems,<sup>32-37</sup> critical phenomena,<sup>38</sup> and nonlinear maps.<sup>6-10</sup> These mode coupling equations may exhibit a critical dependence on the coupling parameters and energy, and provide an important link between classical and quantum spectra. A criterion for stochasticity suggested by this procedure is connected with the dimensionality of the effective harmonic system mapped from the original anharmonic system. When the equations converge after a few iterations the effective harmonic system will be of small size and will correspond to a "regular" spectrum. Slow convergence or divergence of the map implies that an infinite number of harmonic oscillators are needed to reproduce the spectrum. This may serve as an operational definition of quantum chaos.

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The plan of this paper is as follows: In Sec. II we define the basic generating function (quasiprobability) and introduce the general REM. In Sec. III we analyze its behavior for harmonic systems and in Sec. IV we derive the exact REM valid for an arbitrary anharmonic system at zero temperature. Finally, in Sec. V, we derive the self-consistent equations and bring them to the standard mode-coupling form. For the sake of clarity, we included much of the details in the Appendices, and the reader may get the main physical ideas and results without being buried in mathematical details.

## II. THE GENERATING FUNCTION

The absorption line shape, such as the molecular vibrational spectrum, is the power spectrum of the correlation function of the dipole operator.<sup>25</sup> In general, the correlation function of two dynamical variables  $A$  and  $B$  is defined by

$$\langle A(t)B(0) \rangle \equiv \text{Tr} [A(t)B(0)\rho], \quad (1)$$

where  $A(t)$  is in the Heisenberg representation

$$A(t) = \exp(iHt/\hbar)A \exp(-iHt/\hbar) \quad (2)$$

with  $H$  being the Hamiltonian of the system (without the radiation field), and  $\rho$  is the density matrix

$$\rho = \exp(-H/kT)/\text{Tr}[\exp(-H/kT)]. \quad (3)$$

We shall be interested in the calculation of correlation functions of dynamical variables which depend on  $n$  coordinates

$$(Q_1, Q_2, \dots, Q_n) \equiv \mathbf{Q}. \quad (4)$$

{The dipole operator may usually be taken to be a function of nuclear coordinates only and does not depend on the momentum variables. This choice [Eq. (4)] is therefore sufficient for the calculation of dipole correlation functions.}  $\mathbf{Q}$  may be a partial set or a complete set of the coordinate variables of the system.

Any function of the coordinates  $Q_i (i = 1, \dots, n)$  may be formally expressed as

$$f(\mathbf{Q}) = \int d\mathbf{q} f(\mathbf{q}) \delta(\mathbf{q} - \mathbf{Q}), \quad (5)$$

where

$$d\mathbf{q} \equiv dq_1 dq_2 \dots dq_n$$

and  $\delta(\mathbf{q} - \mathbf{Q})$  is the  $n$ -dimensional delta function

$$\delta(\mathbf{q} - \mathbf{Q}) \equiv \prod_{i=1}^n \delta(q_i - Q_i). \quad (6)$$

Note that the integration variables  $q_i (i = 1, \dots, n)$  in Eq. (5) are  $c$  numbers. We shall now introduce the following quantities<sup>27</sup>:

$$g(\mathbf{q}) \equiv \langle \delta(\mathbf{q} - \mathbf{Q}) \rangle, \quad (7)$$

$$P(\mathbf{q}, t; \mathbf{q}') \equiv \langle \delta(\mathbf{q} - \mathbf{Q}(t)) \delta(\mathbf{q}' - \mathbf{Q}(0)) \rangle. \quad (8)$$

$g(\mathbf{q})$  is the equilibrium distribution function, i.e., the probability density for  $\mathbf{Q}$  to assume the value  $\mathbf{q}$ . It allows us to calculate the expectation value of any dynamical variable which is a function of  $\mathbf{Q}$ , by an integration over  $\mathbf{q}$ . If  $A = a(\mathbf{Q})$ , then

$$\langle A \rangle = \int d\mathbf{q} a(\mathbf{q})g(\mathbf{q}). \quad (9)$$

Similarly,  $P(\mathbf{q}, t; \mathbf{q}')$  of Eq. (8) allows us to calculate the corre-

lation function of any two dynamical variables which are functions of  $\mathbf{Q}$ . If  $A = a(\mathbf{Q})$  and  $B = b(\mathbf{Q})$ , then

$$\langle A(t)B(0) \rangle = \int d\mathbf{q} d\mathbf{q}' a(\mathbf{q})b(\mathbf{q}')P(\mathbf{q}, t; \mathbf{q}'). \quad (10)$$

In other words,  $P$  is the generating function for all correlation functions of this type. In classical mechanics,  $P$  is actually the joint probability distribution for  $\mathbf{Q}$  to assume the value  $\mathbf{q}'$  at time 0 and the value  $\mathbf{q}$  at time  $t$ . In quantum mechanics, however,  $P$  is a complex quantity so that it cannot be strictly interpreted as a probability.<sup>27</sup>

Using methods of nonlinear dynamics,<sup>38-42</sup> it was shown that the generating function  $P$  always obeys the following reduced equation of motion (REM)<sup>27</sup>:

$$\frac{dP(\mathbf{q}, t; \mathbf{q}')}{dt} = \int d\mathbf{q}'' R(\mathbf{q}, \mathbf{q}'', t)P(\mathbf{q}'', t; \mathbf{q}'), \quad (11)$$

where

$$R(\mathbf{q}, \mathbf{q}'', t) = \dot{\chi} \cdot \chi^{-1} \quad (12)$$

and

$$\chi(\mathbf{q}, \mathbf{q}', t) \equiv \langle \delta(\mathbf{q} - \mathbf{Q}(t)) \delta(\mathbf{q}' - \mathbf{Q}) \rangle. \quad (13)$$

The initial condition for Eq. (11) is

$$P(\mathbf{q}, 0; \mathbf{q}') = g(\mathbf{q})\delta(\mathbf{q} - \mathbf{q}'). \quad (14)$$

Equation (11), as it stands, is equivalent to the formal identity  $\dot{P} = (\dot{P}/P)P$ . If we can find useful approximations for  $R$  then it may be extremely helpful for getting approximations for  $P$ . In the following sections, we shall derive exact explicit expressions for the REM.

## III. HARMONIC SYSTEMS

In this section we shall examine the form of the REM and the generating function for harmonic systems which are exactly solvable. This is a necessary step in developing the self-consistent formalism for general anharmonic systems. For a harmonic system, the potential energy is a quadratic function of the coordinate variables and the Hamiltonian is given by

$$H = \frac{1}{2} \sum_{\lambda=1}^N (P_{\lambda}^2 + \omega_{\lambda}^2 X_{\lambda}^2). \quad (15)$$

Here,  $X_{\lambda}$  are the normal modes and  $P_{\lambda}$  is the conjugate momentum of  $X_{\lambda}$ .  $\omega_{\lambda}$  is the frequency of the  $\lambda$  mode. Let us focus first on a single coordinate  $Q$ ,

$$Q \equiv \sum_{\lambda} c_{\lambda} X_{\lambda}. \quad (16)$$

$\mathbf{Q}$  may be, e.g., a specific bond in a large polyatomic molecule. The generating function for any correlation function associated with this  $Q$ ,  $P(q, t; q')$  may be developed by a direct expansion of Eqs. (11)–(13) using standard many body techniques.<sup>43-46</sup> The details are given in Appendix A and the final exact result for the REM is

$$\frac{\partial P}{\partial t} = -\frac{\dot{\rho}(t)}{\rho(t)} \left( \frac{\partial}{\partial q} (qP) + \Delta^2 \frac{\partial^2 P}{\partial q^2} \right), \quad (17)$$

where

$$\Delta^2 \equiv \langle Q^2 \rangle = \sum_{\lambda} c_{\lambda}^2 \langle X_{\lambda}^2 \rangle \quad (18)$$

and

$$\rho(t) = \langle Q(t)Q(0) \rangle / \langle Q^2 \rangle = \sum_{\lambda} c_{\lambda}^2 \langle X_{\lambda}(t)X_{\lambda} \rangle / \Delta^2. \quad (19)$$

Here

$$\langle X_{\lambda}^2 \rangle = (2\bar{n}_{\lambda} + 1), \quad (20)$$

$$\langle X_{\lambda}(t)X_{\lambda} \rangle = (\bar{n}_{\lambda} + 1)\exp(-i\omega_{\lambda}t) + \bar{n}_{\lambda} \exp(i\omega_{\lambda}t), \quad (21)$$

and

$$\bar{n}_{\lambda} = [\exp(\hbar\omega_{\lambda}/kT) - 1]^{-1}. \quad (22)$$

In the classical limit ( $kT \gg \hbar\omega_{\lambda}$ ), we have

$$\Delta^2 = \sum_{\lambda} \frac{kT}{\omega_{\lambda}^2} c_{\lambda}^2 \quad (23)$$

and

$$\rho(t) = \sum_{\lambda} \frac{kT}{\omega_{\lambda}^2} \frac{c_{\lambda}^2}{\Delta^2} \cos \omega_{\lambda}t. \quad (24)$$

We further have

$$g(q) = \frac{1}{\sqrt{2\pi}\Delta} \exp(-q^2/2\Delta^2). \quad (25)$$

The solution of Eq. (17) with the initial condition (14) is<sup>27</sup>

$$P(q,t;q') = \frac{1}{\sqrt{2\pi}\Delta \sqrt{1-\rho^2}} \exp\left[-\frac{(q-q'\rho)^2}{2\Delta^2(1-\rho^2)}\right] g(q'). \quad (26)$$

Equations (17) and (26) bear a striking similarity with the Fokker-Planck equation and the joint probability distribution in the theory of Brownian motion.<sup>47</sup> The velocity distribution of a Brownian particle subject to a stationary Gaussian Markovian random force satisfies Eqs. (17) and (26) with

$$\rho(t) = \exp(-\gamma t), \quad (27a)$$

so that

$$\dot{\rho}/\rho = -\gamma. \quad (27b)$$

The coordinate  $q$  in a harmonic system therefore behaves like a stationary Gaussian, but non-Markovian process.<sup>47,48</sup> Physically, what happens is that for a single oscillator,  $P(q,t;q')$  is a *quasiperiodic* function undergoing dephasing and rephasing. For a Brownian particle on the other hand, the dephasing is irreversible, as implied by Eqs. (27). The addition of anharmonicities to the Hamiltonian [Eq.(15)] will change the nature of the quasiperiodic time evolution [Eq. (21)] and may turn it to be irreversible on the relevant time scales. Infinite harmonic lattices may also exhibit the irreversible behavior of Eq. (27a).<sup>49-50</sup> In the coming sections, we shall explore the consequences of anharmonicities on these equations.

If we wish to consider explicitly  $n$  coordinates  $Q_i$  which are linear combinations of  $N$  normal mode coordinates  $X_{\lambda}$  ( $n \leq N$ ), i.e.,

$$Q_i = \sum_{\lambda=1}^N c_{i\lambda} X_{\lambda} \quad (i = 1, \dots, n), \quad (28)$$

then the generating function defined by Eq. (8) satisfies the following *exact* reduced equation of motion (REM):

$$\frac{\partial P(\mathbf{q},t;\mathbf{q}')}{\partial t} = - \sum_{ij} \frac{\partial}{\partial q_i} [\dot{M}(t)M^{-1}(t)M(0)]_{ij} g(\mathbf{q}) \frac{\partial}{\partial q_j} \frac{P(\mathbf{q},t;\mathbf{q}')}{g(\mathbf{q})}, \quad (29a)$$

or in the matrix notation

$$\frac{\partial P(\mathbf{q},t;\mathbf{q}')}{\partial t} = - \frac{\partial}{\partial \mathbf{q}} \dot{M}(t)M^{-1}(t)M(0)g(\mathbf{q}) \frac{\partial}{\partial \mathbf{q}} \frac{P(\mathbf{q},t;\mathbf{q}')}{g(\mathbf{q})}, \quad (29b)$$

where  $M(t)$  is the  $n \times n$  matrix of the coordinate correlation functions

$$M_{ij}(t) \equiv \langle Q_i(t)Q_j(0) \rangle. \quad (30)$$

In Eq. (29) and in the following equations,  $\tilde{A}$  denotes the transposed matrix of  $A$ , and  $\tilde{\mathbf{v}}$  and  $\mathbf{v}$  are a row vector and a column vector, respectively. The equilibrium distribution  $g(\mathbf{q})$  is a Gaussian

$$g(\mathbf{q}) = \frac{1}{\sqrt{(2\pi)^n \det M(0)}} \exp\left[-\frac{1}{2}\tilde{\mathbf{q}}M^{-1}(0)\mathbf{q}\right]. \quad (31)$$

Note that the matrix  $M(0)$ , i.e., the value of  $M(t)$  at  $t = 0$ ,

$$M_{ij}(0) = \langle Q_i Q_j \rangle \quad (32)$$

is a symmetric matrix. We further note that the matrix  $M(t)$  is diagonal if the chosen variables  $Q_i$  are the normal modes  $X_{\lambda}$ . By using Eq. (31), one can write the REM (29) in another form

$$\begin{aligned} \frac{\partial P(\mathbf{q},t;\mathbf{q}')}{\partial t} = & - \frac{\partial}{\partial \mathbf{q}} \dot{M}(t)M^{-1}(t)M(0) \frac{\partial}{\partial \mathbf{q}} P(\mathbf{q},t;\mathbf{q}') \\ & - \frac{\partial}{\partial \mathbf{q}} \dot{M}(t)M^{-1}(t)\mathbf{q}P(\mathbf{q},t;\mathbf{q}'). \end{aligned} \quad (33)$$

Equations (33) and (31) are straightforward generalizations of Eqs. (17) and (25), whereby the ordinary Gaussian distribution function becomes a multivariable Gaussian distribution. They can be proven by a direct calculation which will be an extension of Appendix A. This procedure, however, is quite tedious and in Appendix B we present an alternative derivation. The solution of Eq. (29) or Eq. (33) with the initial condition Eqs. (14) and (31) can be explicitly written as (Appendix B)

$$P(\mathbf{q},t;\mathbf{q}') = \frac{1}{\sqrt{(2\pi)^n \det W(t)}} \exp\left[-\frac{1}{2}\tilde{\mathbf{V}}(t)W^{-1}(t)\mathbf{V}(t)\right] g(\mathbf{q}'), \quad (34)$$

where

$$W(t) \equiv M(0) - M(t)M^{-1}(0)\tilde{M}(t), \quad (35a)$$

and where

$$\mathbf{V}(t) \equiv \mathbf{q} - M(t)M^{-1}(0)\mathbf{q}'. \quad (35b)$$

We note that the generating function in harmonic systems is a Gaussian function of  $\mathbf{q}$  and  $\mathbf{q}'$ . The coordinate correlation functions  $M(t)$  of Eq. (30) can be calculated in the standard way. Making use of Eqs. (21) and (28), we get

$$\begin{aligned} M_{ij}(t) &= \sum_{\lambda} c_{i\lambda} c_{j\lambda} \langle X_{\lambda}(t)X_{\lambda}(0) \rangle \\ &= \sum_{\lambda} c_{i\lambda} c_{j\lambda} \frac{\hbar}{2\omega_{\lambda}} [(\bar{n}_{\lambda} + 1) \\ &\quad \times \exp(-i\omega_{\lambda}t) + \bar{n}_{\lambda} \exp(i\omega_{\lambda}t)]. \end{aligned} \quad (36)$$

It should be noted that the matrix  $M(t)$  is complex so that the

generating function  $P$  of Eq. (34) is a complex Gaussian function.

As noted earlier,  $P(\mathbf{q}, t; \mathbf{q}')$  allows us to calculate any correlation function of variables which depend on  $Q_i$  ( $i = 1, \dots, n$ ). In general, the REM (29) or Eq. (33) is time dependent (i.e., it contains time-dependent coefficients), and is time local (i.e., it does not contain a memory kernel)<sup>29-31</sup> There is a special case where the differential operator in the REM becomes time independent. The condition for this is that (i) the system is at zero temperature and (ii) the number  $n$  of the relevant variables  $Q_i$  is taken to be equal to the total number of degrees of freedom of the system  $N$ . Condition (ii) implies that the coordinates  $\mathbf{Q}$  are obtained by a linear transformation of the normal modes  $\mathbf{X}$ . If we choose  $\mathbf{Q}$  to be the normal modes, then the matrix  $\mathbf{M}(t)$  of Eq. (36) becomes diagonal, i.e.,

$$M_{ij}(t) = \delta_{ij} \frac{\hbar}{2\omega_i} [(\bar{n}_i + 1) \exp(-i\omega_i t) + \bar{n}_i \exp(i\omega_i t)], \quad (37)$$

and it can then be easily shown that the coefficients  $\mathbf{M}(t)\mathbf{M}^{-1}(t)$  in the REM (29) become independent of time at zero temperature. Consequently, this will also be the case for the REM (29) using any choice of the coordinates  $\mathbf{Q}$  obtained by a (time-independent) linear transformation of the normal modes. The final result can be written as

$$\frac{\partial P(\mathbf{q}, t; \mathbf{q}')}{\partial t} = \frac{i\hbar}{2} \frac{\partial}{\partial \mathbf{q}} \mathbf{G} g(\mathbf{q}) \frac{\partial P(\mathbf{q}, t; \mathbf{q}')}{\partial \mathbf{q} g(\mathbf{q})}, \quad (38)$$

or, alternatively

$$\frac{\partial P(\mathbf{q}, t; \mathbf{q}')}{\partial t} = \left[ \frac{i\hbar}{2} \frac{\partial}{\partial \mathbf{q}} \mathbf{G} \frac{\partial}{\partial \mathbf{q}} + i \frac{\partial}{\partial \mathbf{q}} \mathbf{\Omega} \mathbf{q} \right] P(\mathbf{q}, t; \mathbf{q}'), \quad (39)$$

where  $\mathbf{G}$  and  $\mathbf{\Omega}$  are in the inverse mass matrix, and the frequency matrix, respectively, defined by writing the Hamiltonian in terms of the coordinates  $\mathbf{Q}$  and their conjugate momenta  $\mathbf{P}$  as

$$H = \frac{1}{2} \mathbf{\tilde{P}} \mathbf{G} \mathbf{P} + \frac{1}{2} \mathbf{Q} \mathbf{\Omega} \mathbf{Q}. \quad (40)$$

We note that the form of the REM (38) or REM (39) is the same as the Fokker-Planck equation<sup>47</sup> except that it contains pure imaginary coefficients.

#### IV. ANHARMONIC SYSTEMS AT ZERO TEMPERATURE

We shall now consider a general system of  $N$  coupled anharmonic oscillators described by the Hamiltonian

$$H = \frac{1}{2} \sum_{i,j=1}^N P_i G_{ij} P_j + U(Q_1, \dots, Q_N)$$

or

$$H = \frac{1}{2} \mathbf{\tilde{P}} \mathbf{G} \mathbf{P} + U(\mathbf{Q}), \quad (41)$$

where  $U(\mathbf{Q})$  is an anharmonic potential.

It is shown in Appendix C that, if (i) the temperature is zero and (ii) we choose all the coordinates as the relevant variables of Eq. (4), i.e.,  $n = N$ , then the generating function  $P$  obeys an exact REM of the same form as Eq. (38):

$$\frac{\partial P(\mathbf{q}, t; \mathbf{q}')}{\partial t} = \frac{i\hbar}{2} \frac{\partial}{\partial \mathbf{q}} \mathbf{G} g(\mathbf{q}) \frac{\partial P(\mathbf{q}, t; \mathbf{q}')}{\partial \mathbf{q} g(\mathbf{q})}. \quad (42)$$

Here  $g(\mathbf{q})$  is the exact ground state distribution for the anharmonic system. This REM (42) is valid for any form of the

potential  $U(\mathbf{Q})$ , including harmonic potentials. Equation (42) is more general than Eq. (29) since it holds for an arbitrary anharmonic potential, whereas Eq. (29) is restricted to harmonic systems. On the other hand, Eq. (29) is not restricted to zero temperature or by the condition  $n = N$ , and in this sense it is more general than Eq. (42). When the system is anharmonic and at finite temperature, or when  $n < N$ , the REM is more complicated and will contain higher derivatives in  $\mathbf{q}$ . This can be easily shown by a perturbative calculation of the kernel  $R$  in Eq. (11), in terms of the anharmonicities.

Hereafter, we confine ourselves to the REM (42), i.e., we consider the system at zero temperature and choose all the coordinates as the relevant variables. The REM (42) can be rewritten in the form

$$\frac{\partial P(\mathbf{q}, t; \mathbf{q}')}{\partial t} = \left[ \frac{i\hbar}{2} \frac{\partial}{\partial \mathbf{q}} \mathbf{G} \frac{\partial}{\partial \mathbf{q}} + i \frac{\partial}{\partial \mathbf{q}} \mathbf{u}(\mathbf{q}) \right] P(\mathbf{q}, t; \mathbf{q}'), \quad (43)$$

where the vector  $\mathbf{u}(\mathbf{q})$  is defined by

$$\mathbf{u}(\mathbf{q}) = -\frac{\hbar}{2} \mathbf{G} \left( \frac{\partial}{\partial \mathbf{q}} \ln g(\mathbf{q}) \right). \quad (44)$$

It is further shown in Appendix D that the function  $\mathbf{u}(\mathbf{q})$  satisfies the equation

$$-\frac{\hbar}{2} \frac{\partial}{\partial \mathbf{q}} \mathbf{u}(\mathbf{q}) + \frac{1}{2} \tilde{\mathbf{u}}(\mathbf{q}) \mathbf{G}^{-1} \mathbf{u}(\mathbf{q}) = U(\mathbf{q}) - E_0, \quad (45)$$

where  $E_0$  is the ground state energy.

The REM (42) or REM (43) can be rewritten also in the form of the equation of continuity

$$\frac{\partial P}{\partial t} + \frac{\partial}{\partial \mathbf{q}} (\mathbf{V} P) = 0, \quad (46)$$

where the local velocity is given by

$$\mathbf{V} \equiv \frac{i\hbar}{2} \mathbf{G} \left[ \frac{\partial \ln P}{\partial \mathbf{q}} - \frac{\partial \ln g}{\partial \mathbf{q}} \right]. \quad (47)$$

This form of the local velocity  $\mathbf{V}$  implies that the deviation of  $P$  from the equilibrium distribution  $g$  is the driving force for the time evolution of  $P$ . Equations (46) and (47) have a striking resemblance with the hydrodynamic formulation of quantum mechanics.<sup>51-53</sup> If we define

$$\Psi \equiv \sqrt{\rho} \exp(iS/\hbar), \quad (48)$$

where  $\Psi$  is the wave function, then the Schrödinger equation can be recast in the form

$$\frac{\partial \rho}{\partial t} + \frac{\partial}{\partial \mathbf{q}} (\mathbf{V}_R \rho) = 0, \quad (49)$$

where  $\mathbf{V}_R$  is the real part of the velocity

$$\Psi^{-1} \left[ \frac{\hbar}{i} \frac{\partial}{\partial \mathbf{q}} \right] \Psi = \mathbf{G}^{-1} \mathbf{V} \equiv \mathbf{G}^{-1} (\mathbf{V}_R + i\mathbf{V}_I) \quad (50)$$

and where

$$\mathbf{V}_R = \mathbf{G} \frac{\partial}{\partial \mathbf{q}} S, \quad (51a)$$

$$\mathbf{V}_I = -\frac{\hbar}{2} \mathbf{G} \frac{\partial}{\partial \mathbf{q}} \ln \rho. \quad (51b)$$

Our  $\mathbf{V}$  [Eq. (47)] is analogous to the imaginary part of the hydrodynamic velocity ( $\mathbf{V}_I$ ).<sup>53</sup>

Equations (43) and (44) or (46) and (47) are a major result

of the present work. It should be emphasized again that they are *exact* and allow us to develop useful approximation schemes towards the calculation of  $M(t)$ . We should note in passing that as can be easily verified using Appendix C, Eq. (42) holds not only at zero temperature but for any quantum system which is in a pure state  $\Psi_n$ .  $g(\mathbf{q})$  is then equal to  $|\Psi_n|^2$ . Nodal points of the wave function where  $g(\mathbf{q}) = 0$  are singular points of Eq. (42). In the case of the ground state, however,  $\Psi_0$  is always positive<sup>54</sup> and Eq. (42) does not have such a singularity.

In the case of a harmonic system [Eq. (40)],  $\mathbf{u}(\mathbf{q})$  of Eq. (44) is linear in  $\mathbf{q}$ , i.e.,

$$\mathbf{u}(\mathbf{q}) = \Omega \mathbf{q}, \quad (52)$$

and Eq. (43) reduces to Eq. (39) (see Appendix D). In the case of anharmonic systems, we write the potential as a sum

$$U(\mathbf{Q}) = \frac{1}{2} \tilde{\mathbf{Q}} \tilde{\Omega} \mathbf{G}^{-1} \Omega \mathbf{Q} + V(\mathbf{Q}), \quad (53)$$

where the first and the second terms correspond to the harmonic and the residual anharmonic potentials, respectively. Then  $\mathbf{u}(\mathbf{q})$  of Eq. (44) may be written as

$$\mathbf{u}(\mathbf{q}) = \Omega \mathbf{q} + \mathbf{v}(\mathbf{q}) \quad (54)$$

so that the REM (43) assumes the form

$$\frac{\partial P(\mathbf{q}, t; \mathbf{q}')}{\partial t} = K(\mathbf{q}) P(\mathbf{q}, t; \mathbf{q}'). \quad (55a)$$

Here the differential operator  $K(\mathbf{q})$  consists of the harmonic and the anharmonic parts

$$K(\mathbf{q}) \equiv K_0(\mathbf{q}) + K'(\mathbf{q}), \quad (55b)$$

$$K_0(\mathbf{q}) \equiv \frac{i\hbar}{2} \frac{\partial}{\partial \mathbf{q}} \mathbf{G} \frac{\partial}{\partial \mathbf{q}} + i \frac{\partial}{\partial \mathbf{q}} \Omega \mathbf{q}, \quad (55c)$$

and

$$K'(\mathbf{q}) = i \frac{\partial}{\partial \mathbf{q}} \mathbf{v}(\mathbf{q}). \quad (55d)$$

$$\begin{aligned} \exp(Kt) &= \exp(K_0 t) \exp_+ \left[ \int_0^t dt K'[\tau] \right] \\ &= \exp(K_0 t) \left[ 1 + \int_0^t dt_1 K'[t_1] + \int_0^t dt_1 \int_0^{t_1} dt_2 K'[t_1] K'[t_2] + \dots \right], \end{aligned} \quad (59)$$

where

$$K'[\tau] \equiv \exp(-K_0 \tau) K' \exp(K_0 \tau). \quad (60)$$

The correlation function of Eq. (57) may be calculated without obtaining an explicit expression for  $P(\mathbf{q}, t; \mathbf{q}')$ . Making use of Eq. (58), we have

$$M_{ij}(t) = \int d\mathbf{q} q_i \exp(Kt) g(\mathbf{q}) q_j. \quad (61)$$

Substitution of Eq. (59) into Eq. (61) yields the perturbation expansion of the correlation function. Alternatively, the cumulant expansion may be used to generate a nonperturbative approximation for  $M(t)$ . This is done by postulating the following equation for  $M(t)$ :

$$\frac{dM(t)}{dt} = F(t) M(t), \quad (62a)$$

The relation between the quantities  $\mathbf{v}(\mathbf{q})$  in  $K'(\mathbf{q})$  and the anharmonic potential  $V(\mathbf{q})$  is further discussed in Appendix D.

## V. THE SELF-CONSISTENT EQUATIONS

We shall now apply the REM (55) to the calculation of the correlation functions

$$M_{ij}(t) = \langle Q_i(t) Q_j \rangle \quad (56)$$

which are relevant, e.g., to molecular vibrational spectra. Our procedure consists of three steps:

(1) To solve Eq. (45) with Eq. (44) for  $g(\mathbf{q})$ . This determines  $\mathbf{u}(\mathbf{q})$  in the REM and the initial condition (14).

(2) To solve the REM (55) for the generating function  $P(\mathbf{q}, t; \mathbf{q}')$  with the initial condition (14).

(3) To calculate the correlation functions by

$$M_{ij}(t) = \int d\mathbf{q} d\mathbf{q}' q_i q_j' P(\mathbf{q}, t; \mathbf{q}'), \quad (57)$$

where

$$d\mathbf{q} \equiv dq_1 \dots dq_N.$$

The first step is a purely static problem. Although we cannot usually find an exact expression for  $g(\mathbf{q})$ , it is not difficult to generate a reasonable approximation for the ground state distribution. We shall therefore suppose that we have solved step (1) and proceed to the second and third steps. The formal solution of the REM (55a) with the initial condition (14) is written as

$$P(\mathbf{q}, t; \mathbf{q}') = \exp[K(\mathbf{q})t] g(\mathbf{q}) \delta(\mathbf{q} - \mathbf{q}'). \quad (58)$$

The simplest way to evaluate Eq. (58) is by a perturbative expansion of the propagator where  $K'$  (the anharmonic part) serves as the perturbation, i.e.,

i.e.,

$$M(t) = \exp_+ \left[ \int_0^t d\tau F(\tau) \right] M(0). \quad (62b)$$

A perturbative expansion for  $F$  in terms of the anharmonicities ( $K'$ ) may be obtained by expanding  $M$  [Eq. (61)] in  $K'$  and using the relation  $F = \dot{M} M^{-1}$  [Eq. (62a)]. When the latter is substituted in Eq. (62b) it will generate a nonperturbative approximation for  $M(t)$ . Since we shall be primarily interested in cases whereby the effects of anharmonicities are very significant (e.g., transition from quasiperiodic to chaotic types of motion), we shall attempt to derive an improved *self-consistent equation* (SCE) for  $M(t)$ .

The self-consistent approach is based on the following idea: Let us consider a large system of  $\hat{N}$  harmonic oscillators  $X_\lambda$  ( $\hat{N} \gg N$ ) and imagine that our  $N$  coordinates  $Q_i$  ( $i = 1, \dots, N$ )

are linear combinations of these harmonic coordinates i.e.,

$$Q_i = \sum_{\lambda=1}^N c_{i\lambda} X_{\lambda}, \quad i = 1, \dots, N. \quad (63)$$

We shall further denote the  $N \times N$  correlation function matrix calculated for this effective harmonic system by  $\hat{M}(t)$ . It is clear that we can always construct a large enough harmonic system for which  $\hat{M}(t)$  will be identical to our original anharmonic correlation matrix  $M(t)$ . Making use of the exact eigenstates of the anharmonic system  $|\alpha\rangle$  with the eigenenergies  $E_{\alpha}$ , the correlation function  $M(t)$  of Eq. (56) at zero temperature is written as

$$M_{ij}(t) = \sum_{\alpha} \langle 0|Q_i|\alpha\rangle \langle \alpha|Q_j|0\rangle \exp\left[-\frac{i}{\hbar}(E_{\alpha} - E_0)t\right], \quad (64)$$

where  $|0\rangle$  is the ground state. On the other hand, the correlation function for a harmonic system at zero temperature is obtained from Eq. (36) as

$$\hat{M}_{ij}(t) = \sum_{\lambda=1}^N c_{i\lambda} c_{j\lambda} \frac{\hbar}{2\omega_{\lambda}} \exp(-i\omega_{\lambda}t). \quad (65)$$

Setting the number of harmonic oscillators in Eq. (65) equal to the number of the eigenstates in Eq. (64), one can always determine the parameters  $\omega_{\lambda}$  and  $c_{i\lambda}$  in Eq. (65) so that  $M_{ij}(t)$  of Eq. (64) is identical with  $\hat{M}_{ij}(t)$  of Eq. (65):

$$\left[ \text{i.e., } \omega_{\lambda} = \frac{1}{\hbar}(E_{\lambda} - E_0), \text{ and } c_{i\lambda} = \sqrt{2\omega_{\lambda}/\hbar} \langle 0|Q_i|\alpha\rangle \right].$$

This implies that, as long as we are concerned with the correlation functions  $M(t)$ , the true (anharmonic) generating function  $P$  in Eq. (57) may be replaced by the generating function  $\hat{P}$  of the harmonic system introduced above. We shall call  $\hat{P}(\mathbf{q}, t; \mathbf{q}')$  the effective generating function. It should be noted that the effective generating function depends on the same number of relevant variables  $Q_i$  (i.e.,  $N$ ) as the true generating function but that the number of oscillators (i.e.,  $\hat{N}$ ) is much larger since the number of *degrees of freedom* in the effective system is equal to the number of *states* in the original anharmonic system. It should further be noted that higher order correlation functions e.g.,  $\langle Q_i^2(t)Q_j \rangle$  etc., predicted by  $\hat{P}$  will be different from the actual ones given by  $P$ , only the  $\langle Q_i(t)Q_j \rangle$  correlation functions, which are of interest to us, will be the same. In Sec. III, we have shown that the generating function for such harmonic oscillators obeys the REM (33) or

$$\frac{\partial \hat{P}(\mathbf{q}, t; \mathbf{q}')}{\partial t} = \hat{K}(t) \hat{P}(\mathbf{q}, t; \mathbf{q}'), \quad (66a)$$

$$\hat{K}(t) = -\frac{\partial}{\partial \mathbf{q}} \hat{F}(t) \hat{M}(0) \frac{\partial}{\partial \mathbf{q}} - \frac{\partial}{\partial \mathbf{q}} \hat{F}(t) \mathbf{q}, \quad (66b)$$

where

$$\hat{F}(t) \equiv \hat{M}(t) \hat{M}^{-1}(t). \quad (66c)$$

The initial condition for  $\hat{P}$  is [in analogy with Eq. (14)]

$$\hat{P}(\mathbf{q}, 0; \mathbf{q}') = \hat{g}(\mathbf{q}) \delta(\mathbf{q} - \mathbf{q}'), \quad (66d)$$

$\hat{g}(\mathbf{q})$  being a multivariate Gaussian distribution. We have also shown in Sec. III that the generating function  $\hat{P}$  for harmonic systems is Gaussian. Therefore, the procedure described above may be viewed as a Gaussian approximation for  $P$ . The effective generating function  $\hat{P}$  is the Gaussian function

of  $\mathbf{q}$  and  $\mathbf{q}'$  whose correlation matrix  $\hat{M}(t)$  [Eq. (57)] is equal to that of the true generating function

$$M(t) = \hat{M}(t), \quad (67a)$$

i.e.,

$$\int d\mathbf{q} \mathbf{q} \exp(Kt) \hat{g}(\mathbf{q}) = \int d\mathbf{q} \mathbf{q} \exp_+ \left[ \int_0^t d\tau \hat{K}(\tau) \right] \hat{g}(\mathbf{q}). \quad (67b)$$

This equation forms the basis for the construction of our self-consistent equation (SCE).

Assuming that we know the exact  $\hat{M}(t)$ , we can use it to construct  $\hat{K}(t)$  [Eq. (66b)]. The operator  $K$  in the exact REM (55a) may then be repartitioned into this harmonic part  $\hat{K}(t)$  and the residual part

$$K \equiv \hat{K}(t) + \Delta \hat{K}(t). \quad (68)$$

Note that both  $\hat{K}$  and  $\Delta \hat{K}$  are time dependent although  $K$  itself is independent of time. We next expand the propagator  $\exp(Kt)$  in Eq. (58) in terms of  $\Delta K(t)$ :

$$\begin{aligned} \exp(Kt) &= \exp_+ \left[ \int_0^t d\tau \hat{K}(\tau) \right] \cdot \exp_+ \left[ \int_0^t dt \Delta \hat{K}(t) \right] \\ &= \exp_+ \left[ \int_0^t d\tau \hat{K}(\tau) \right] \cdot \left\{ 1 + \int_0^t dt_1 \Delta \hat{K}(t_1) \right. \\ &\quad \left. + \int_0^t dt_1 \int_0^{t_1} dt_2 \Delta \hat{K}(t_1) \Delta \hat{K}(t_2) + \dots \right\}. \end{aligned} \quad (69)$$

Substituting Eq. (69) into Eq. (67b), we get our most general form for the SCE (Appendix E):

$$\begin{aligned} \int d\mathbf{q} q_i \left\{ \exp_+ \left[ \int_0^t d\tau \Delta \hat{K}(\tau) \right] - 1 \right\} q_j g(\mathbf{q}) \\ = 0, \quad i, j = 1, 2, \dots, N, \end{aligned} \quad (70a)$$

where

$$\begin{aligned} \Delta \hat{K}(\tau) &\equiv \frac{\partial}{\partial \mathbf{q}} \left[ \frac{i\hbar}{2} \mathbf{G} + F(\tau) \mathbf{M}(0) \right] \frac{\partial}{\partial \mathbf{q}} \\ &\quad + \frac{\partial}{\partial \mathbf{q}} [i\Omega \mathbf{q} + F(\tau) \mathbf{q} + iv(\mathbf{q})], \end{aligned} \quad (70b)$$

$$\Delta \hat{K}(\tau) \equiv \exp_- \left[ - \int_0^{\tau} ds \hat{K}(s) \right] \Delta \hat{K}(\tau) \exp_+ \left[ \int_0^{\tau} ds \hat{K}(s) \right], \quad (70c)$$

and

$$\hat{K}(s) \equiv -\frac{\partial}{\partial \mathbf{q}} F(s) \left[ \mathbf{M}(0) \frac{\partial}{\partial \mathbf{q}} + \mathbf{q} \right]. \quad (70d)$$

In Eqs. (70), we have replaced  $\hat{M}(0)$  and  $\hat{F}(t)$  by  $M(0)$  and  $F(t)$ . This is a direct consequence of Eq. (67a).  $M(0)$  which is an input to Eqs. (70) may be calculated using Eq. (9), i.e.,

$$M_{ij}(0) = \int d\mathbf{q} q_i q_j g(\mathbf{q}). \quad (70e)$$

Equation (70) bears close formal similarity with a general time-domain SCE developed recently for mode-coupling problems in general.<sup>55</sup> Equation (70) is an *exact* closed self-consistent equation for  $F(t)$ . Note that we have  $N^2$  equations and  $N^2$  unknown functions  $F_{ij}(t)$ . Once we have solved for  $F(t)$ ,  $M(t)$  can be obtained by solving Eq. (62a):

$$\frac{dM(t)}{dt} = F(t)M(t). \quad (70f)$$

It should be noted that we have considered here all the elements of the matrix  $M(t)$  as the quantities which should be determined self-consistently. An alternative exact SCE may be obtained by taking into account only the diagonal elements  $M_{ii}(t)$  as the quantities to be determined self-consistently. In this case we shall have only  $N$  equations with  $N$  unknown  $F_{ii}(t)$ . ( $F_{ij}$  for  $i \neq j$  will be taken to be zero).

Approximate and simplified self-consistent equations may be obtained by truncating the time-ordered exponential in Eq. (70a) at a given order. For example, it is shown in Appendix E that, if we take into account the contribution of the time-ordered exponential up to the second-order cumulant, the self-consistent equations may be transformed into a set of simple autonomous differential equations by introducing new variables  $Y_\alpha(t)$  such that

$$F_{ij}(t) = -i\Omega'_{ij} - i \sum_{\alpha} B_{i,j,\alpha} Y_{\alpha}(t) \quad (71a)$$

with some known coefficients  $\Omega'_{ij}$  and  $B_{i,j,\alpha}$ .  $Y_{\alpha}(t)$  satisfy the following equations:

$$\frac{dY_{\alpha}(t)}{dt} = C_{\alpha} + i \sum_{\beta} D_{\alpha\beta} Y_{\beta}(t) + \sum_{\beta\gamma} L_{\alpha\beta\gamma} Y_{\beta}(t) Y_{\gamma}(t), \quad (71b)$$

where  $C_{\alpha}$ ,  $D_{\alpha\beta}$ , and  $L_{\alpha\beta\gamma}$  are again some known coefficients. (See Appendix E for the details.) The initial conditions for Eqs. (71b) are

$$Y_{\alpha}(0) = 0. \quad (71c)$$

Equation (71b) thus obtained is a prototype of nonlinear mode-coupling equations which appear in nonlinear hydrodynamics,<sup>32-37</sup> chemical reactions,<sup>56,57</sup> critical phenomena,<sup>38</sup> etc. If we rewrite it in the frequency domain, we get

$$i\omega Y_{\alpha}(\omega) = C_{\alpha} \delta(\omega) + i \sum_{\beta} D_{\alpha\beta} Y_{\beta}(\omega) + \sum_{\beta\gamma} L_{\alpha\beta\gamma} \int d\omega' Y_{\beta}(\omega - \omega') Y_{\gamma}(\omega'). \quad (72)$$

In this form it is isomorphous with the mode-coupling formulation of Kawasaki.<sup>32-34</sup> There is an extensive literature on the dynamical behavior of the solutions of such equations.<sup>6-10,58</sup> It is well known that this type of equation can show various stages of periodic or chaotic motion depending upon parameters and initial conditions. If the solution of Eq. (71b) shows chaotic behavior, this leads to chaotic behavior of the correlation function  $M(t)$  by Eq. (70 f). Thus, the investigation of Eq. (71) for various anharmonic systems will allow us to discuss the regular vs chaotic behavior in molecular vibrational spectra.

The mode-coupling equation (72) may be solved by iteration starting from the harmonic (linear) equation ( $L_{\alpha\beta\gamma} = 0$ ). In each step, new functions  $Y_{\alpha}(\omega)$  are obtained from Eq. (72) by substituting the old functions  $Y_{\alpha}(\omega)$  of the previous step into the bilinear (convolution) term in Eq. (72). An obvious criterion for stochasticity suggested by this procedure is connected to the convergence properties of our nonlinear iteration procedure [Eq. (72)]. Rapid convergence implies that the spectrum of the anharmonic system is equivalent to that of a harmonic system with a few more degrees of freedom. Slow convergence or divergence may

imply that we need infinite number of harmonic degrees of freedom to reproduce the spectrum. This may serve as an operational criterion for quantum chaos.

## APPENDIX A: DERIVATION OF EQ. (17)

We introduce a complete set of polynomials which satisfy the orthonormality conditions with the weighting function being given by the equilibrium distribution  $g(q)$ , i.e.,

$$\int dq g(q) \phi_n(q) \phi_m(q) = \delta_{nm}. \quad (A1)$$

The delta function  $\delta(q - Q)$  is expanded in this basis set as

$$\delta(q - Q) = \sum g(q) \phi_n(q) \phi_n(Q) \quad (A2)$$

so that the matrix  $\chi(q, q')$  of Eq. (13) is written as

$$\chi(q, q', t) = g(q)g(q') \sum_n \sum_m \phi_n(q) \phi_m(q') \langle \phi_n(Q(t)) \phi_m(Q) \rangle. \quad (A3)$$

It can be easily shown by using standard techniques<sup>43-45</sup> that when the equilibrium distribution  $g(q)$  is a Gaussian, i.e.,

$$g(q) = \frac{1}{\sqrt{2\pi}\Delta} \exp\left[-\frac{q^2}{2\Delta^2}\right], \quad (A4)$$

with

$$\Delta^2 = \langle Q^2 \rangle, \quad (A5)$$

then the orthonormal polynomials  $\phi_n(q)$  are given by

$$\phi_n(q) = \frac{1}{\sqrt{2^n n!}} H_n\left(\frac{q}{\sqrt{2\Delta}}\right), \quad (A6)$$

where  $H_n(x)$  are the Hermite polynomials<sup>46</sup>

$$H_n(x) = (-1)^n \exp(x^2) \frac{d^n}{dx^n} \exp(-x^2). \quad (A7)$$

By using properties of the Hermite polynomials, one can show the following equations:

$$\frac{\partial \phi_n(q)}{\partial q} = \frac{\sqrt{n}}{\Delta} \phi_{n-1}(q), \quad (A8)$$

$$\frac{\partial}{\partial q} [\phi_n(q)g(q)] = -\frac{\sqrt{n}}{\Delta} \phi_{n+1}(q)g(q). \quad (A9)$$

We now return to Eq. (A3). It can be easily shown by using standard many-body techniques<sup>43-46</sup> that

$$\langle \phi_n(Q(t)) \phi_m(Q) \rangle = \sum_{r=0}^{\min(n,m)} \frac{1}{r!} \left\langle \frac{\partial^r \phi_n(Q)}{\partial Q^r} \right\rangle \left\langle \frac{\partial^r \phi_m(Q)}{\partial Q^r} \right\rangle \langle Q(t)Q \rangle^r. \quad (A10)$$

By using Eq. (A8), we then have

$$\left\langle \frac{\partial^r \phi_n(Q)}{\partial Q^r} \right\rangle = \frac{1}{\Delta^r} \sqrt{\frac{n!}{(n-r)!}} \langle \phi_{n-r}(Q) \rangle. \quad (A11)$$

However, from the orthogonality condition (A1)

$$\begin{aligned} \langle \phi_{n-r}(Q) \rangle &= \int dq \phi_{n-r}(q) g(q) \\ &= \int dq \phi_{n-r}(q) \phi_0(q) g(q) = \delta_{n-r,0}. \end{aligned} \quad (A12)$$

We therefore obtain from Eqs. (A10)–(A12)

$$\langle \phi_n(Q(t))\phi_m(Q) \rangle = \delta_{nm} [\rho(t)]^n, \quad (\text{A13})$$

$$\rho(t) \equiv \langle Q(t)Q \rangle / \Delta^2. \quad (\text{A14})$$

Substituting Eq. (A13) into Eq. (A3), we get

$$\chi(q, q', t) = g(q)g(q') \sum_n [\rho(t)]^n \phi_n(q)\phi_n(q'), \quad (\text{A15})$$

so that

$$\chi(q, q'', t) = g(q)g(q'') \sum_n n [\rho(t)]^{n-1} \dot{\rho}(t) \phi_n(q)\phi_n(q'') \quad (\text{A16})$$

and

$$\chi^{-1}(q'', q', t) = \sum_n [\rho(t)]^{-n} \phi_n(q'')\phi_n(q'). \quad (\text{A17})$$

Here the inverse  $\chi^{-1}$  of a matrix  $\chi$  is defined by the equation

$$\int dq'' \chi(q, q'') \chi^{-1}(q'', q') = \delta(q - q'). \quad (\text{A18})$$

Using Eqs. (A16) and (A17), we may calculate  $R$  [Eq. (12)]:

$$R(q, q', t) = g(q) \frac{\dot{\rho}}{\rho} \sum_n n \phi_n(q)\phi_n(q'). \quad (\text{A19})$$

Then, the REM (11) is written as

$$\frac{\partial P(q, t; q')}{\partial t} = \frac{\dot{\rho}}{\rho} \int dq'' \sum_n n g(q)\phi_n(q)\phi_n(q'') P(q'', t; q'). \quad (\text{A20})$$

By using Eq. (A9), Eq. (A20) can be rewritten in the form

$$\begin{aligned} \frac{\partial P(q, t; q')}{\partial t} &= \frac{\dot{\rho}}{\rho} \Delta^2 \int dq'' \sum_n \left[ \frac{\partial}{\partial q} g(q)\phi_n(q) \right] \\ &\times \left[ \frac{\partial}{\partial q''} g(q'')\phi_n(q'') \right] \frac{P(q'', t; q')}{g(q'')} \end{aligned} \quad (\text{A21})$$

and by partial integration we get

$$\begin{aligned} \frac{\partial P(q, t; q')}{\partial t} &= -\frac{\dot{\rho}}{\rho} \Delta^2 \frac{\partial}{\partial q} \int dq'' \sum_n g(q)\phi_n(q)g(q'')\phi_n(q'') \\ &\times \frac{\partial}{\partial q''} \frac{P(q'', t; q')}{g(q'')}. \end{aligned} \quad (\text{A22})$$

Making use of

$$\sum_n g(q)\phi_n(q)\phi_n(q'') = \delta(q - q''), \quad (\text{A23})$$

we finally get

$$\frac{\partial P(q, t; q')}{\partial t} = -\Delta^2 \frac{\dot{\rho}}{\rho} \frac{\partial}{\partial q} g(q) \frac{\partial}{\partial q} \frac{P(q, t; q')}{g(q)}. \quad (\text{A24})$$

Equation (A24) may be easily recast in the form of Eq. (17) by making use of Eq. (A4).

## APPENDIX B: DERIVATION OF EQ. (34)

Let us introduce the Fourier transforms of  $g(\mathbf{q})$  and  $P(\mathbf{q}, t; \mathbf{q}')$ :

$$\begin{aligned} g(\mathbf{k}) &\equiv \int d\mathbf{q} \exp(i\tilde{\mathbf{k}}\mathbf{q})g(\mathbf{q}) \\ &= \langle \exp(i\tilde{\mathbf{k}}\mathbf{Q}) \rangle, \end{aligned} \quad (\text{B1})$$

$$\begin{aligned} P(\mathbf{k}, \mathbf{k}', t) &\equiv \int d\mathbf{q} d\mathbf{q}' \exp(i\tilde{\mathbf{k}}\mathbf{q} + i\tilde{\mathbf{k}}'\mathbf{q}') P(\mathbf{q}, t; \mathbf{q}') \\ &= \langle \exp[i\tilde{\mathbf{k}}\mathbf{Q}(t)] \exp[i\tilde{\mathbf{k}}'\mathbf{Q}(0)] \rangle. \end{aligned} \quad (\text{B2})$$

Using the standard techniques<sup>43-46</sup>, Eqs. (B1) and (B2) reduce to

$$g(\mathbf{k}) = \exp[-\frac{1}{2} \tilde{\mathbf{k}}\mathbf{M}(0)\mathbf{k}], \quad (\text{B3})$$

$$P(\mathbf{k}, \mathbf{k}', t) = \exp[-\frac{1}{2} \{ \tilde{\mathbf{k}}\mathbf{M}(0)\mathbf{k} + \tilde{\mathbf{k}}'\mathbf{M}(0)\mathbf{k}' + 2\tilde{\mathbf{k}}\mathbf{M}(t)\mathbf{k}' \}], \quad (\text{B4})$$

where

$$\mathbf{M}(t) \equiv \langle \mathbf{Q}(t)\tilde{\mathbf{Q}}(0) \rangle. \quad (\text{B5})$$

From Eq. (B4), we get

$$\frac{\partial}{\partial t} P(\mathbf{k}, \mathbf{k}', t) = -\tilde{\mathbf{k}}\dot{\mathbf{M}}(t)\mathbf{k}' P(\mathbf{k}, \mathbf{k}', t) \quad (\text{B6})$$

and

$$\frac{\partial}{\partial \mathbf{k}} P(\mathbf{k}, \mathbf{k}', t) = -[\mathbf{M}(0)\mathbf{k} + \mathbf{M}(t)\mathbf{k}'] P(\mathbf{k}, \mathbf{k}', t). \quad (\text{B7})$$

By eliminating the term  $\mathbf{k}' P(\mathbf{k}, \mathbf{k}', t)$  from Eqs. (B6) and (B7), we obtain

$$\frac{\partial}{\partial t} P(\mathbf{k}, \mathbf{k}', t) = \tilde{\mathbf{k}}\dot{\mathbf{M}}(t)\mathbf{M}^{-1}(t) \left[ \mathbf{M}(0)\mathbf{k} + \frac{\partial}{\partial \mathbf{k}} \right] P(\mathbf{k}, \mathbf{k}', t). \quad (\text{B8})$$

The Fourier transformation of Eq. (B8) into  $\mathbf{q}$  space yields

$$\frac{\partial}{\partial t} P(\mathbf{q}, t; \mathbf{q}') = -\frac{\partial}{\partial \mathbf{q}} \dot{\mathbf{M}}(t)\mathbf{M}^{-1}(t) \left[ \mathbf{M}(0) \frac{\partial}{\partial \mathbf{q}} + \mathbf{q} \right] P(\mathbf{q}, t; \mathbf{q}'), \quad (\text{B9})$$

which is identical to Eq. (33). From Eqs. (B3) and (B4), one can also easily get the explicit expressions of Eqs. (31) and (34) by performing a Fourier transformation.

## APPENDIX C: REM FOR ANHARMONIC OSCILLATORS AT ZERO TEMPERATURE

Since at zero temperature the equilibrium average is simply the expectation value for the ground state  $|0\rangle$ , the generating function is calculated as (we put  $\hbar = 1$ )

$$\begin{aligned} P(\mathbf{q}, t; \mathbf{q}') &= \langle 0 | \delta(\mathbf{q} - \mathbf{Q}(t)) \delta(\mathbf{q}' - \mathbf{Q}) | 0 \rangle \\ &= \langle 0 | \exp(iHt) \delta(\mathbf{q} - \mathbf{Q}) \exp(-iHt) \delta(\mathbf{q}' - \mathbf{Q}) | 0 \rangle \\ &= \exp(iE_0 t) \langle 0 | \delta(\mathbf{q} - \mathbf{Q}) \exp(-iHt) \delta(\mathbf{q}' - \mathbf{Q}) | 0 \rangle, \end{aligned} \quad (\text{C1})$$

where  $E_0$  is the ground state energy. We introduce the eigenvectors for the coordinate variables  $\mathbf{Q} = (Q_1, \dots, Q_n)$ :

$$\mathbf{Q}|\mathbf{q}\rangle = \mathbf{q}|\mathbf{q}\rangle. \quad (\text{C2})$$

By using the completeness condition



$$\int d\mathbf{q} |\mathbf{q}\rangle \langle \mathbf{q}| = 1, \quad (\text{C3})$$

we rewrite Eq. (C1) as follows:

$$\begin{aligned} P(\mathbf{q}, t; \mathbf{q}') &= \exp(iE_0 t) \langle 0 | \delta(\mathbf{q} - \mathbf{Q}) \int d\mathbf{q}'' |\mathbf{q}''\rangle \langle \mathbf{q}'' | \exp(-iHt) \delta(\mathbf{q}' - \mathbf{Q}) | 0 \rangle \\ &= \exp(iE_0 t) \int d\mathbf{q}'' \langle 0 | \mathbf{q}'' \rangle \delta(\mathbf{q} - \mathbf{q}'') \langle \mathbf{q}'' | \exp(-iHt) \delta(\mathbf{q}' - \mathbf{Q}) | 0 \rangle \\ &= \Psi_0(\mathbf{q}) \langle \mathbf{q} | \exp[-i(H - E_0)t] \delta(\mathbf{q}' - \mathbf{Q}) | 0 \rangle, \end{aligned} \quad (\text{C4})$$

where

$$\Psi_0(\mathbf{q}) \equiv \langle 0 | \mathbf{q} \rangle$$

is the ground state wave function. Differentiating Eq. (C4) with respect to  $t$ , we get

$$\frac{\partial P(\mathbf{q}, t; \mathbf{q}')}{\partial t} = -i \Psi_0(\mathbf{q}) \langle \mathbf{q} | (H - E_0) \exp[-i(H - E_0)t] \delta(\mathbf{q}' - \mathbf{Q}) | 0 \rangle. \quad (\text{C5})$$

By using the local coordinates representation of the Hamiltonian

$$\langle \mathbf{q} | H(\mathbf{P}, \mathbf{Q}) | \Psi \rangle = H\left(-i\frac{\partial}{\partial \mathbf{q}}, \mathbf{q}\right) \langle \mathbf{q} | \Psi \rangle, \quad (\text{C6})$$

Eq. (C5) is written as

$$\frac{\partial P(\mathbf{q}, t; \mathbf{q}')}{\partial t} = -i \Psi_0(\mathbf{q}) \left[ H\left(-i\frac{\partial}{\partial \mathbf{q}}, \mathbf{q}\right) - E_0 \right] \frac{P(\mathbf{q}, t; \mathbf{q}')}{\Psi_0(\mathbf{q})}. \quad (\text{C7})$$

The equilibrium distribution  $g(\mathbf{q})$  is given by

$$g(\mathbf{q}) = \langle 0 | \delta(\mathbf{q} - \mathbf{Q}) | 0 \rangle = |\langle 0 | \mathbf{q} \rangle|^2 = |\Psi_0(\mathbf{q})|^2. \quad (\text{C8})$$

Hereafter, without loss of generality, the ground state wave function  $\Psi_0(\mathbf{q})$  is chosen to be real.<sup>54</sup> We write Eq. (C7) in the form

$$\begin{aligned} \frac{\partial P(\mathbf{q}, t; \mathbf{q}')}{\partial t} &= i \Psi_0(\mathbf{q}) [H - E_0] \Psi_0(\mathbf{q}) \frac{P(\mathbf{q}, t; \mathbf{q}')}{g(\mathbf{q})} \\ &= -i \Psi_0(\mathbf{q}) [H\Psi_0(\mathbf{q}) - (H\Psi_0(\mathbf{q}))] \frac{P(\mathbf{q}, t; \mathbf{q}')}{g(\mathbf{q})}. \end{aligned} \quad (\text{C9})$$

Here the parentheses of  $(H\Psi_0)$  implies that the differential operator  $H$  acts only on the functions of  $\mathbf{q}$  which are inside the parentheses. For the Hamiltonian (41):

$$H\Psi_0 - (H\Psi_0) = -\frac{1}{2} \left[ \frac{\partial}{\partial \mathbf{q}} \mathbf{G} \frac{\partial}{\partial \mathbf{q}} \Psi_0 - \left( \frac{\partial}{\partial \mathbf{q}} \mathbf{G} \frac{\partial}{\partial \mathbf{q}} \Psi_0 \right) \right], \quad (\text{C10})$$

so that we can write

$$\begin{aligned} \Psi_0 [H\Psi_0 - (H\Psi_0)] &= -\frac{1}{2} \Psi_0 \left[ \Psi_0 \frac{\partial}{\partial \mathbf{q}} \mathbf{G} \frac{\partial}{\partial \mathbf{q}} + 2 \left( \frac{\partial \Psi_0}{\partial \mathbf{q}} \right) \mathbf{G} \frac{\partial}{\partial \mathbf{q}} \right] \\ &= -\frac{1}{2} \frac{\partial}{\partial \mathbf{q}} \Psi_0^2 \mathbf{G} \frac{\partial}{\partial \mathbf{q}}. \end{aligned} \quad (\text{C11})$$

We therefore finally get

$$\frac{\partial P(\mathbf{q}, t; \mathbf{q}')}{\partial t} = \frac{i\hbar}{2} \frac{\partial}{\partial \mathbf{q}} \mathbf{G} g(\mathbf{q}) \frac{\partial}{\partial \mathbf{q}} \frac{P(\mathbf{q}, t; \mathbf{q}')}{g(\mathbf{q})}, \quad (\text{C12})$$

which is equivalent to Eq. (42).

#### APPENDIX D: EVALUATION OF $u(\mathbf{q})$

Let us start from the Schrödinger equation for the ground state wave function  $\Psi_0(\mathbf{q})$ :

$$\left[ -\frac{\hbar^2}{2} \frac{\partial}{\partial \mathbf{q}} \mathbf{G} \frac{\partial}{\partial \mathbf{q}} + U(\mathbf{q}) - E_0 \right] \Psi_0(\mathbf{q}) = 0 \quad (\text{D1})$$

or

$$\frac{\hbar^2}{2} \frac{1}{\Psi_0(\mathbf{q})} \frac{\partial}{\partial \mathbf{q}} \mathbf{G} \frac{\partial}{\partial \mathbf{q}} \Psi_0(\mathbf{q}) = U(\mathbf{q}) - E_0. \quad (\text{D2})$$

One can easily show the following identity:

$$\begin{aligned} \frac{1}{\Psi_0} \frac{\partial}{\partial \mathbf{q}} \mathbf{G} \frac{\partial}{\partial \mathbf{q}} \Psi_0 &= \frac{1}{2} \frac{\partial}{\partial \mathbf{q}} \mathbf{G} \frac{\partial}{\partial \mathbf{q}} \frac{\partial}{\partial \mathbf{q}} \Psi_0^2 \\ &+ \frac{1}{4} \frac{1}{\Psi_0^4} \left( \frac{\partial \Psi_0^2}{\partial \mathbf{q}} \right) \mathbf{G} \left( \frac{\partial \Psi_0^2}{\partial \mathbf{q}} \right). \end{aligned} \quad (\text{D3})$$

By using Eq. (D3) and

$$g(\mathbf{q}) = \Psi_0(\mathbf{q})^2,$$

Equation (D2) is written as

$$\frac{\hbar^2}{2} \left[ \frac{1}{2} \frac{\partial}{\partial \mathbf{q}} \mathbf{G} \frac{\partial}{\partial \mathbf{q}} \ln g(\mathbf{q}) + \frac{1}{4} \frac{\partial \ln g(\mathbf{q})}{\partial \mathbf{q}} \mathbf{G} \frac{\partial \ln g(\mathbf{q})}{\partial \mathbf{q}} \right] = U(\mathbf{q}) - E_0. \quad (\text{D4})$$

If we substitute

$$\mathbf{u}(\mathbf{q}) \equiv -\frac{\hbar}{2} \mathbf{G} \left( \frac{\partial}{\partial \mathbf{q}} \ln g(\mathbf{q}) \right), \quad (\text{D5})$$

then Eq. (D4) reads

$$-\frac{\hbar}{2} \frac{\partial}{\partial \mathbf{q}} \mathbf{u}(\mathbf{q}) + \frac{1}{2} \tilde{\mathbf{u}}(\mathbf{q}) \mathbf{G}^{-1} \mathbf{u}(\mathbf{q}) = U(\mathbf{q}) - E_0, \quad (\text{D6})$$

which is identical to Eq. (45). The quantity  $\mathbf{u}(\mathbf{q})$  satisfies

$$\langle \mathbf{u}(\mathbf{q}) \rangle \equiv \int d\mathbf{q} g(\mathbf{q}) \mathbf{u}(\mathbf{q}) = 0. \quad (\text{D7})$$

This may be shown as follows:

$$\begin{aligned} \int d\mathbf{q} g(\mathbf{q}) \mathbf{u}(\mathbf{q}) &= - \int d\mathbf{q} g(\mathbf{q}) \frac{\hbar}{2} \mathbf{G} \frac{\partial}{\partial \mathbf{q}} \ln g(\mathbf{q}) \\ &= -\frac{\hbar}{2} \mathbf{G} \int d\mathbf{q} \frac{\partial}{\partial \mathbf{q}} g(\mathbf{q}) \\ &= 0. \end{aligned}$$

Here we have used the condition

$$\lim_{|\mathbf{q}| \rightarrow \infty} g(\mathbf{q}) = 0. \quad (\text{D8})$$

In the case of a harmonic potential

$$U(\mathbf{q}) = \frac{1}{2} \tilde{\mathbf{q}} \tilde{\mathbf{\Omega}} \mathbf{G}^{-1} \mathbf{\Omega} \mathbf{q}, \quad (\text{D9})$$

the solution of Eq. (D6) is

$$\mathbf{u}(\mathbf{q}) = \mathbf{\Omega} \mathbf{q}. \quad (\text{D10})$$

When an anharmonic potential is added to this harmonic part as

$$U(\mathbf{q}) = \frac{1}{2} \tilde{\mathbf{q}} \tilde{\mathbf{\Omega}} \mathbf{G}^{-1} \mathbf{\Omega} \mathbf{q} + \lambda V(\mathbf{q}), \quad (\text{D11})$$

$\mathbf{u}(\mathbf{q})$  is written in the form

$$\mathbf{u}(\mathbf{q}) = \mathbf{\Omega} \mathbf{q} + \mathbf{v}(\mathbf{q}). \quad (\text{D12})$$

Let us expand  $\mathbf{v}(\mathbf{q})$  in terms of the anharmonicity parameter  $\lambda$ :

$$\mathbf{v}(\mathbf{q}) = \sum_{m=1}^{\infty} \lambda^m \mathbf{v}^{(m)}(\mathbf{q}). \quad (\text{D13})$$

Substituting Eqs. (D13) and (D12) into Eq. (D6), one gets equations for each order in  $\lambda$ . The first order equation is

$$\frac{\hbar}{2} \frac{\partial}{\partial \mathbf{q}} \mathbf{v}^{(1)}(\mathbf{q}) + \tilde{\mathbf{q}} \tilde{\mathbf{\Omega}} \mathbf{G}^{-1} \mathbf{v}^{(1)}(\mathbf{q}) = V(\mathbf{q}) - \Delta E_0^{(1)}, \quad (\text{D14})$$

where  $\Delta E_0^{(1)}$  is the first order correction of the ground state energy. This equation indicates that, if  $V(\mathbf{q})$  is a  $p$ th order polynomial of  $q_i$ 's then  $\mathbf{v}^{(1)}(\mathbf{q})$  must be  $(p-1)$ th order polynomials. For example, if the anharmonic potential  $V(\mathbf{q})$  is cubic, i.e.,

$$V(\mathbf{q}) = \sum_{ijk} V_{ijk} q_i q_j q_k, \quad (\text{D15})$$

where  $V_{ijk}$  is a symmetric tensor, then, by inspection, the solution of Eq. (D14) is in a quadratic form

$$v_i^{(1)}(\mathbf{q}) = \sum_{jk} v_{ijk} q_j q_k + \text{const.} \quad (\text{D16})$$

From Eqs. (D5) and (D12), the coefficients  $v_{ijk}$  should be written in the form

$$v_{ijk} = \sum_l G_{il} S_{ljk}, \quad (\text{D17})$$

where  $S_{ljk}$  is a symmetric tensor which is invariant to permutation of its indices. Substituting Eqs. (D15)–(D17) into Eq. (D14), one obtains

$$2 \sum_l (S_{jkl} \Omega_{li} + S_{ikl} \Omega_{lj} + S_{ijl} \Omega_{lk}) = 6V_{ijk}. \quad (\text{D18})$$

If we use the normal mode coordinates with which the harmonic part of the potential is written in the form in Eq. (15), then  $G_{ij} = \delta_{ij}$  and  $\Omega_{ij} = \delta_{ij} \omega_i$ , so that Eqs. (D17) and (D18) yield

$$v_{ijk} = \frac{V_{ijk}}{\frac{1}{3}(\omega_i + \omega_j + \omega_k)}. \quad (\text{D19})$$

From Eqs. (D7) and (D12), we have the following identity:

$$\langle \mathbf{v}(\mathbf{q}) \rangle = -\mathbf{\Omega} \langle \mathbf{q} \rangle. \quad (\text{D20})$$

Therefore, if we choose the origin of the coordinates so that  $\langle \mathbf{q} \rangle = 0$ , then  $\langle \mathbf{v}(\mathbf{q}) \rangle = 0$ . Thus, Eq. (D16) may be written, including a constant term,

$$v_i^{(1)}(\mathbf{q}) = \sum_{jk} \frac{V_{ijk}}{\frac{1}{3}(\omega_i + \omega_j + \omega_k)} (q_j q_k - \langle q_j q_k \rangle). \quad (\text{D21})$$

Highest order terms in Eq. (D13) can be obtained successively. It can be shown that the  $m$ th order term  $v_i^{(m)}(\mathbf{q})$  is a  $\{m(p-2)+1\}$ th order polynomial if the potential  $V(\mathbf{q})$  is a  $p$ th order polynomial in  $q_i$ 's.

## APPENDIX E: THE MODE COUPLING EQUATIONS

First we shall show that Eq. (70a) is equivalent to Eq. (67). By making use of the expansion of Eq. (69),  $\mathbf{M}(t)$  of Eq. (61) is written as

$$\begin{aligned} \mathbf{M}(t) &= \int d\mathbf{q} \mathbf{q} \exp_+ \left[ \int_0^t d\tau \hat{K}(\tau) \right] \\ &\times \exp_+ \left[ \int_0^t d\tau \Delta \hat{K}(\tau) \right] \mathbf{q} g(\mathbf{q}), \end{aligned} \quad (\text{E1})$$

where, from Eqs. (66b), (66c), and (67a)  $\hat{K}$  is written as

$$\hat{K}(\tau) = -\frac{\partial}{\partial \mathbf{q}} F(\tau) \mathbf{M}(0) \frac{\partial}{\partial \mathbf{q}} - \frac{\partial}{\partial \mathbf{q}} F(\tau) \mathbf{q} \quad (\text{E2})$$

and  $\Delta \hat{K}(\tau)$  is given by Eqs. (70b) and (70c). By partial integration, the operator  $\hat{K}(\tau)$  in Eq. (E1) may be replaced by its

adjoint operator  $\hat{K}^{\dagger}(\tau)$  which acts on functions of  $\mathbf{q}$  to the left:

$$\hat{K}^{\dagger}(\tau) = -\frac{\partial}{\partial \mathbf{q}} F(\tau) \mathbf{M}(0) \frac{\partial}{\partial \mathbf{q}} + \frac{\partial}{\partial \mathbf{q}} F(\tau) \mathbf{q}. \quad (\text{E3})$$

It can be easily shown that

$$\mathbf{q} \exp_+ \left[ \int_0^t d\tau \hat{K}^{\dagger}(\tau) \right] = \exp_+ \left[ \int_0^t d\tau F(\tau) \right] \mathbf{q}, \quad (\text{E4})$$

so that Eq. (E1) is rewritten as

$$\mathbf{M}(t) = \exp_+ \left[ \int_0^t d\tau F(\tau) \right] \int d\mathbf{q} \mathbf{q} \exp_+ \left[ \int_0^t d\tau \Delta \hat{K}[\tau] \right] \hat{\mathbf{q}} g(\mathbf{q}). \quad (\text{E5})$$

On the other hand, from Eq. (62a),  $\mathbf{M}(t)$  is written as

$$\mathbf{M}(t) = \exp_+ \left[ \int_0^t d\tau F(\tau) \right] \mathbf{M}(0), \quad (\text{E6})$$

where

$$\mathbf{M}(0) = \int d\mathbf{q} \mathbf{q} \hat{\mathbf{q}} g(\mathbf{q}). \quad (\text{E7})$$

From Eqs. (E5)–(E7) we obtain

$$\int d\mathbf{q} \mathbf{q} \exp_+ \left[ \int_0^t d\tau \Delta \hat{K}[\tau] \right] \hat{\mathbf{q}} g(\mathbf{q}) = \int d\mathbf{q} \mathbf{q} \hat{\mathbf{q}} g(\mathbf{q}), \quad (\text{E8})$$

which is equivalent to Eq. (70a).

We now approximate the self-consistent equation (E8). First, we replace the distribution  $g(\mathbf{q})$  by the effective Gaussian distribution

$$\hat{g}(\mathbf{q}) = \frac{1}{\sqrt{(2\pi)^N \det \mathbf{M}(0)}} \exp \left[ -\frac{1}{2} \hat{\mathbf{q}} \mathbf{M}^{-1}(0) \hat{\mathbf{q}} \right]. \quad (\text{E9})$$

Next, postulating the left-hand side of Eq. (E8) to be in the form

$$\exp_+ \left[ \int_0^t d\tau S(\tau) \right] \mathbf{M}(0), \quad (\text{E10})$$

we calculate  $S(t)$  up to the second order in  $\Delta \hat{K}$ :

$$S(t) = S^{(1)}(t) + S^{(2)}(t). \quad (\text{E11})$$

Note that the self-consistent condition Eq. (E8) is equivalent to

$$S(t) \equiv 0. \quad (\text{E12})$$

By comparing the expansion of Eq. (E10) and that of the left-hand side of Eq. (E8) term by term, the first and the second order terms in Eq. (E11) can be written as

$$S^{(1)}(t) = \langle \mathbf{q} \Delta \hat{K}[t] \hat{\mathbf{q}} \rangle \mathbf{M}^{-1}(0), \quad (\text{E13a})$$

$$S^{(2)}(t) = \int_0^t ds \left[ \langle \mathbf{q} \Delta \hat{K}[t] \Delta \hat{K}[s] \hat{\mathbf{q}} \rangle - \langle \mathbf{q} \Delta \hat{K}[t] \hat{\mathbf{q}} \rangle \mathbf{M}^{-1}(0) \langle \mathbf{q} \Delta \hat{K}[s] \hat{\mathbf{q}} \rangle \right] \mathbf{M}^{-1}(0), \quad (\text{E13b})$$

where

$$\langle \dots \rangle \equiv \int d\mathbf{q} \dots \hat{g}(\mathbf{q}). \quad (\text{E13c})$$

By using Eq. (E4) and

$$\begin{aligned} \exp_+ \left[ \int_0^t d\tau \hat{K}(\tau) \right] g(\mathbf{q}) \hat{\mathbf{q}} &= g(\mathbf{q}) \hat{\mathbf{q}} \mathbf{M}^{-1}(0) \\ &\times \exp_+ \left[ \int_0^t d\tau F(\tau) \right] \mathbf{M}(0) \end{aligned} \quad (\text{E14})$$

and also the adjoint operator of  $\Delta \hat{K}(t)$

$$\begin{aligned} \overleftarrow{\Delta \hat{K}}(t) &= \frac{\partial}{\partial \mathbf{q}} \left[ \frac{i\hbar}{2} \mathbf{G} + F(t) \mathbf{M}(0) \right] \frac{\partial}{\partial \mathbf{q}} \\ &- \frac{\partial}{\partial \mathbf{q}} [i\Omega + F(t)] \mathbf{q} - i \frac{\partial}{\partial \mathbf{q}} \mathbf{v}(\mathbf{q}), \end{aligned} \quad (\text{E15})$$

Eqs. (E13) can be calculated as

$$\begin{aligned} S^{(1)}(t) &= \exp_- \left[ - \int_0^t d\tau F(\tau) \right] \\ &\times [ -i\Omega - F(t) - i\Delta \Omega ] \exp_+ \left[ \int_0^t d\tau F(\tau) \right], \end{aligned} \quad (\text{E16a})$$

and

$$\begin{aligned} S^{(2)}(t) &= \exp_- \left[ \int_0^t d\tau F(\tau) \right] \int_0^t ds \langle [ -iv(\mathbf{q}) - i\Delta \Omega \mathbf{q} ] \\ &\times \exp_+ \left[ \int_s^t d\tau \hat{K}(\tau) \right] \Delta \hat{K}(s) \hat{\mathbf{q}} \rangle \\ &\times \mathbf{M}^{-1}(0) \exp_+ \left[ \int_0^s d\tau F(\tau) \right], \end{aligned} \quad (\text{E16b})$$

where

$$\Delta \Omega \equiv \langle \mathbf{v}(\mathbf{q}) \hat{\mathbf{q}} \rangle \mathbf{M}^{-1}(0). \quad (\text{E16c})$$

From Eqs. (E16), our self-consistent equation (E12) in this approximation [Eq. (E11)] is obtained as

$$\begin{aligned} F(t) &= -i(\Omega + \Delta \Omega) - i \int_0^t ds \langle [\Delta \Omega \mathbf{q} + \mathbf{v}(\mathbf{q})] \\ &\times \exp_+ \left[ \int_s^t d\tau \hat{K}(\tau) \right] \Delta \hat{K}(s) \hat{\mathbf{q}} \rangle \mathbf{M}^{-1}(0) \\ &\times \exp_- \left[ - \int_s^t d\tau F(\tau) \right]. \end{aligned} \quad (\text{E17})$$

Let us consider the case where the anharmonic term  $\mathbf{v}(\mathbf{q})$  in the REM (55) has the form

$$v_i(\mathbf{q}) = \sum_{v_1, \dots, v_m} V_{i v_1 \dots v_m} (q_{v_1} \dots q_{v_m} - \langle q_{v_1} \dots q_{v_m} \rangle), \quad (\text{E18})$$

where the second term guarantees that  $\langle \mathbf{v}(\mathbf{q}) \rangle = 0$  as mentioned in Appendix D. Hereafter, we omit the symbol of summation over suffixes according to the standard tensor notation. We define the following quantities:

$$\begin{aligned} Y(t)_{v_1 \dots v_j}^{(r)} &\equiv \int_0^t ds \langle q_{v_1} \dots q_{v_j} \exp_+ \left[ \int_s^t d\tau \hat{K}(\tau) \right] \Delta \hat{K}(s) q_k \rangle \\ &\times \left( \mathbf{M}^{-1}(0) \exp_- \left[ - \int_s^t d\tau F(\tau) \right] \right)_{kj}. \end{aligned} \quad (\text{E19})$$

Then the self-consistent equation (E17) can be written in the form

$$F_{ij}(t) = -i(\Omega + \Delta \Omega)_{ij} - i(\Delta \Omega)_{il} Y(t)_{lj}^{(1)} - iV_{i v_1 \dots v_m} Y(t)_{v_1 \dots v_m}^{(m)}. \quad (\text{E20})$$

By differentiating Eq. (E19) and noting that

$$\prod_{i=1}^r q_{v_i} \hat{K}(t) = \sum_l (F(t) \mathbf{q})_{v_l} \prod_{i=1, i \neq l}^r q_{v_i} - \sum_{l,k} (F(t) \mathbf{M}(0))_{v_l v_k} \prod_{i=1, i \neq l, k}^r q_{v_i}, \quad (\text{E21})$$

we obtain

$$\begin{aligned} \dot{Y}(t)_{\nu_1 \dots \nu_r, j}^{(r)}(t) &= A_{\nu_1 \dots \nu_r, j}^{(r)} + \sum_I F_{\nu \mu, I}(t) B_{\nu_1 \dots \nu_{l-1} \mu \nu_{l+1} \dots \nu_r, j}^{(r)} \\ &\quad - \sum_{ik} \sum (F(t) M(0))_{\nu \nu_k} B_{\nu_1 \dots \nu_r, j}^{(r-2)} \\ &\quad + \sum_I F_{\nu \mu, I}(t) Y(t)_{\nu_1 \dots \nu_{l-1} \mu \nu_{l+1} \dots \nu_r, j}^{(r)} \\ &\quad - \sum_{ik} \sum (F(t) M(0))_{\nu \nu_k} Y(t)_{\nu_1 \dots \nu_r, j}^{(r-2)} - Y(t)_{\nu_1 \dots \nu_r, j}^{(r)} F_{ij}(t), \end{aligned} \quad (E22a)$$

where

$$A_{\nu_1 \dots \nu_r, j}^{(r)} \equiv \langle q_{\nu_1} \dots q_{\nu_r} K q_I \rangle M^{-1}(0)_{I, j}, \quad (E22b)$$

$$B_{\nu_1 \dots \nu_r, j}^{(r)} \equiv \langle q_{\nu_1} \dots q_{\nu_r} q_I \rangle M^{-1}(0)_{I, j}. \quad (E22c)$$

In Eq. (E22a), the index  $\nu_1 \dots \nu_r$  in  $B^{(r-2)}$  and  $Y^{(r-2)}$  does not include  $\nu_l$  and  $\nu_k$ . Writing Eq. (E22) for  $r = m$  and substituting Eq. (E20) into it, we get an equation for  $\dot{Y}^{(m)}(t)$ , which depends on  $Y^{(m-2)}(t)$  and  $Y^{(1)}(t)$ . Thus, if we write a set of equations corresponding to Eq. (E22) for

$$r = m, m-2, m-4, \dots (r > 0),$$

and for  $r = 1$ , then those equations form a closed set of equations. Since  $F$  of Eq. (E20) are linear in  $Y$  and the right-hand side of Eq. (E22a) is bilinear in  $F$  and  $Y$ , the closed equations are all in the form of Eq. (71b). If  $\mathbf{v}(\mathbf{q})$  is not necessarily in the form of Eq. (E18), but  $m$ th order polynomials in general, then  $Y^{(r)}(t)$  of Eq. (E19) for  $r = 1, 2, \dots, m$  are sufficient to construct closed equations.

For example, if  $\mathbf{v}(\mathbf{q})$  is in the form of Eq. (D21), then  $\Delta \hat{\Omega}$  of Eq. (E16c) vanishes so that the variables that must be taken into account are  $Y(t)_{\nu_1 \nu_2}^{(2)}$  only. From the symmetry for the permutation of  $\nu_1$  and  $\nu_2$  implied in the definition of Eq. (E19), there are  $N^2(N+1)/2$  independent  $Y^{(2)}$ . For a two-dimensional system ( $N = 2$ ), such as the Henon-Heiles potential,<sup>2</sup> these are

$$\{ Y_\alpha^{(2)} \} = \{ Y_{11}^{(2)}, Y_{12}^{(2)}, Y_{22}^{(2)}, Y_{21}^{(2)}, Y_{121}^{(2)} = Y_{211}^{(2)}, Y_{122}^{(2)} = Y_{212}^{(2)} \}. \quad (E23)$$

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