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Two-Dimensional Spectroscopy of Coupled Vibrations with the Optimized Mean-Trajectory Approximation

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Abstract

The optimized mean-trajectory (OMT) approximation is a semiclassical representation of the nonlinear vibrational response function used to compute multidimensional infrared spectra. In this method, response functions are calculated from a sequence of classical trajectories linked by discontinuities representing the effects of radiation-matter interactions, thus providing an approximation to quantum dynamics using classical inputs. This approach was previously formulated and assessed numerically for a single anharmonic degree of freedom. Our previous work is generalized here in two respects. First, the derivation of the OMT is extended to any number of coupled anharmonic vibrations by determining semiclassical approximations for pairs of double-sided Feynman diagrams. Second, an efficient numerical procedure is developed for calculating two-dimensional infrared spectra of coupled anharmonic vibrations in the OMT approximation. The OMT approximation is shown to reproduce the fundamental features of the quantum response function including both coherence and population dynamics.

Keywords

nonlinear spectroscopy; vibrational echoes; semiclassical dynamics

I. INTRODUCTION

Multidimensional infrared spectroscopy probes interactions among molecular vibrations in condensed phase and biomolecular systems.^{1–10} Complete interpretation of nonlinear vibrational spectra requires atomistic level modeling of the experimental observables. Quantum dynamical calculations are generally impractical for large anharmonic systems and classical mechanical treatments of nonlinear response functions become increasingly inaccurate over long time scales.^{11–22} One strategy for treating quantum dynamical effects for many degrees of freedom is to partition the system into a quantum subsystem and a bath treated classically or semiclassically.^{23–36} Here we pursue the alternative approach of developing a semiclassical approximation^{37–58} to quantum dynamics that can in principle be applied uniformly to all degrees of freedom.

Computing a thermally averaged response function semiclassically requires approximating the time-evolution of the density operator. Replacing each instance of the quantum time-evolution operator with a semiclassical approximation^{59–66} leads to a treatment in which the dynamics are computed from pairs of classical trajectories^{20,21,67} representing the evolution of the ket and bra aspects of the density operator. Such calculations typically involve evaluating high-dimensional integrals over strongly oscillatory integrands. Gruenbaum and

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Loring^{68–71} developed the mean-trajectory approximation for vibrational response functions in which the dynamics of the density operator are represented by a single mean classical trajectory, removing some of the numerical challenges associated with treating trajectory pairs. When applied to thermal ensembles of single anharmonic oscillators and pairs of oscillators, the mean-trajectory approach was shown to accurately treat coherence dynamics associated with the first and third propagation times of the third-order response function, but to treat qualitatively incorrectly the dynamics during the second propagation period or waiting time.²⁸

We have developed an optimized mean-trajectory approximation (OMT) for nonlinear vibrational response functions that can provide an accurate description of the dynamics probed by all three propagation times in the third-order response function.⁷² Like the previous mean-trajectory approximation, two-dimensional infrared spectra are calculated from sequences of classical trajectories linked by discontinuities representing radiation-matter interactions. The OMT approximation is constructed⁷² by considering the double-sided Feynman diagrams (2FDs) conventionally used to represent quantum mechanical processes contributing to a nonlinear optical signal.^{5,73–75} A semiclassical approximation is made to the sum of two 2FDs, generating a single semiclassical diagram. These semiclassical diagrams are similar to contributions to the original mean-trajectory approximation,⁷⁰ but differ in the points along the semiclassical paths at which classical state information is collected and in the statistical weights assigned to these contributions. We have demonstrated⁷² the accuracy of this method for all time arguments of the third-order response function for thermal ensembles of noninteracting anharmonic oscillators. Both mean-trajectory and OMT methods rely on the identification of classical action and angle variables, and so are limited to systems with quasiperiodic dynamics for which these variables may be defined. The OMT approach may be regarded as an application to density matrix dynamics of quasiclassical methods⁷⁶ in which quantum dynamics are represented by classical trajectories with quantized action variables.

In Sec. II we construct the OMT approximation for collections of coupled anharmonic oscillators based on the semiclassical analysis of 2FDs. A numerically efficient procedure for calculating the third-order vibrational response function with the OMT is presented in Sec. III. Numerical results are reported in Sec. IV and conclusions are made in Sec. V.

II. SEMICLASSICAL RESPONSE OF COUPLED VIBRATIONS

The quantum mechanical third-order vibrational response function^{5,74} associated with the four-wave mixing signal at a given phase-matching condition is

$$R_{\gamma\beta\alpha}^{(3)}(t_3, t_2, t_1) = \left(\frac{i}{\hbar}\right)^3 \text{Tr} \left(\hat{q}_a^\delta \hat{K}(t_3) \left[\hat{q}_a^\gamma, \hat{K}(t_2) \left[\hat{q}_a^\beta, \hat{K}(t_1) \times [\hat{q}_a^\alpha, \hat{\rho}] \hat{K}^\dagger(t_1) \right] \hat{K}^\dagger(t_2) \right] \hat{K}^\dagger(t_3) \right). \quad (1)$$

The labels α, β, γ , and δ take on the signs $\pm$ constrained so that two are $+$ and two $-$. The sample is assumed to interact sequentially with applied electric fields labeled 1, 2, and 3, so that this response function generates the signal with wavevector $\alpha\mathbf{k}_1 + \beta\mathbf{k}_2 + \gamma\mathbf{k}_3$. The electric dipole operator is taken to be proportional to the coordinate $\hat{q}_a$, with the constant of proportionality suppressed. This coordinate is written in terms of boson creation and

annihilation operators $\hat{b}_a^\dagger$ and $\hat{b}_a$ as $\hat{q}_a = \hat{q}_a^+ + \hat{q}_a^-$, with $\hat{q}_a^+ = \hat{b}_a^\dagger \sqrt{\hbar/2m_a\omega_a}$ and $\hat{q}_a^- = (\hat{q}_a^+)^\dagger$. The rotating wave approximation has been invoked.⁷⁴ Expanding the three nested commutators in Eq. (1) yields 8 terms that are conventionally represented by double-sided Feynman diagrams^{5,73–75} (2FDs) that depict the allowed sequences of radiation-matter interactions. A

pair of 2FDs is shown in panel (a) of Fig. 1 for $R_{+-}^{(3)}$ and in panel (b) for $R_{-++}^{(3)}$. Time increases upwards, the vertical solid lines on the left and right represent, respectively, the ket and bra aspects of the density operator and horizontal arrows represent radiation-matter interactions.

In the OMT approximation,⁷² the response function is calculated from sequences of classical trajectories linked by discontinuities representing radiation-matter interactions. The OMT approximation to $R_{\gamma\beta\alpha}^{(3)}$ was developed by constructing semiclassical diagrams corresponding to sums of pairs of 2FDs as shown in Fig. 1. Examples of OMT diagrams are shown to the right of the 2FDs in panels (a) and (b) of Fig. 1. In these diagrams, time increases from left to right, horizontal solid lines represent classical trajectories and vertical dashed lines connecting distinct trajectories indicate the effect of radiation-matter interactions. Colored dots label classical states included in the calculation of the response function.⁷² The uppermost OMT diagram in each panel of Fig. 1 involves a single vibrational mode and therefore has the same appearance as the diagrams presented in Ref. 72 for the single-mode case. We briefly review the OMT procedure for the single-mode case, referring to these two diagrams. The remaining OMT diagrams will be discussed below in connection with the multimode case.

For a single degree of freedom,⁷² radiation-matter interactions the OMT approximation are represented by changes in the classical action variable J at fixed classical angle variable ϕ . The correspondence between 2FDs and OMT diagrams is based on the choice of the classical action associated with each trajectory in the semiclassical calculation. This action is determined by evaluating 2FDs in the limit of harmonic dynamics in which the quantum mechanical energy is related to quantum number n by $E = (n + 1/2)\hbar\omega$ and the classical energy is related to action J by $E = J\omega$, yielding the correspondence $J = (n + 1/2)\hbar$. If the density operator in a 2FD has the form $|n_l\rangle\langle n_r|$, the average energy of the ket and bra aspects of the density operator is $(n_l + n_r + 1)\hbar\omega/2$ corresponding to an average action of $J = (n_l + n_r + 1)\hbar/2$. In the OMT approximation the corresponding classical trajectory is assigned this action, so that the quantum dynamics of the density operator $|n_l\rangle\langle n_r|$ are represented by a classical trajectory with action $J = (n_l + n_r + 1)\hbar/2$. Interactions with the field are taken to obey harmonic selection rules so that each interaction either increases or decreases J by $\hbar/2$. Because the density matrix is initially diagonal, the initial value of J in each OMT diagram is a half-odd-integral multiple of $\hbar$. The final value of J must also be a half-odd-integral multiple of $\hbar$ since each diagram represents a contribution to a trace. In Fig. 1, action values that are half-odd-integral multiples of $\hbar$ are indicated by horizontal dotted lines and values that are integral multiples of $\hbar$ are shown by horizontal dashed lines. Each OMT diagram therefore begins and ends on a horizontal dotted line, with each transition connecting adjacent horizontal lines. The initial dotted vertical lines in an OMT diagram represent either an increase or a decrease in action by $\hbar/2$. The increase is associated with the 2FD in each pair that begins with an excitation, for example the first 2FD in panel (a) of Fig. 1. The decrease in action is associated with the other member of the pair, for example the second 2FD in panel (a), which begins with a deexcitation event. Both of these processes are included in a single OMT diagram.

While OMT semiclassical paths are constructed to correspond with the harmonic limit of 2FDs, the OMT diagrams are evaluated numerically using exact classical trajectories for the full anharmonic Hamiltonian. Furthermore, for a single degree of freedom the good action variable is quantized, providing a semiclassical approximation to the dynamics of quantum eigenstates for the true Hamiltonian. The OMT calculation thus approximately includes the effects of anharmonicity. It should be emphasized that the nonlinear response function in Eq. (1) necessarily vanishes for a harmonic potential. This vanishing may be described as a

cancellation among the 8 2FDs generated by the commutators in Eq. (1). However, individual 2FDs are nonzero in the harmonic limit, as are the sums of pairs that we associate with OMT diagrams. The fact that the cancellation among 2FDs occurs at the level of all 8 diagrams permits the use of the harmonic limit of individual pairs in our analysis.

Here we extend the development of Ref. 72 to a collection of f coupled anharmonic vibrations with quantum Hamiltonian

$$\hat{H} = \sum_{i=1}^f \hat{H}_{\text{HO}}^{(i)} + \sum_{i < j} c_{ij} \sqrt{m_i m_j} \omega_i \omega_j \hat{q}_i \hat{q}_j + \hat{V}. \quad (2)$$

The harmonic Hamiltonian for a local mode q_i with mass m_i and angular frequency ω_i is denoted $\hat{H}_{\text{HO}}^{(i)}$. One of these modes is the bright mode a coupled to radiation in Eq. (1). The second term in Eq. (2) is a bilinear coupling between local modes and the third term contains all local mode anharmonicities and anharmonic couplings. By analogy to the $f = 1$ case, we construct OMT diagrams based on 2FDs in the harmonic limit which amounts to neglecting $\hat{V}$ in Eq. (2). In this case, $\hat{H}$ can be written in terms of noninteracting normal modes, $\{x_j\}$. The OMT diagrams are constructed from 2FDs that are evaluated for this harmonic system in the basis of eigenstates of these normal modes. As for the $f = 1$ case just described, the numerical evaluation of OMT diagrams in the multimode case is performed using classical trajectories for the full anharmonic Hamiltonian and quantization is applied approximately to the good action variables, thereby including anharmonic effects.

The bright coordinate q_a in Eq. (1) may be written as a linear combination of normal modes,

$$q_a = \sum_{i=1}^f \kappa_{ai} x_i. \quad (3)$$

If all of the coefficients $\{\kappa_{ai}\}$ are nonzero, then each of the radiation-matter interactions in Eq. (1) can excite or deexcite any one of the f normal modes. Therefore, in the multimode case both 2FDs and OMT diagrams indicate the identity of the normal mode involved in each interaction. In principle, the four interactions in each 2FD generate f^4 combinations of interactions with normal modes, but this total includes combinations that do not satisfy the trace condition in the harmonic limit and hence are excluded from the OMT calculation. All OMT diagrams associated with the 2FDs in panels (a) and (b) of Fig. 1 are shown in that figure. The boxed labels 1–4 indicate successive interactions with the field. The first normal mode interacting with the field is labeled in red, and the second distinct interacting mode, if any, is labeled in blue. The uppermost OMT diagram in each panel describes a process in which all interactions occur with the same mode and the remaining OMT diagrams in each panel represent the same sequences of interactions but with two normal modes. There are three combinations of interactions involving two interactions with each of the red and blue normal modes, but in general only two of these satisfy the trace condition in the harmonic limit. Therefore of the f^4 possible combinations of interactions with different normal modes only $2f^4 - f$ satisfy the harmonic trace condition, of which f possibilities involve all interactions with one mode and $2f(f - 1)$ involve interactions with a pair of modes.

Since the 2FDs and OMT diagrams in Fig. 1 are constructed for noninteracting normal modes, the correspondence between the quantum and semiclassical diagrams is a straightforward generalization of the $f = 1$ case previously described.⁷² The quantum dynamics of the multimode density operator $|n_{1l}, n_{2l}, \dots\rangle\langle n_{1r}, n_{2r}, \dots|$ is represented by a

classical trajectory in which the action of each normal mode j is $\hbar(n_{jl} + n_{jr} + 1)/2$. At the start of the first horizontal line in each OMT diagram in Fig. 1, the action of the red mode must be an integral multiple of $\hbar$ representing a one-quantum coherence, while the action of the blue mode must be a half-odd-integral multiple of $\hbar$ representing a population. All other modes not interacting directly with the field in a given diagram are propagated at constant action equal to a half-odd-integral multiple of $\hbar$ for the entire time interval $t_1 + t_2 + t_3$. The trajectories of these modes are not indicated explicitly in the OMT diagrams in Fig. 1. The initial actions of all modes are independently averaged so that in the two-mode OMT diagrams in Fig. 1, the relative vertical positions of the red and blue portions of the diagram have no significance.

Within the OMT for f degrees of freedom and with one local mode labeled a interacting with radiation, $R_{\gamma\beta\alpha}^{(3)}$ includes processes that reflect interactions with either one or two normal modes,

$$R_{\gamma\beta\alpha}^{(3)}(t_3, t_2, t_1) = \sum_{r=1}^f \kappa_{ar}^4 \rho_{\gamma\beta\alpha}^r(t_3, t_2, t_1) + \sum_{r=1}^f \sum_{s \neq r}^f \kappa_{ar}^2 \kappa_{as}^2 \rho_{\gamma\beta\alpha}^{r,s}(t_3, t_2, t_1). \quad (4)$$

The first sum in Eq. (4) contains contributions from processes such as the uppermost OMT diagrams in Fig. 1, and the second sum contains contributions from OMT diagrams such as the lower two diagrams in each panel of Fig. 1. Modes weakly coupled to a may be neglected as their contributions to Eq. (4) scale as either κ_{ai}^2 or κ_{ai}^4 . The contribution to Eq. (4) from processes in which all interactions occur with a single normal mode r is

$$\begin{aligned} \rho_{\gamma\beta\alpha}^r(t_3, t_2, t_1) &= \frac{i}{2^4 \hbar^2 f + 3} \sum_{p=1}^4 \varepsilon_p \int d\mathbf{z}_1 \int d\mathbf{z}_2 \int d\mathbf{z}_3 \\ &\times \Gamma_r(\mathbf{z}_1) \Delta f_{\text{cl}}^r(\mathbf{z}_1) \delta(\varphi_2 - \varphi_{1t_1}) \delta(\varphi_3 - \varphi_{2t_2}) \Delta_{1p}^r \Delta_{2p}^r \\ &\times Q_{\alpha}^r(\mathbf{z}_1) Q_{\beta}^r(\mathbf{z}_p') Q_{\gamma}^r(\mathbf{z}_p'') Q_{\delta}^r(\mathbf{z}_{3t_3}), \end{aligned} \quad (5)$$

$$\Gamma_r(\mathbf{z}_1) \equiv \hbar^f \sum_{n_r=1}^{\infty} \delta(J_{1r} - n_r \hbar) \times \prod_{s' \neq r} \sum_{n_{s'}=0}^{\infty} \delta(J_{1s'} - (n_{s'} + 1/2) \hbar), \quad (6)$$

$$\Delta f_{\text{cl}}^r(\mathbf{z}_1) \equiv f_{\text{cl}}^r(\mathbf{z}_1)|_{J_{1r} \rightarrow J_{1r} - \hbar/2} - f_{\text{cl}}^r(\mathbf{z}_1)|_{J_{1r} \rightarrow J_{1r} + \hbar/2}, \quad (7)$$

$$\Delta_{j\pm}^r \equiv \hbar^f \delta(J_{j+1,r} - (J_{jr} \pm \hbar/2)) \times \prod_{s' \neq r} \delta(J_{j+1,s'} - J_{js'}), \quad (8)$$

$$Q_{\pm}^r \equiv x_r \mp ip_r / (m_r \omega_r). \quad (9)$$

This quantity is expressed as an integral over three $2f$ -dimensional phase-space variables $\mathbf{z}_j$, representing the start of each of the three classical trajectories in the OMT diagrams of Fig. 1. The factor Γ_r in Eq. (6) quantizes the action of each mode after the first interaction with

radiation. As previously discussed, mode r which interacts with radiation has an action J_{1r} quantized to an integral multiple of $\hbar$, while the other modes not interacting with radiation have actions quantized to a half-odd-integral multiple of $\hbar$. The statistical weight for the classical state $\mathbf{z}_1$ is set by Δ_{cl}^r in Eq. (7), the multimode generalization of the corresponding quantity in Eq. (14) of Ref. 72. The subtraction in this weight arises from the summation of pairs of 2FDs as in Fig. 1. The factors $\delta(\phi_j - \phi_l)$ in Eq. (5) ensure that angle variables for each mode are unchanged after each radiation-matter interaction, while the factors $\Delta_{j\pm}^r$ in Eq. (8) constrain the action of the mode interacting with radiation to increase or decrease by $\hbar/2$ and the actions of all other modes to remain the same. The index p labels the four semiclassical paths in which radiation interacts with a single mode, presented in Fig. 4 of Ref. 72 for $f=1$. The uppermost diagrams in panels (a) and (b) of Fig. 1 each represent one of these four paths for two possible phase-matching conditions. The sign $\varepsilon_p = \pm 1$ in Eq. (5) is determined as described in Ref. 72. One of each pair of 2FDs contributing to a semiclassical path begins with an excitation. If an even number of interactions occur on the right-hand (bra) side of this 2FD, then $\varepsilon_p = 1$, and otherwise $\varepsilon_p = -1$. For example, in the first semiclassical paths in panels (a) and (b) of Fig. 1, $\varepsilon_p = 1$. The classical states $\mathbf{z}_p'$ and $\mathbf{z}_p''$ in Eq. (5) are determined by the path p , and are designated by the placement of the second and third dots along the path. For example, in the first path in panel (a) of Fig. 1, $\mathbf{z}_p' = \mathbf{z}_{1t_1}$ and $\mathbf{z}_p'' = \mathbf{z}_3$, as indicated by the locations of the middle two red dots. In Eq. (9), p_r is the momentum conjugate to the normal mode coordinate x_r . For the single oscillator case Eq. (5) reduces to the expression for the third-order response function in Eq. (15) of Ref. 72.

The OMT response in Eq. (4) also includes a contribution from processes in which the radiation interacts twice with mode r (labeled red in Fig. 1) and twice with mode s (labeled blue in Fig. 1),

$$\begin{aligned} \rho_{\gamma\beta\alpha}^{r,s}(t_3, t_2, t_1) = & \frac{i}{2^4 \hbar^2 f + 3} \sum_{p=1}^8 \varepsilon_p \int d\mathbf{z}_1 \int d\mathbf{z}_2 \int d\mathbf{z}_3 \\ & \times \Gamma_r(\mathbf{z}_1) \Delta_{\text{cl}}^r(\mathbf{z}_1) \delta(\varphi_2 - \varphi_{1t_1}) \delta(\varphi_3 - \varphi_{2t_2}) \Delta_{1p}^{r,s} \Delta_{2p}^{r,s} \\ & \times Q_{\alpha p}^{r,s}(\mathbf{z}_1) Q_{\beta p}^{r,s}(\mathbf{z}_p') Q_{\gamma p}^{r,s}(\mathbf{z}_p'') Q_{\delta p}^{r,s}(\mathbf{z}_{3t_3}). \end{aligned} \quad (10)$$

As illustrated in Fig. 1, the number of paths with two interacting modes is double the number of paths with all radiation-matter interactions occurring with a single mode, so that contributions from 8 semiclassical paths are summed here. The factors $\Delta_{jp}^{r,s}$ and $Q_{\sigma p}^{r,s}$ depend on two mode indices, since the identity of the mode interacting with radiation, r or s , is determined by the path p . These factors are otherwise defined as in Eqs. (8) and (9). For example, in the second semiclassical path in panel (a) of Fig. 1, these path-dependent factors in Eq. (10) are $\Delta_{1+}^r \Delta_{2-}^s Q_{-}^r(\mathbf{z}_1) Q_{+}^r(\mathbf{z}_{1t_1}) Q_{+}^s(\mathbf{z}_3) Q_{-}^s(\mathbf{z}_{3t_3})$. Equations (4)–(10) present the central result of this work: the OMT approximation to the phase-matched third-order vibrational response function for coupled vibrations. In Section III, we discuss an efficient numerical implementation of this method.

III. COMPUTATIONAL METHODS

Implementing the OMT approximation in Sec. II for multiple coupled vibrations presents three significant challenges. First, classical trajectories with quantized good action variables must be determined. The good action variables are generalized momenta such that the Hamiltonian is independent of the conjugate coordinate variables.⁷⁷ Each horizontal solid line in the OMT diagrams of Fig. 1 represents one such trajectory. Second, discrete jumps in action must be carried out at constant angles. Each vertical dashed line in Fig. 1 represents

one such transition. Third, computation of semiclassical paths must be carried out efficiently, since the evaluation of an OMT diagram for specified evolution times t_1 , t_2 and t_3 requires a phase-space average over $2f$ degrees of freedom, with the computation of spectra then requiring the variation of all three time variables. We have addressed these challenges through an approximate procedure for efficiently generating and averaging semiclassical paths, which is described next.

To construct classical trajectories with specified good action values, initial classical states corresponding to these action values can be propagated numerically. To approximate the desired initial conditions perturbation theory in anharmonicity, as discussed in Ref. 76, was used. The central object⁷⁶ in this approach is a type 2 generating function⁷⁷ associated with the canonical transformation from zeroth-order action and angle variables $(\mathbf{I}, \boldsymbol{\theta})$ to good variables $(\mathbf{J}, \boldsymbol{\phi})$. The zeroth-order variables are correct for the harmonic Hamiltonian specified by Eq. (2) with $V = 0$. The generating function, which depends on $\mathbf{J}$ and $\boldsymbol{\theta}$, is expanded in a Fourier series in $\boldsymbol{\theta}$ and the Fourier coefficients are determined perturbatively in anharmonicity. For the calculations shown here, V is expanded to fourth order in coordinates and the Fourier coefficients are determined to second order in cubic anharmonicity and to first order in quartic anharmonicity. This procedure results in expressions for normal mode coordinates and momenta as functions of good actions and harmonic angles, $x_s(\mathbf{J}, \boldsymbol{\theta})$ and $p_s(\mathbf{J}, \boldsymbol{\theta})$. The focus in Ref. 76 is the calculation of semiclassical energies, which does not require expressing harmonic angle variables $\boldsymbol{\theta}$ in terms of $\mathbf{J}$ and $\boldsymbol{\phi}$. In our calculation such relations are necessary in order to write normal mode coordinates and momenta as $x_s(\mathbf{J}, \boldsymbol{\phi})$ and $p_s(\mathbf{J}, \boldsymbol{\phi})$. Differentiating the generating function with respect to the good action variables yields $\boldsymbol{\phi}$ as a function of $\mathbf{J}$ and $\boldsymbol{\theta}$ to the appropriate order in perturbation theory. Numerical inversion of these relations yields $\boldsymbol{\theta}$ in terms of $\mathbf{J}$ and $\boldsymbol{\phi}$, allowing the determination of initial conditions for each classical trajectory.

Carrying out a transition in action at fixed angle values requires changing the normal mode coordinates and momenta according to $\{(x_s'(\mathbf{J}_i, \boldsymbol{\phi}), p_s'(\mathbf{J}_i, \boldsymbol{\phi}))\} \rightarrow \{(x_s'(\mathbf{J}_f, \boldsymbol{\phi}), p_s'(\mathbf{J}_f, \boldsymbol{\phi}))\}$. In principle, implementing this transition requires determining the values of the angle variables in the initial state at the moment of transition. Rather than reapplying the perturbation theory described above to do so, we use an approximate procedure that avoids the need to calculate the values of angle variables. In the harmonic limit, the appropriate transition would result from scaling both the coordinate and momentum of the normal mode

interacting with radiation, r , by a factor of $\sqrt{J_{f,r}/J_{i,r}}$. As described next, the OMT approximation to the vibrational response function is calculated from a collection of discretized classical trajectories at quantized action values. Action jumps at fixed angle values between an initial classical state along one trajectory and a final classical state along a target trajectory are approximated by scaling the initial coordinate and momentum of the normal mode interacting with radiation in this manner and then selecting the discrete classical state along the target trajectory that minimizes the phase-space distance to the scaled initial state.

Computing a trajectory with quantized action values by the method outlined above requires numerical inversion of multidimensional nonlinear equations to obtain the initial conditions, followed by numerical propagation of the trajectory. Determining a transition at fixed angles requires a multidimensional minimization, as just described. For efficient calculation of the OMT response function, the number of these computations should be kept as small as possible. At a minimum, a single trajectory with each desired set of actions must be computed. If the trajectories are long enough and the frequencies associated with all angle variables are incommensurate, all possible angle values are sampled in each trajectory.

Mappings approximating constant angle transitions can then be determined between pairs of trajectories connected by an OMT transition. Each state on the initial trajectory is mapped onto a state on the target trajectory, representing the destination after a transition in action at constant angle values. Because of the approximations involved, the mappings from one trajectory to another need not be the inverses of the mappings from the latter trajectory to the former.

The calculations supporting the evaluation of OMT diagrams are indicated schematically in Fig. 2. Each horizontal arrow represents an action-quantized trajectory, with boxes indicating discrete classical states. Dashed arrows indicate mappings between states on different trajectories representing transitions in action at fixed angle values. Once the trajectories and mappings have been computed, time evolution at specified action values is reduced to incrementing the index of the classical state along the appropriate trajectory. Similarly, performing transitions between trajectories at constant angle values is reduced to using the appropriate map to identify the starting index on the target trajectory. To further increase computational efficiency, the phase-space average over initial angles can be approximated as a time average, by varying the starting state indicated by the first blue box in Fig. 2. This procedure greatly reduces the computational labor of the calculation because a set of trajectories and mappings is computed only once for a given Hamiltonian. Colored boxes show one implementation of a semiclassical path. Depending on the identities of the three trajectories, this schematic could represent any OMT diagram.

Because the good action and angle variables are approximated with perturbation theory, numerical trajectories initialized with different approximate angle values may be confined to different invariant subspaces of phase space. Discrepancies between spectra computed with different initial sets of angles provide a measure of the cumulative effects of the approximations we have made and hence of the applicability of this approach to a given model. If spectra computed from different initial sets of angles differ from each other markedly, longer trajectories may be required or the model may lie outside the domain of applicability of this method. Such a lack of reproducibility may arise from the approximate method for carrying out transitions in action, from the perturbative identification of action and angle variables, or from the nonexistence of good action and angle variables. Testing the dependence of final results on initial sets of angle values provides an empirical assessment of the applicability of the theory to a given model.

IV. NUMERICAL RESULTS

We present calculations of the third-order vibrational response function for a local mode a interacting directly with radiation bilinearly coupled to a local mode b . The bright mode a is a Morse oscillator with well depth D_a and harmonic frequency ω_a and the dark mode is either a harmonic oscillator or a second Morse oscillator. The model is characterized by the mass ratio $\gamma_m \equiv m_b/m_a$, the frequency ratio $\gamma_\omega \equiv \omega_b/\omega_a$, $\beta\hbar\omega_a$ with $\beta \equiv 1/k_B T$, which represents the importance of quantum mechanics, c_{ab} the intermode coupling constant in Eq. (2), βD_a which represents the anharmonicity of the bright Morse oscillator, and if applicable, βD_b . All times are scaled by ω_a and the response function is scaled by $m_a^2 \omega_a D_a$.

OMT calculations from Eqs. (4)–(10) are compared to numerically exact quantum mechanical calculations from Eq. (1) with a harmonic product state basis using 15 basis functions per mode. OMT results were computed using the implementation described in Sec. III. For each set of parameters, randomly chosen angle values were used to define the trajectories' initial conditions. For all of the systems studied varying the initial angles caused small amplitude changes and frequency shifts in the calculated spectra. Increasing anharmonicity and allowing γ_ω to approach unity increases the size of these variations.

Initial actions for each oscillator vary between $\hbar/2$ and $5\hbar/2$ in steps of $\hbar$, requiring 58 classical trajectories in which the normal mode actions vary between $\hbar/2$ and $4\hbar$ in steps of $\hbar/2$.

We calculate the response functions associated with the two phase-matched signals discussed in connection with Fig. 1: $-\mathbf{k}_1+\mathbf{k}_2+\mathbf{k}_3$ ($R_{++-}^{(3)}$) and $\mathbf{k}_1+\mathbf{k}_2-\mathbf{k}_3$ ($R_{-++}^{(3)}$). The dependence of each of these response functions on the propagation times t_1 , t_2 , and t_3 may be qualitatively interpreted by expressing each response function as a sum of 2FDs as in Fig. 1 and considering each 2FD for a harmonic system. For both signals, during t_1 and t_3 one oscillator evolves in a one-quantum coherence and the other oscillator evolves in a population. In the $R_{++-}^{(3)}$ signal, each oscillator evolves in a population during the t_2 waiting time, while the $R_{-++}^{(3)}$ signal has contributions from two distinct processes during the waiting time. If both normal modes interact with radiation as in the lower two OMT diagrams in panel (b) of Fig. 1, then both modes will evolve as populations. If the radiation only interacts directly with one normal mode as in the upper OMT diagram in panel (b) of Fig. 1, then that mode will evolve in a two-quantum coherence during the waiting time and the other mode will evolve as a population. This contribution is expected to dominate the t_2 -dependence in this signal for the present model since it displays appreciable dynamics even in the harmonic limit.

Results are displayed as the absolute square of the fast Fourier transform of the response function with respect to $t_1 = t_3 = t$ in Fig. 3 and with respect to t_2 in Fig. 4. Numerically exact quantum spectra are shown with gray dashed lines and the OMT results are given with solid blue lines. The zero frequency component has been omitted in all figures. The model has neither dissipation nor static disorder so apparent linewidths are artifacts of computing the Fourier transform over a finite time interval. Therefore, peak areas were computed, and each spectrum is scaled so that the dominant peak has unit area. OMT peak areas are shown as open blue circles and quantum peak areas as gray dots. Because of this normalization, absolute intensities of the quantum and OMT spectra cannot be compared in Figs. 3 and 4. For the cases shown in rows (a)–(c), amplitudes are in good agreement, but for the case in row (d), the OMT calculation underestimates the signal strength by an order of magnitude due to the use of the classical phase-space distributions in Eq. (7) at low temperatures. The frequency range in each plot is selected to show the dominant contributions to the signal.

The response function for a particular phase-matching condition, $R_{\gamma\beta\alpha}^{(3)}(t_3, t_2, t_1)$ in Eq. (1), is complex-valued and the absolute square of its Fourier transform with respect to time arguments need not be even in frequency. Both positive and negative frequencies are shown for the $R_{++-}^{(3)}$ signal in Fig. 3. In other plots, only positive frequencies are shown, either because the signal is nearly symmetric in ω , as for the $R_{-++}^{(3)}$ signal in Fig. 4, or because there is no significant contribution at negative frequencies, as for the $R_{-++}^{(3)}$ signal in Figs. 3 and 4.

Panels (ai)–(di) in the left-hand column of Fig. 3 show the absolute square of the Fourier transform of $R_{++-}^{(3)}(t, 0, t)$, the vibrational echo signal, and panels (aii)–(dii) in the right-hand column show the absolute square of the Fourier transform of $R_{-++}^{(3)}(t, 0, t)$. In rows (a)–(c), the bright Morse oscillator is coupled to a harmonic oscillator with $\beta D_a = 40$, $\beta \hbar \omega_a = 2$, $\gamma_m = 1$, and various degrees of interaction. In row (a), $c_{ab} = 0$, giving the signal for a thermal ensemble of noninteracting Morse oscillators.⁷² The dominant peak in the $R_{++-}^{(3)}$ signal in panel (ai) is at $-\Delta$, with $\Delta = \hbar \omega_a^2 / 2D_a$ the anharmonic frequency of a Morse

oscillator. It has been previously shown⁶⁹ that the vibrational echo for a Morse oscillator filters out frequencies other than this anharmonic frequency. The agreement between OMT and quantum calculations for a single anharmonic oscillator in row (a) of Fig. 3 demonstrates the accuracy of the approximate schemes for action quantization and for action transitions described in Sec. III. Row (b) shows calculations for coupled oscillators, with $c_{ab} = 0.05$ and $\gamma_{\omega} = 0.9$. For the $R_{++-}^{(3)}$ signal in panel (bi), coupling shifts the dominant peak to lower $|\omega|$ and introduces other peaks of smaller amplitude. Both effects are reproduced by the OMT calculation. For the $R_{-++}^{(3)}$ signal in panel (bii), the primary effect of the coupling is to introduce frequency shifts, which are also shown by the OMT result. In row (c), the coupling $c_{ab} = 0.05$ is maintained, but the interaction is increased by bringing the oscillators closer to resonance with $\gamma_{\omega} = 0.95$. The effects of interactions in this case relative to the uncoupled case of row (a) are more pronounced than in row (b). The OMT does not reproduce all peak amplitudes quantitatively, but does show many of the effects of interactions between the oscillators.

The parameters used in rows (a)–(c) of Fig. 3 correspond at room temperature to oscillators of relatively low frequency and high anharmonicity. Row (d) shows calculations more appropriate to high-frequency modes at room temperature. Signals are shown for two interacting Morse oscillators, with $\beta D_a = \beta D_b = 410$, $\beta \hbar \omega_a = 8$, $\gamma_m = 1$, $\gamma_{\omega} = 0.994$, and $c_{ab} = 0.05$. At room temperature, these parameters correspond to local mode frequencies of approximately 1650 cm^{-1} and anharmonicity of $\Delta \approx 16 \text{ cm}^{-1}$, roughly the frequency and anharmonicity characterizing a peptide unit in an amide I mode.⁷⁸ The OMT well reproduces the effects of interactions in this case.

The dependence of the signals on waiting time t_2 is examined in Fig. 4, which shows the absolute square of the Fourier transforms of $R_{++-}^{(3)}(5, t, 0)$ in column (i) and of $R_{-++}^{(3)}(5, t, 0)$ in column (ii). The parameters in each panel are the same as in Fig. 3. For uncoupled oscillators in panel (ai), the $R_{++-}^{(3)}$ signal is not well reproduced by the OMT approximation. All contributions in this case arise from transitions forbidden under harmonic selection rules⁷² and hence occur at relatively low amplitude, which is not apparent in the figure because of normalization. When coupling is introduced in panel (bi), low frequency peaks appear in the quantum response corresponding to frequencies of energy transfer between local modes. For a harmonic system this frequency corresponds to the frequency difference between states in which one normal mode is singly excited and the other is in the ground state, or approximately 0.11 for this case. The quantum response shows a peak shifted to lower frequency, indicating the effects of anharmonicity. The OMT does not reproduce the amplitude of these peaks in panel (bi), but does show a response near this frequency. In panel (ci), the energy transfer peak is dominant in the quantum calculation and greatly increased in amplitude in the OMT response. In the OMT spectrum the energy transfer peak at approximately 0.055 is incorrectly split into two nearly resonant features. For the lower anharmonicity case of panel (di), the OMT reproduces well the $R_{++-}^{(3)}$ signal.

The OMT and quantum calculations in panel (aii) in Fig. 4 agree well, showing that for a single anharmonic oscillator, the OMT describes the time-evolution of two-quantum coherences. As the interaction between the oscillators is introduced in panel (bii) and increased in panel (cii), the OMT reproduces well the resulting frequency shifts relative to the uncoupled case, although the dominant quantum peak in panel (cii) is again split into two near resonant peaks in the OMT response. The OMT performs well for the high frequency, low anharmonicity case in panel (dii). The calculations in Figs. 3 and 4 demonstrate the accuracy of the OMT calculations for dynamics probed in all three

propagation periods of the third-order response function, including the time-evolution of two-quantum coherences and energy transfer between local modes.

V. CONCLUSIONS

The OMT approximation to a vibrational response function, previously developed and implemented for a single anharmonic degree of freedom,⁷² represents the quantum dynamics of a density operator with a single quantized classical trajectory and represents the radiation-matter interaction by a transition in action at fixed angle. In the present work, we have extended the OMT to any number of interacting anharmonic oscillators, with the significant proviso that action and angle variables exist and can be determined. The OMT approximation in the multimode case was developed by semiclassically approximating sums of pairs of 2FDs, which represent contributions to the quantum mechanical response. Each OMT diagram is constructed from a harmonic limit of these 2FDs, in which the system is taken to be composed of noninteracting normal modes. The OMT approximation then introduces anharmonicity into the response function calculation in two ways. First, the quantization rules derived for the normal modes are applied to approximations to the good action variables of the exact Hamiltonian. Second, all trajectories are run with the full anharmonic Hamiltonian.

In principle, implementing this approximation even for a few degrees of freedom is computationally laborious. Coordinates and momenta must be expressed in terms of good action and angle variables to provide initial conditions for classical trajectories and to permit transitions in action at constant angles to be performed. For fixed values of the three time arguments of the response function, semiclassical paths such as those shown in Fig. 1 must be evaluated repeatedly in performing a thermal average over initial conditions. Furthermore, calculating a two-dimensional spectrum at several values of the waiting time requires the repeated determination of such semiclassical paths as the three propagation times of the response function are varied. We propose an approximate implementation of the OMT scheme, which greatly reduces computational effort. The relation between normal mode coordinates and momenta and good action and angle variables is determined using second-order perturbation theory in anharmonicity.⁷⁶ A single classical trajectory is computed for each set of action variables, which can then be applied to describe time evolution in any OMT diagram containing a trajectory with these actions. Mappings between classical states on distinct trajectories connected by a transition are constructed within a harmonic approximation to transitions at constant angle variables. OMT transitions are implemented by changing trajectories according to these mappings. All necessary trajectories and mappings are calculated once, before the determination of the response function. The thermal average over initial angles is then approximated by a time average along the initial trajectory of each diagram.

The OMT with this implementation was tested on thermal ensembles of pairs of interacting oscillators, with a bright anharmonic local mode coupled to a dark mode that was either harmonic or anharmonic. The responses associated with four-wave-mixing signals in phase-matched directions $-\mathbf{k}_1 + \mathbf{k}_2 + \mathbf{k}_3$ and $\mathbf{k}_1 + \mathbf{k}_2 - \mathbf{k}_3$ were determined, and dependences on all time arguments of $R_{\gamma\beta\alpha}^{(3)}(t_3, t_2, t_1)$ were considered. The OMT approximation reproduced well both the dynamics of single-quantum and two-quantum coherences and the dynamics of energy transfer between local modes. As the interaction between the modes increases, either from increasing the coupling term in the potential energy or from bringing the two modes more closely into resonance, the OMT calculation becomes less accurate. The performance of the OMT approximation and its efficient implementation here suggest that the method may be practically applied to larger systems, in which the required classical trajectories are generated from molecular dynamics simulations. For interacting vibrational chromophores

coupled to a larger system that induces dissipation,¹⁷ the presence of dephasing processes will place an upper limit on relevant time intervals. The level of accuracy required for the semiclassical quantization of trajectories for a large system may then be expected to be less than that demonstrated here for two degrees of freedom.

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FIG. 1.

All semiclassical diagrams corresponding to a pair of 2FDs contributing to (a)

$R_{++-}^{(3)}(t_3, t_2, t_1)$ and (b) $R_{-++}^{(3)}(t_3, t_2, t_1)$ are shown. Colored boxes labeled 1–4 indicate the identities of the normal modes interacting with radiation. The normal mode interacting earliest is labeled as red, and if there is a second interacting mode it is labeled as blue. At most, each diagram shows explicitly two modes. Horizontal solid lines indicate classical trajectories, and dashed vertical lines represent interactions with radiation. Colored dots on the semiclassical path represent phase points used to evaluate the OMT response function.

FIG. 2.

The computation of semiclassical paths used to evaluate OMT diagrams is shown schematically. A single trajectory is computed for each set of actions. Boxes represent discretized classical states along the trajectories, depicted by horizontal arrows. Maps approximating constant angle jumps are represented by dashed arrows connecting classical states on different trajectories. A possible time evolution is shown by colored boxes.

FIG. 3.

The squared absolute magnitudes of the Fourier transforms of $R_{++-}^{(3)}(t, 0, t)$ and $R_{-++}^{(3)}(t, 0, t)$ are shown respectively in the left and right columns. Row (a) shows spectra for a thermal ensemble of Morse oscillators with $\beta D_a = 40$ and $\beta \hbar \omega_a = 2$. Rows (b) and (c) show results for a thermal ensemble of these Morse oscillators each coupled to a dark harmonic oscillator with $\gamma_m = 1$. In row (b), $\gamma_\omega = 0.9$ and $c_{ab} = 0.05$, and in row (c) the frequency ratio has been increased to $\gamma_\omega = 0.95$ with $c_{ab} = 0.05$. Row (d) shows spectra for a thermal ensemble of two bilinearly coupled Morse oscillators with $\beta D_a = \beta D_b = 410$, $\beta \hbar \omega_a = 8$, $\gamma_m = 1$, $\gamma_\omega = 0.994$ and $c_{ab} = 0.05$. The quantum mechanical responses are given as gray dashed lines and the OMT results in solid blue. Peak areas are indicated for the quantum responses by gray dots while the OMT peak areas are shown as blue circles.

FIG. 4.

The squared absolute magnitudes of the Fourier transforms of $R_{+-}^{(3)}(5, t, 0)$ and $R_{-++}^{(3)}(5, t, 0)$ are shown respectively in the left and right columns for the same parameters as in the corresponding panels in Fig. 3.