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SELF CONSISTENT MODE-COUPLING FORMULATION OF
SPECTRA OF NONLINEAR (ANHARMONIC) SYSTEMS

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INTRODUCTION

The calculation of spectra of nonlinearly coupled oscillators is a basic problem in nonequilibrium statistical mechanics which has broad range of implications (e.g. the vibrational spectra of polyatomic molecules). It is well established that classical trajectories of nonlinear systems may be classified as "quasiperiodic" or "stochastic" (chaotic) depending on the nonlinear coupling and the initial conditions.¹⁻³ The quantum mechanical significance of these concepts is however not at all clear and is the subject of numerous current studies.^{4,5} 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 behaviour in detail. In the present paper, 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. The latter assumes the form of a nonlinear map analogous to those used in classical nonlinear dynamics and may exhibit critical dependence on the anharmonic potential.⁶ The present approach is based on the mode-coupling formalism⁷ and utilizes a new type of reduced equation of motion developed recently.^{8,9}

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THE GENERATING FUNCTION

We shall be interested in calculating correlation functions of the form

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

where A and B are dynamical variables which are functions of some coordinates $(Q_1, \dots, Q_n) \equiv \underline{Q}$. \underline{Q} may be a partial set or a complete set of the coordinates of the system. To that end we introduce the generating function^{7,9}

$$P(\underline{q}, t; \underline{q}') \equiv \langle \delta(\underline{q} - \underline{Q}(t)) \delta(\underline{q}' - \underline{Q}(0)) \rangle , \quad (2)$$

which allows us to calculate the correlation function (eq. (1)) as

$$\langle A(t)B(0) \rangle = \int d\underline{q}^n d\underline{q}'^n A(\underline{q}) B(\underline{q}') P(\underline{q}, t; \underline{q}') . \quad (3)$$

In classical mechanics, the generating function P corresponds to the joint probability distribution for \underline{Q} to assume the value \underline{q}' at time 0 and the value \underline{q} at time t. In quantum mechanics, however, P is a complex quantity⁹ so that it cannot be strictly interpreted as a probability.⁹

In the following, we shall show that $P(\underline{q}, t; \underline{q}')$ obeys an exact reduced equation of motion (REM). The initial condition for the REM is given by

$$P(\underline{q}, 0; \underline{q}') = g(\underline{q}) \delta(\underline{q} - \underline{q}') , \quad (4)$$

where $g(\underline{q}) \equiv \langle \delta(\underline{q} - \underline{Q}) \rangle$ is the equilibrium distribution for \underline{Q} to assume the value \underline{q} .

HARMONIC OSCILLATORS

Let us first consider a harmonic system whose hamiltonian is given by:

$$H = \frac{1}{2} \sum_{\lambda=1}^N (P_{\lambda}^2 + \omega_{\lambda}^2 X_{\lambda}^2) . \quad (5)$$

It can be shown that the generating function $P(\underline{q}, t; \underline{q}')$ associated with n coordinates $Q_i = \sum_{\lambda=1}^N C_{i\lambda} X_{\lambda}$ ($i=1, \dots, n$) (and $n \leq N$) obeys the following REM^{9,10}

$$\frac{\partial P(\underline{q}, t; \underline{q}')}{\partial t} = - \frac{\partial}{\partial \underline{q}} \cdot \overset{-1}{\underline{M}(t) \underline{M}(t) \underline{M}(0)} \frac{\partial}{\partial \underline{q}} P(\underline{q}, t; \underline{q}') - \frac{\partial}{\partial \underline{q}} \cdot \overset{-1}{\underline{M}(t) \underline{M}(t) \underline{q}} P(\underline{q}, t; \underline{q}'), \quad (6)$$

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

$$M_{ij}(t) \equiv \langle Q_i(t) Q_j(0) \rangle = \sum c_{i\lambda} c_{j\lambda} \langle X_\lambda(t) X_\lambda(0) \rangle. \quad (7a)$$

Here

$$\langle X_\lambda(t) X_\lambda(0) \rangle = (\bar{n}_\lambda + 1) \exp(-i\omega_\lambda t) + \bar{n}_\lambda \exp(i\omega_\lambda t), \quad (7b)$$

and

$$\bar{n} = [\exp(\hbar\omega_\lambda/kT) - 1]^{-1}. \quad (7c)$$

The equilibrium distribution $g(\underline{q})$ is a Gaussian

$$g(\underline{q}) = \frac{1}{\sqrt{(2\pi)^n \det \underline{M}(0)}} \exp\left[-\frac{1}{2} \underline{\overset{-1}{q}} \underline{\overset{-1}{M}(0)} \underline{q}\right]. \quad (8)$$

The solution of eq. (6) with the initial condition eqs. (4) and (8) can be explicitly written as

$$P(\underline{q}, t; \underline{q}') = \frac{1}{\sqrt{(2\pi)^n \det \underline{W}(t)}} \exp\left[-\frac{1}{2} (\underline{\overset{-1}{q}} - \underline{\overset{-1}{M}(t) \underline{M}(0)} \underline{\overset{-1}{q}'}) \underline{\overset{-1}{W}(t)} (\underline{\overset{-1}{q}} - \underline{\overset{-1}{M}(t) \underline{M}(0)} \underline{\overset{-1}{q}'})\right] \cdot g(\underline{q}'), \quad (9a)$$

where

$$\underline{\overset{-1}{W}(t)} \equiv \underline{\overset{-1}{M}(0)} - \underline{\overset{-1}{M}(t) \underline{M}(0) \underline{M}(t)}. \quad (9b)$$

We note that the generating function in harmonic systems is a Gaussian function of \underline{q} and \underline{q}' .

Equations (6) and (9) bear a striking similarity with the Fokker Planck equation and the joint probability distribution in the theory of Brownian motion.¹¹ The coordinates \underline{q} in a harmonic system therefore behave like a stationary Gaussian but non Markov process. We note that, as long as the number N of oscillators is finite, the correlation functions $\underline{M}(t)$ of eq. (7) are quasiperiodic functions of t , so that $P(\underline{q}, t; \underline{q}')$ is a quasiperiodic function as well, undergoing dephasing and rephasing. For a Brownian particle on the other hand, the dephasing is irreversible. The addition of anharmonicities to

the hamiltonian eq. (5) will change the nature of the quasiperiodic time evolution and may turn it to be irreversible on the relevant time scales. In the following, we shall explore the consequences of anharmonicities on these equations.

ANHARMONIC SYSTEMS AT ZERO TEMPERATURE

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

$$H = \frac{1}{2} \sum_{i,j=1}^N P_i G_{ij} P_j + U(Q_1, \dots, Q_N). \quad (10)$$

Let us take a complete set of the coordinates $(Q_1, \dots, Q_N) \equiv \underline{Q}$. We have shown¹⁰ that the generating function $P(\underline{q}, t; \underline{q}')$ associated with \underline{Q} obeys the following exact REM at zero temperature:

$$\frac{\partial P(\underline{q}, t; \underline{q}')}{\partial t} = -\frac{\hbar}{2} \frac{\partial}{\partial \underline{q}} G \frac{\partial}{\partial \underline{q}} P(\underline{q}, t; \underline{q}') + i \frac{\partial}{\partial \underline{q}} \underline{u}(\underline{q}) P(\underline{q}, t; \underline{q}'), \quad (11)$$

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

$$\underline{u}(\underline{q}) = -\frac{\hbar}{2} G \frac{\partial}{\partial \underline{q}} \ln g(\underline{q}). \quad (12)$$

Here $g(\underline{q})$ is now the ground state distribution function of the system. If the potential $U(Q)$ is harmonic (quadratic in \underline{q}) then $g(\underline{q})$ is Gaussian and $\underline{u}(\underline{q})$ is linear in \underline{q} . When $U(\underline{q})$ is anharmonic, $\underline{u}(\underline{q})$ will contain higher order (quadratic, cubic etc.) terms in \underline{q} .

Eq. (11) is a major result of this work. It is exact and holds for an arbitrary anharmonic potential. Since it allows us to calculate only correlation functions of dynamical variables which depend on the coordinates (\underline{Q}) and not on the momenta (\underline{P}), it provides a reduced level of description and contains less information than the complete propagator for the system. The REM(11) is a second order differential equation in \underline{q} , similarly to eq. (6) in the harmonic case but with time-independent coefficients. The difference comes from the fact that the REM(11) is derived under the conditions that (i) the variables $\underline{q}(\underline{q}')$ are chosen to be a complete set of the coordinates ($n=N$) and (ii) the system is at zero temperature. Eq. (6) on the other hand is not restricted by conditions (i) and (ii) but it holds only for harmonic systems.

The REM(11) may be rewritten in the form of the equation of continuity

$$\frac{\partial P}{\partial t} + \frac{\partial}{\partial \underline{q}} (\underline{V}P) = 0, \quad (13)$$

where the local velocity is given by:

$$\underline{V} \equiv \frac{i\hbar}{2} \frac{\partial \ln P}{\partial \underline{q}} - \frac{\partial \ln g}{\partial \underline{q}}. \quad (14)$$

This form of the local velocity \underline{V} indicates that the deviation of P from the equilibrium distribution g is the driving force for the time evolution of P . Eqs. (13) and (14) have a striking resemblance with the hydrodynamic formulation of quantum mechanics.¹²

THE SELF CONSISTENT EQUATIONS

We now apply the REM(11) to the calculation of the correlation functions

$$M_{ij}(t) \equiv \langle Q_i(t)Q_j \rangle = \int d\underline{q}^n d\underline{q}'^n q_i q_j' P(\underline{q}, t; \underline{q}'), \quad (15)$$

which are relevant e.g. to the infrared spectra of supercooled anharmonic molecules.^{4,5} First we need to calculate the ground state distribution $g(\underline{q})$. Although in general we cannot obtain an exact solution for $g(\underline{q})$, it is not difficult to generate a reasonable approximation for the ground state distribution since usually the change of the ground state from the harmonic one due to anharmonicity is small. Let us suppose that we have solved this problem and proceed to the next step of solving the REM(11). Since the exact solution of the REM may be obtained only for harmonic systems, let us partition it in the form

$$\frac{\partial P(\underline{q}, t; \underline{q}')}{\partial t} = K(\underline{q})P(\underline{q}, t; \underline{q}'), \quad (16a)$$

where the differential operator $K(\underline{q})$ consists of the harmonic and the anharmonic parts:

$$K(\underline{q}) \equiv K_0(\underline{q}) + K'(\underline{q}), \quad (16b)$$

$$K_0(\underline{q}) \equiv \frac{i\hbar}{2} \frac{\partial}{\partial \underline{q}} \frac{\partial}{\partial \underline{q}} + 1 \frac{\partial}{\partial \underline{q}} \Omega \underline{q}, \quad (16c)$$

and

$$K'(\underline{q}) \equiv i \frac{\partial}{\partial \underline{q}} v(\underline{q}) \quad (16d)$$

The simplest way to evaluate the solution $P(\underline{q}, t; \underline{q}')$ of eq. (16) is by a perturbative expansion of the propagator $\exp(Kt)$, which governs the time evolution of $P(\underline{q}, t; \underline{q}')$ of eq. (16a), in terms of the anharmonic part K' of eq. (16d). Suppose we calculate the expansion terms, say, up to the second order. Then eq. (15) immediately yields a corresponding approximate expression for the correlation functions $\underline{M}(t)$. Since we shall be primarily interested in cases where the effects of anharmonicities are very significant (e.g. transition from quasiperiodic to chaotic types of motion) we shall derive an improved self consistent approximation for $\underline{M}(t)$. This is based on the following idea: We can always construct a large system of harmonic oscillators such that the correlation matrix $\underline{M}(t)$ calculated for this system will be identical with that of our original anharmonic system. As long as we are concerned with the correlation functions $\underline{M}(t)$, the true (anharmonic) generating function $P(\underline{q}, t; \underline{q}')$ in eq. (18) may be replaced by the generating function $\hat{P}(\underline{q}, t; \underline{q}')$ of an equivalent harmonic system. We shall call $\hat{P}(\underline{q}, t; \underline{q}')$ the effective generating function. It should be noted that the effective generating function depends on the same number of relevant variables Q_i as the true generating function but that the number of oscillators 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 , and only the $\langle Q_i(t) Q_j \rangle$ correlation functions in which we are interested will be the same.

As shown before, the generating function for harmonic systems is Gaussian, so that the procedure described above may be viewed as a Gaussian approximation for $P(\underline{q}, t; \underline{q}')$: The effective generating function $\hat{P}(\underline{q}, t; \underline{q}')$ is the Gaussian function of \underline{q} and \underline{q}' whose second moment $\underline{M}(t)$ is equal to that of the true generating function, i.e.

$$\hat{\underline{M}}(t) = \underline{M}(t). \quad (17)$$

This equation forms the basis for the construction of the self consistent equation in the following. We first decompose the operator $K(\underline{q})$ of eq. (16) into the effective harmonic part

$$\hat{K}(t) = - \frac{\partial}{\partial \underline{q}} \hat{M}(t) \hat{M}(t) \hat{M}(0) - \frac{\partial}{\partial \underline{q}} \hat{M}(t) \hat{M}(t) \hat{q} \quad (18)$$

and the residual part $\Delta K(t) \equiv K - \hat{K}(t)$. Note that both K and ΔK are time-dependent although K is independent of time. Next we write an expression for the perturbation expansion of the true correlation function $M(t)$ in terms of $\Delta K(t)$. By truncating the expansion, say, at the second order, we get an approximate expression for $M(t)$ as a functional of $\hat{M}(t)$, since $\hat{K}(t)$ of eq. (18) depends on $\hat{M}(t)$. By inserting this expression into the right hand side of eq. (17), we obtain a closed, self consistent equation for the correlation function $\hat{M}(t)$.¹⁰

We have shown that the self consistent equation may be transformed into a set of simple autonomous differential equations by introducing new variables $Y_\alpha(t)$ such that¹⁰

$$\frac{d\hat{M}_{ij}(t)}{dt} = \sum_k [i\Omega'_{ik} - i \sum_\alpha B_{ik,\alpha} Y_\alpha(t)] \hat{M}_{kj}(t) \quad (19a)$$

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

$$\frac{dY_\alpha(t)}{dt} = C_\alpha + i \sum_\beta D_{\alpha\beta} Y_\beta(t) + \sum_{\beta,\gamma} L_{\alpha\beta\gamma} Y_\beta(t) Y_\gamma(t), \quad (19b)$$

where C_α , $D_{\alpha\beta}$ and $L_{\alpha\beta\gamma}$ are some known coefficients which may be calculated using the anharmonic potential $U(q)$.¹⁰ Eqs. (19) are our final self consistent equations. We have first to solve eq. (19b) with the initial conditions $Y_\alpha(0) = 0$. $\hat{M}(t)$ is subsequently obtained by solving eq. (19a). Eq. (19b) may be alternatively written in the frequency domain:

$$i\omega Y_\alpha(\omega) = C_\alpha \delta(\omega) + i \sum_\beta D_{\alpha\beta} Y_\beta(\omega) + \sum_{\beta,\gamma} L_{\alpha\beta\gamma} \int d\omega' Y_\beta(\omega-\omega') Y_\gamma(\omega') \quad (20)$$

This is a typical nonlinear mode-coupling equation similar to those which appear in nonlinear hydrodynamics, chemical reactions and critical phenomena⁷. There is an extensive literature on the dynamical behaviour of the solutions of such equations. It is well known that this type of equations can show various stages of periodic motion and chaotic motion depending upon parameters and initial conditions.^{13,14} If the solution of eq. (19b) or (20) shows chaotic behaviour, this leads to chaotic behaviour of the correlation function $\hat{M}(t)$ via eq. (19a). Thus the investigation of eq. (19) for various anharmonic systems will allow us to discuss the regular vs. chaotic behavior in molecular vibrational spectra.

The mode-coupling equation (20) may be solved by iteration starting from the harmonic (linear) equation ($L_{\text{obs}} = 0$). In each step new functions $Y_{\alpha}(\omega)$ are obtained from eq. (20) by substituting the old functions $Y_{\alpha}(\omega)$ of the previous step into the bilinear (convolution) term in eq. (20). An obvious criterion for stochasticity suggested by this procedure is connected to the convergence properties of our nonlinear mapping (eq. 20). Rapid convergence implies that the spectra of the anharmonic system are equivalent to those of a harmonic system with fewer more degrees of freedom. Slow convergence may imply that we need infinite number of harmonic degrees of freedom to reproduce the spectrum.

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