Vibrational coherence and energy transfer in two-dimensional spectra with the optimized mean-trajectory approximation

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The optimized mean-trajectory (OMT) approximation is a semiclassical method for computing vibrational response functions from action-quantized classical trajectories connected by discrete transitions that represent radiation-matter interactions. Here, we extend the OMT to include additional vibrational coherence and energy transfer processes. This generalized approximation is applied to a pair of anharmonic chromophores coupled to a bath. The resulting 2D spectra are shown to reflect coherence transfer between normal modes. © 2015 AIP Publishing LLC. [<http://dx.doi.org/10.1063/1.4916644>]

I. INTRODUCTION

Multidimensional infrared spectroscopy probes interactions among molecular vibrations, providing both structural and dynamical perspectives on biomolecular and condensed phase systems.^{1–5} Multidimensional spectra can be computed from nonlinear response functions⁶ involving equilibrium dynamics in the experimentally attainable limit in which spectra reflect only the lowest-order nonlinearity. To reveal a maximally detailed picture of both structure and dynamics, these response function calculations should treat atomistic models.^{7–15} Numerically exact quantum dynamical calculations of response functions are generally impractical while purely classical calculations may be qualitatively incorrect except at the shortest time scales.^{16–23} These challenges motivate the development of approximate methods for computing response functions. One successful strategy is to treat a subsystem of interest with an implementation of quantum dynamics and to treat the rest of the system with classical or semiclassical mechanics.^{24–33} An alternative approach is to treat all degrees of freedom consistently with a semiclassical approximation to quantum dynamics.^{19,20,34–40} Kryvohuz and Cao⁴¹ have developed a semiclassical approximation of response functions in terms of classical dynamics in action-angle variables⁴² with action variables subject to quantization conditions. This approach results from expressing response functions exactly as phase space integrals of Wigner-transformed operators and then evaluating the Wigner transforms within a semiclassical approximation. The optimized mean trajectory (OMT) approximation^{43–45} also evaluates response functions through classical trajectories with semiclassical quantization of action variables. However, the OMT approximation differs both in its derivation and in its final form from the approximation based on semiclassical Wigner transforms.

The OMT approximation derives from an analysis of double-sided Feynman diagrams (2FDs), which provide a visualization of the quantum time-evolution underlying nonlinear spectra.^{1,4,6,46} These diagrams represent density oper-

ator dynamics treated perturbatively in the radiation-matter interaction. The mapping between quantum and semiclassical dynamics in the OMT is established by evaluating 2FDs for a harmonic potential. While a harmonic system has zero nonlinear response, implying that the sum of all 2FDs vanishes, individual 2FDs do not vanish for a harmonic potential and may be considered in this limit. In the OMT, the time evolution of the density matrix element $|n_i\rangle\langle n_j|$ is mapped onto a classical trajectory with action corresponding to the energy of a quantum harmonic oscillator with quantum number $(n_i + n_j)/2$. Although the semiclassical diagrams are determined from this correspondence in the harmonic limit, they are evaluated numerically using the full anharmonic potential with quantization rules applied to the “good” action and angle variables, thus incorporating anharmonic effects. The OMT approach therefore requires constructing canonical transformations between Cartesian coordinates and momenta and approximations to action and angle variables and is limited to the regime of quasiperiodic dynamics⁴⁷ in which action variables can be defined, or in practice, to situations that approximate such dynamics over the relevant experimental time scales.

This approximate correspondence between 2FDs and semiclassical diagrams results in continuous classical trajectories linked by transitions representing the effect of each radiation-matter interaction. Trajectories are propagated at quantized action values and the transitions between them increase or decrease action values at fixed angles. Depending on the values of the action variables and the phase of the interactions, these classical trajectories can approximate the dynamics of quantum coherences or populations. We have previously applied the OMT to calculate the third-order vibrational response of a thermal ensemble of noninteracting anharmonic oscillators,⁴³ pairs of coupled oscillators,⁴⁴ and an anharmonic oscillator coupled to a dissipative bath^{45,48} and have demonstrated the accuracy and practicality of the method.

The set of OMT diagrams that represent a response function calculation can be determined by enumerating a complete set of 2FDs. While the exact quantum calculation of a nonlinear response function is basis independent, its expression as a sum

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of 2FDs is not. For example, a vibrational response function calculated in a basis of stationary states is expressed as a sum of 2FDs that do not include population and coherence transfer processes. If an alternative basis is used, population and coherence transfer among non-stationary vibrational states should be included in the response function calculation. Therefore, evaluating the response function in this alternative basis requires a larger set of 2FDs that includes population and coherence transfer²⁶ in the structure of the diagrams. The structure of the corresponding OMT diagrams similarly depends on the identity of the phase space variables employed in the classical dynamics. Evaluating the response function within the OMT approach using good action and angle variables, assuming such exist, will require only diagrams in which action variables remain constant during propagation. However, if the phase space variables only approximate action and angle variables, then the conjugate momenta are not constants of the motion and the set of OMT diagrams would have to explicitly include nonradiative changes in these values.

Previous applications^{43–45} of the OMT approach employed approximate canonical transformations between Cartesian coordinates and momenta and action and angle variables based on low order perturbation theory in anharmonicity of the potential.⁴⁹ We have demonstrated⁴⁴ the accuracy of this approach for several coupled oscillator models. However, for sufficiently strong anharmonic couplings, perturbation theory will yield action variables that vary significantly in time. A possible conclusion is that low-order perturbation theory is inadequate and must be replaced with a more accurate method for computing action-angle variables. The calculation could also be regarded as outside the domain of applicability of the method. Here, we instead increase the number of 2FDs to incorporate vibrational coherence and energy transfer and hence enlarge the corresponding set of OMT diagrams to explicitly allow energy transfer among classical trajectories. We interpret this generalization as extending the domain of applicability of the OMT method to include systems with stronger anharmonic couplings. This enlarged set of OMT diagrams is then applied to a model of near-resonant coupled anharmonic chromophores interacting with a dissipative bath.

The model is presented and the form of the third-order vibrational response function is reviewed in Sec. II. In Sec. III, the third-order response function is formulated as a sum of OMT diagrams whose structure explicitly reflects the possibility of energy transfer among vibrational modes. In a previous treatment of an anharmonic oscillator coupled to a dissipative bath,⁴⁵ we proposed an implementation of the OMT employing forward-backward dynamics^{50–53} which greatly enhanced the efficiency of the calculation. The possibility of significant time variation of the approximate action variables poses challenges to this implementation which are addressed in Sec. IV and the Appendix. Two-dimensional spectra for the model of Sec. II are presented and interpreted in Sec. V. Our conclusions are summarized in Sec. VI.

II. RESPONSE FUNCTION AND MODEL

We treat a model in which two anharmonic local chromophore modes a and b are coupled to a bath of harmonic

oscillators,^{54–56}

$$\hat{H} = \hat{H}_a + \hat{H}_b + c_{ab}\hat{q}_a\hat{q}_b + \sum_{j=1}^{N_B} \frac{\hat{p}_j^2}{2m_j} + \frac{m_j\omega_j^2}{2} \left(\hat{q}_j - \frac{c_j V(\hat{q}_a, \hat{q}_b)}{m_j\omega_j^2} \right)^2. \quad (1)$$

Here, $\hat{H}_j$ are uncoupled local mode Hamiltonians, N_B is the number of bath modes, m_j and ω_j are the mass and frequency of mode j , c_{ab} determines the direct bilinear coupling between the chromophores, and c_j quantifies the coupling between bath mode j and the chromophore modes. The dependence of this coupling on the chromophore coordinates is determined by $V(\hat{q}_a, \hat{q}_b)$, which has dimensions of length. We will take this coupling to be first order in both coordinates,⁴⁸

$$V(\hat{q}_a, \hat{q}_b) = \hat{q}_a + \hat{q}_b. \quad (2)$$

The bath coupling coefficients and frequencies can be obtained from a specified spectral density, $J(\omega) \equiv \sum_j c_j^2 / (2m_j\omega_j) \delta(\omega - \omega_j)$. We take $J(\omega)$ in the continuum limit to be Ohmic with a Lorentzian cutoff,^{48,54–56}

$$J(\omega) = \frac{\eta}{\pi} \frac{\gamma^2 \omega}{\gamma^2 + \omega^2}, \quad (3)$$

where γ controls the width of $J(\omega)$ and η is the classical friction coefficient. This continuous distribution can be approximated by a discrete bath of oscillators with linearly spaced frequencies, $\omega_j = (j-1)\Omega/(N_B-1)$, and maximum frequency Ω by taking the coupling constants c_j to be⁵⁷

$$\frac{c_j^2}{m_j\omega_j^2} = \frac{2\eta\Omega}{\pi(N_B-1)} \frac{\gamma^2}{\gamma^2 + \omega_j^2}, \quad j = 2, \dots, N_B-1. \quad (4)$$

To better approximate a continuous bath, the $j=1$ mode is taken to have zero frequency⁵⁷ which contributes a frequency shift to the chromophore modes. The coupling constants for bath modes 1 and N_B are given by half of the right side of Eq. (4).

The Hamiltonian in Eq. (1) governs two local chromophore modes a and b and N_B local bath modes. Suppressing anharmonicity in the local mode Hamiltonians $\hat{H}_a$ and $\hat{H}_b$ allows the construction of $f = N_B + 2$ normal modes with coordinates denoted $\hat{x}_j$. For an off-resonant bath, two normal modes are dominated by contributions from the local chromophore modes, with the remaining normal modes representing perturbed bath modes. We label the chromophore normal modes 1 and 2, with labels $3, \dots, f$ referring to bath normal modes. These normal modes are coupled by anharmonic terms in $\hat{H}_a$ and $\hat{H}_b$.

The quantum mechanical third order vibrational response function for the signal with wavevector $\mathbf{k}_s = \alpha\mathbf{k}_1 + \beta\mathbf{k}_2 + \gamma\mathbf{k}_3$ generated by incident fields with wavevectors $\mathbf{k}_1$, $\mathbf{k}_2$, and $\mathbf{k}_3$ at times t_1 , $t_1 + t_2$, and $t_1 + t_2 + t_3$, respectively is⁶

$$R_{\gamma\beta\alpha}^{(3)}(t_3, t_2, t_1) = \left(\frac{i}{\hbar} \right)^3 \text{Tr}(\hat{\mu}^\delta \mathcal{G}(t_3) [\hat{\mu}^\gamma, \mathcal{G}(t_2) [\hat{\mu}^\beta, \mathcal{G}(t_1) [\hat{\mu}^\alpha, \hat{\rho}]]]), \quad (5)$$

with α, β, γ , and δ either $+$ or $-$ and the restriction that two signs are $+$ and two $-$. The rotating-wave approximation has been applied.⁶ We take the dipole operator to be proportional to

the sum of the chromophore normal mode coordinates $\hat{x}_1 + \hat{x}_2$ with the constant of proportionality suppressed. The operators $\hat{\mu}^\pm$ can then be expressed in terms of boson creation and annihilation operators, $\hat{\mu}^+ = \hat{b}_1^\dagger(\hbar/2m_1\omega_1)^{1/2} + \hat{b}_2^\dagger(\hbar/2m_2\omega_2)^{1/2}$ and $\hat{\mu}^- = (\hat{\mu}^+)^\dagger$. The equilibrium density operator is given by $\hat{\rho}$ and $\mathcal{G}(t)\hat{A} = e^{-i\hat{H}t/\hbar}\hat{A}e^{i\hat{H}t/\hbar}$. The purely absorptive spectrum,^{4,48} $R_{\text{abs}}(\omega_3, \omega_1; t_2)$, is obtained by combining the rephasing, $R_I \equiv R_{++-}$, and nonrephasing, $R_{II} \equiv R_{+--}$, responses,

$$R_{\text{abs}}(\omega_3, \omega_1; t_2) \equiv \text{Im} \left[\tilde{R}_I^{(3)}(\omega_3, -\omega_1; t_2) + \tilde{R}_{II}^{(3)}(\omega_3, \omega_1; t_2) \right], \quad (6)$$

with $\tilde{R}^{(3)}(\omega_3, \omega_1; t_2)$ the one-sided Fourier transform of $R^{(3)}(t_3, t_2, t_1)$ with respect to t_1 and t_3 . Calculations of R_{abs} for the model of Eqs. (1)–(4) are presented in Sec. V.

III. OPTIMIZED MEAN-TRAJECTORY APPROXIMATION WITH COHERENCE AND ENERGY TRANSFER

We review and generalize the OMT, focusing on computing the third-order response function in Eq. (5) for a pair of local modes weakly coupled to a bath as described in Eq. (1). The method is extended to include coherence and energy transfer processes.

The OMT method is based on an approximate evaluation of the quantum mechanical 2FDs^{1,4,6,46} that compose the response function. This approximation is carried out in a harmonic limit as follows. First, the Hamiltonian is treated to harmonic order and a canonical transformation to normal modes is applied. The quantum evolution of the density operator for normal mode r , $|n_i^r\rangle\langle n_j^r|$ is then represented in the OMT as the evolution of a classical oscillator with action $\hbar(n_i^r + n_j^r + 1)/2$. This is the action of a classical harmonic oscillator with energy equal to that of a quantum harmonic oscillator with quantum number $(n_i^r + n_j^r)/2$. Within this approximation, an interaction of the electric field with mode r will increase or decrease n_i^r or n_j^r by one, corresponding to jumps in action of $\hbar/2$ in the OMT approximation. Quantum mechanical evolution interrupted by transitions between eigenstates is treated in the OMT as classical evolution interrupted by transitions in action at constant angle values. While the OMT is derived within this harmonic approximation, the action quantization conditions are applied to the good action variables⁴³ or approximations to these variables,^{44,45} and time evolution is carried out under the full anharmonic Hamiltonian. This incorporates anharmonic effects into the OMT method.^{43–45}

For the system of two chromophore normal modes coupled to $f - 2$ bath modes described in Sec. II, this procedure yields the approximate response function,⁴⁴

$$R_{\gamma\beta\alpha}^{(3)}(t_3, t_2, t_1) = \sum_{r=1,2} \rho_{\gamma\beta\alpha}^r(t_3, t_2, t_1) + \sum_{r=1,2} \sum_{s=1,2, s \neq r} \rho_{\gamma\beta\alpha}^{r,s}(t_3, t_2, t_1). \quad (7)$$

The OMT diagrams that generate Eq. (7) are derived from pairs of 2FDs that satisfy the trace in Eq. (5) in the harmonic limit. This correspondence results in either one chromophore

mode interacting four times with the electric field, as in the first sum in Eq. (7), or each chromophore mode interacting twice, as in the second sum. Full expressions for $\rho_{\gamma\beta\alpha}^r$ and $\rho_{\gamma\beta\alpha}^{r,s}$ are given in Ref. 44. There are four trace-satisfying OMT diagrams contributing to $\rho_{\gamma\beta\alpha}^r$ resulting from all combinations of either increasing or decreasing the action of the interacting mode r at times t_1 and $t_1 + t_2$. There are eight trace-satisfying contributions to $\rho_{\gamma\beta\alpha}^{r,s}$ resulting from two of the three possible sequences of mode interactions with the field first interacting with mode r and varying in whether the action increases or decreases at t_1 and $t_1 + t_2$. Figure 1 shows the four shared trace-satisfying OMT diagrams contributing to $\rho_{++-}^{1,2}$ and $\rho_{+-+}^{1,2}$ with interaction ordering 1122.^{43,44} Each diagram is a schematic plot of action versus time and is composed of two fragments, representing the time course of each chromophore mode. Bath mode actions are not shown and are taken to be continuous. Dotted horizontal lines indicate actions that are half-odd-integer multiples of $\hbar$ and correspond to the density matrix being diagonal in the eigenstate basis. Actions that are integer multiples of $\hbar$ are indicated by dashed horizontal lines and correspond to single-quantum coherences. To correspond to a diagonal thermal density operator, all normal mode actions must be half-odd-integer multiples of $\hbar$ prior to the first interaction with the field. Additionally, to satisfy the trace, it is necessary that all normal mode actions are half-odd-integer multiples of $\hbar$ following the final interaction with the field. Therefore, the diagram fragment corresponding to each mode in an OMT diagram must begin and end on a dotted line. While this is a necessary condition to satisfy the trace, it is not sufficient since a dotted line corresponding to a half-odd-integer quantized action can also represent a two-quantum coherence.

FIG. 1. Four of the eight OMT diagrams contributing to $\rho_{++-}^{1,2}$ in Eq. (7) or all four contributing to $\rho_{+-+}^{1,2,2}$ in Eq. (8) are shown. In each diagram fragment, action increases vertically. The relative actions of modes 1 and 2 are independently varied so that the relative position of the normal mode actions is arbitrary. Dashed horizontal lines indicate integer quantized actions, representing coherences, while dotted horizontal lines indicate half-odd-integer quantized values which here represent populations.

The OMT diagrams in Fig. 1 are semiclassical representations of quantum 2FDs evaluated in a basis of stationary states so that coherence and population transfer processes are not included in the structure of the diagrams. These 2FDs correspond to OMT diagrams evaluated with quantized values of good action variables. In practice, OMT diagrams are evaluated numerically using perturbative corrections⁴⁹ to the action variables of the normal modes. For some anharmonic couplings, the classical modes may exchange an appreciable amount of energy. This exchange of energy corresponds to quantum coherence or population transfer in 2FDs. To allow for the inclusion of these processes, we must enlarge the collection of 2FDs, and thereby the number of associated OMT diagrams, that contribute to the third order response function.

Example 2FDs with coherence and population-coherence transfer that contribute to the rephasing signal are shown in Figs. 2(a)-2(c), together with their corresponding OMT diagrams. These 2FDs are evaluated in the normal mode basis of the Hamiltonian in Eq. (1), so that the basis states are coupled by anharmonicity. For convenience, all 2FDs shown begin with the chromophore modes in the ground state and do not specify the state of the bath modes. For the high frequency chromophores treated in Sec. V, thermally excited states make a negligible contribution to the response function. The OMT diagrams in Fig. 2, however, could be used to compute the response function at any temperature. These OMT diagrams are obtained from their corresponding 2FDs by applying the same rules used to generate the diagrams in Fig. 1 with the additional wavy vertical lines representing nonradiative energy transfer processes. Since the bath is assumed to be off-resonant, an increase in the energy of one chromophore mode is accom-

panied by a decrease in energy of the other chromophore. For example, in the 2FD in Fig. 2(a), at the start of the t_1 propagation period, mode 1 is in the coherence $|0\rangle\langle 1|$ and mode 2 is in the population $|0\rangle\langle 0|$, while by the end of this period, mode 1 is in the population $|0\rangle\langle 0|$ and mode 2 is in the coherence $|0\rangle\langle 1|$. In the corresponding OMT diagram in Fig. 2(a), this coherence transfer process is represented by the transfer of energy between two classical oscillators during the t_1 period. The action of mode 1 decreases by $\hbar/2$ and the action of mode 2 increases by this amount. The 2FDs in Figs. 2(b) and 2(c) include similar population-coherence and coherence transfer processes during the t_2 and t_3 propagation periods, respectively, and these processes are represented in the associated semiclassical diagrams as energy transfer between classical oscillators during the appropriate time intervals. The 2FDs in Figs. 2(a)-2(c) are trace-satisfying and hence contribute to the response function, as should the corresponding OMT diagrams.

The diagrams in Figs. 2(a)-2(c) cannot be directly incorporated into the OMT calculation since these diagrams are generated numerically only if specific dynamical processes occur. Our strategy for including OMT diagrams such as those in Figs. 2(a)-2(c) is based on consideration of non-trace-satisfying “parent” diagrams that do not explicitly include energy transfer processes, such as the diagram in Fig. 2(d). The 2FD in Fig. 2(d) does not satisfy the trace and hence does not contribute to $R^{(3)}$. The OMT diagram in Fig. 2(d), if evaluated in the harmonic limit, would similarly vanish as a consequence of integration over angle variables. However, if in evaluating the OMT diagram in Fig. 2(d) mode 1 were found to have transferred energy to mode 2 during the t_1 evolution period, the result would be the sequence of events represented by the OMT diagram in 2(a). Similarly, energy transfer between modes 1 and 2 during the t_2 or t_3 trajectories in the OMT diagram in Fig. 2(d) would yield the diagrams in Figs. 2(b) and 2(c), respectively. We will refer to the diagrams in Figs. 2(a)-2(c) as “child” diagrams of the parent in Fig. 2(d). Including the diagram in Fig. 2(d) incorporates the diagrams in 2(a)-2(c) into the OMT through the use of full classical dynamics. The importance of processes such as those represented by the OMT diagrams in Figs. 2(a)-2(c) to the response function is entirely determined by the extent to which the numerical classical trajectories of the coupled chromophores exhibit these processes.

For systems with energy transfer, the response function should be computed from all parent OMT diagrams generated from Eq. (5), including those not satisfying the trace in the harmonic limit. This can be achieved by modifying the OMT response function in Eq. (7) to include contributions from any sequence of chromophore interactions,

$$R_{\gamma\beta\alpha}^{(3)}(t_3, t_2, t_1) = \sum_{r_j=1,2} \rho_{\gamma\beta\alpha}^{r_0, r_1, r_2, r_3}(t_3, t_2, t_1). \quad (8)$$

The indices r_0, r_1, r_2 , and r_3 specify the normal mode interacting with the field at time 0, t_1 , $t_1 + t_2$, and $t_1 + t_2 + t_3$, respectively. There are 16 terms contributing to Eq. (8) corresponding to all sequences of interactions with modes 1 and 2. The contribution to Eq. (8) from a given sequence of interactions is⁴⁴

FIG. 2. Panels (a)-(c) show at left trace-satisfying 2FDs with coherence transfer occurring during the t_1 , t_2 , and t_3 time periods, respectively. Corresponding OMT diagrams are shown at right. These form a subset of the possible “child” diagrams that can be generated from the non-trace-satisfying “parent” diagram in (d) with all-forward time propagation.

$$\begin{aligned} \rho_{+\pm\mp}^{r_0, r_1, r_2, r_3}(t_3, t_2, t_1) = & \frac{i}{24\hbar^{2f+3}} \sum_{p=1}^4 \epsilon_p \int d\mathbf{z}_1 \int d\mathbf{z}_2 \int d\mathbf{z}_3 \\ & \times \Gamma^{r_0}(\mathbf{z}_1) \Delta F^{r_0}(\mathbf{z}_1) \delta(\phi_2 - \phi_1(t_1)) \\ & \times \delta(\phi_3 - \phi_2(t_2)) \Delta_{1\sigma_p}^{r_1} \Delta_{2\sigma'_p}^{r_2} \\ & \times Q_{\mp}^{r_0}(\mathbf{z}_1) Q_{\pm}^{r_1}(\mathbf{z}_{p_1}(t_{p_1})) Q_{+}^{r_2}(\mathbf{z}_{p_2}(t_{p_2})) \\ & \times Q_{-}^{r_3}(\mathbf{z}_{p_3}(t_{p_3})), \end{aligned} \quad (9)$$

$$\Gamma^r(\mathbf{z}) \equiv \hbar^f \sum_{n_r=1}^{\infty} \delta(J^r - n_r \hbar) \prod_{s \neq r} \sum_{n_s=0}^{\infty} \delta(J^s - (n_s + \frac{1}{2}) \hbar), \quad (10)$$

$$\Delta F^r(\mathbf{z}) \equiv F(\mathbf{z})|_{J^r \rightarrow J^r - \hbar/2} - F(\mathbf{z})|_{J^r \rightarrow J^r + \hbar/2}, \quad (11)$$

$$F(\mathbf{z}) \equiv \frac{e^{-\beta H(\mathbf{z})}}{\int d\mathbf{z}' e^{-\beta H(\mathbf{z}')} \prod_{s=1}^f \sum_{n_s=0}^{\infty} \hbar \delta(J^s - (n_s + \frac{1}{2}) \hbar)}, \quad (12)$$

$$\Delta_{\tau\pm}^r \equiv \hbar^f \delta(J_{\tau+1}^r - (J_{\tau}^r(t_{\tau}) \pm \frac{\hbar}{2})) \prod_{s \neq r} \delta(J_{\tau+1}^s - J_{\tau}^s(t_{\tau})), \quad (13)$$

$$Q_{\pm}^r(\mathbf{z}_{\tau}(t)) \equiv x_{\tau}^r(t) \mp i p_{\tau}^r(t) / (m_r \omega_r). \quad (14)$$

While $\rho_{+\pm\mp}$ is given in Eq. (9) as three $2f$ -dimensional integrals, only the integration over $\mathbf{z}_1$ needs to be performed numerically due to the delta functions in angle in Eq. (9) and in action in Eq. (13). The integration over action variables $\mathbf{J}_1$ is further reduced to f sums by $\Gamma^{r_0}(\mathbf{z}_1)$ in Eq. (10). This simplifies the response function calculation to a summation of OMT diagrams which include an average over initial conditions.^{43–45} The index p in Eq. (9) sums over semiclassical diagrams, composed of classical trajectories linked by jumps in the chromophore actions at fixed angle values. Four parent diagrams contribute to each term, corresponding to combinations of either increasing or decreasing the action at the second and third interactions with the field. Only combinations of these two interactions must be considered since both initial interactions are included in a single diagram through the factor ΔF^{r_0} defined in Eq. (11). Therefore, a total of 64 parent diagrams contribute to Eq. (8). Subscripts $\tau = 1, 2, 3$ label the three classical trajectories of the OMT diagram, which are propagated for times t_1 , t_2 , and t_3 , respectively. The action of mode r is increased or decreased following trajectory τ in the OMT diagram according to the subscripts σ in $\Delta_{\tau\sigma}^r$, which can be either + or –, as defined in Eq. (13). Here, the final action values of each trajectory are explicitly given as functions of time, since the assumption that these actions are fixed has been relaxed to allow for energy transfer. In Eqs. (9)–(14), $\mathbf{z}_{\tau}(t)$ refers to the phase space variables $\mathbf{z}$ for trajectory τ of the OMT diagram at time t ; if no time is specified, $t = 0$. The arguments of Q_{σ}^r in Eq. (9) determine the four phase space points in the diagram required to compute the response function. These points are calculated at times t_0 , t_1 , $t_1 + t_2$, and $t_1 + t_2 + t_3$ at action values chosen according to the procedure described in Ref. 44, which ensures the classical evaluation of an OMT diagram and the quantum calculation of its corresponding pair of 2FDs give the same result in the harmonic limit. Superscripts in Eqs. (10)–(14) indicate components of the f -dimensional action, $\mathbf{J}$, or of the normal mode coordinate and its conjugate momentum, $\mathbf{x}$ and $\mathbf{p}$.

The statistical weight of each diagram is determined by F in Eq. (12), the classical equilibrium distribution function renormalized to account for action quantization. In Eq. (11), F is evaluated at the two states prior to the first interaction with the field. The actions of these states are obtained by replacing the initial action of the first mode interacting with the field in trajectory 1, $J_1^{r_0}$, with $J_1^{r_0} - \hbar/2$ or $J_1^{r_0} + \hbar/2$, as indicated in Fig. 1 by the two initial dashed vertical lines. The angle values are held constant in this transition. The terms have opposite sign in Eq. (11) due to the innermost commutator in Eq. (5). In Eq. (9), ϵ_p is an overall sign arising from the remaining commutators.⁴³ For diagrams with one of the middle interactions increasing and the other decreasing the action, $\epsilon_p = -1$, while $\epsilon_p = 1$ for diagrams with both interactions increasing or decreasing the action.⁴³

An example is the evaluation of the $\rho_{+\pm\mp}^{1,1,2,2}$ contribution to the response function generated by the four OMT diagrams in Fig. 1. The first sum in Eq. (10) restricts the action of the first interacting mode in trajectory 1, in this case mode 1, to be an integer multiple of $\hbar$. Red dots in Fig. 1 at the beginning and end of this trajectory represent the points in each diagram where the factors $Q_{\mp}^1(\mathbf{z}_1)$ and $Q_{\pm}^1(\mathbf{z}_1(t_1))$ in Eqs. (9) and (14) are evaluated. At time t_1 , mode 1 interacts with the field a second time, either increasing or decreasing its action by $\hbar/2$. This transition is controlled by the factor $\Delta_{1\sigma_p}^1$ in Eq. (9). All angle values are unchanged during this jump in action as required by $\delta(\phi_2 - \phi_1(t_1))$. Following propagation for time t_2 , mode 2 interacts with the field causing a jump of $\hbar/2$ in this mode's action at constant angles according to the factors $\Delta_{2\sigma'_p}^2$ and $\delta(\phi_3 - \phi_2(t_2))$. The blue dots at the start and end of the third trajectory in the mode 2 fragment of each diagram represent the factors $Q_{+}^2(\mathbf{z}_3)$ and $Q_{-}^2(\mathbf{z}_3(t_3))$, respectively.

The form of the OMT presented in Eqs. (9)–(14) generalizes the OMT of our previous work^{43–45} by including non-trace-satisfying diagrams such as that in Fig. 2(d). In the absence of anharmonic processes, such terms will average to zero under the phase space integration in Eq. (9). Therefore, contributions from non-trace-satisfying diagrams can be attributed to anharmonic processes such as coherence and energy transfer.

IV. FORWARD-BACKWARD IMPLEMENTATION WITH ENERGY TRANSFER

In a naive implementation⁴⁵ of the OMT approximation, diagrams such as those in Figs. 1 and 2 are evaluated from left to right by propagating all trajectories forward in time. For a single high frequency oscillator coupled to a bath, we developed⁴⁵ a forward-backward⁴⁸ implementation of this method that achieves a significant increase in efficiency by factoring OMT diagrams into contributions depending separately on t_1 and t_3 . This factorization is exact for good action-angle variables. The initial state of each diagram is taken to be the end of trajectory 1, $\mathbf{z}_1(t_1)$. The classical trajectory 1 is then propagated backward in time to obtain $\mathbf{z}_1$. Trajectories 2 and 3 are propagated forward in time. This procedure greatly reduces the number of trajectories used to compute the response function but relies on trajectories in the OMT diagram being propagated at constant action, which will not hold for diagrams with energy transfer as in Figs. 2(a)–2(c). Therefore, to include energy

transfer, the forward-backward implementation described in Ref. 45 must be modified.

For an implementation of the OMT approximation to incorporate all energy transfer processes, the response function in Eq. (8) must be evaluated in such a way that all child diagrams generated via energy transfer under all-forward propagation can be reached by dynamical processes. While diagrams are defined independently of an evaluation scheme, the association of a child diagram with its parent is implementation dependent. The primary challenge in extending the forward-backward implementation to include energy transfer is that child diagrams with energy transfer during the t_1 time period are not naturally generated from the 64 parent diagrams evaluated in Eq. (8) in this implementation. For example, Fig. 3(a) shows the child diagram from Fig. 2(a) with energy transfer during the t_1 time period. To identify a parent diagram in the forward-backward implementation, the energy transfer event is removed while the actions at t_1 remain fixed, since these values are now associated with the starting point of the diagram. Following this procedure results in a spurious diagram in which the field first interacts with mode 1 but the result is an increase in the action of mode 2. To include diagrams like that in Fig. 2(a) in the forward-backward implementation, we allow the identity of the interacting mode r_0 in Eq. (8) to vary depending on the chromophore actions at time 0. Specifically, we take the parent diagram for Fig. 3(a) in the forward-backward implementation to be the diagram in Fig. 3(b), in which the first interacting mode is mode 2. In practice, the identity of the first interacting mode is determined by computing the action of the chromophore modes during trajectory 1 as a function of time. We calculate these actions by equating the perturbative expression for the Hamiltonian in action variables with the exact Hamiltonian written as a function of normal mode coordinates and momenta propagated with the exact Hamiltonian. For simplicity, the bath is neglected in solving for the chromophore actions, although propagated trajectories include the bath. The identity of the first interacting mode r_0 is determined by rounding the computed chromophore actions to the nearest properly quantized set of action values, assuming that the sum of their actions is fixed, so that $\Gamma^{r_0}(\mathbf{z}_1)$ in Eq. (9) is most closely satisfied. We denote the first interacting mode in the parent diagram as r'_0 , which may or may not be the same as r_0 . For example, $r'_0 = 2$ for the parent diagram shown in Fig.

3(b). If, in evaluating this diagram, back propagation of the t_1 time period results in the actions of modes 1 and 2 changing from approximately $\hbar/2$ and $\hbar$ to approximately $\hbar$ and $\hbar/2$, as in (a), then the identity of the first interacting mode is taken to be mode 1 rather than mode 2 and $r_0 = 1$. This will result in the diagram being evaluated at $Q_-^1(\mathbf{z}_1)$ as in Fig. 3(a) and not $Q_-^2(\mathbf{z}_1)$ as in Fig. 3(b). As seen in this example, trace-satisfying child diagrams with t_1 energy transfer are generated in the forward-backward implementation from trace-satisfying parent diagrams. In contrast, trace-satisfying diagrams with t_2 and t_3 energy transfer as in Figs. 2(b) and 2(c) will result from non-trace-satisfying parent diagrams as in Fig. 2(d).

Only OMT diagrams with one chromophore mode's action integer quantized and the rest half-odd-integer quantized at time t_1 can be generated in the forward-backward implementation by allowing the first interacting mode to vary. This is sufficient to ensure that the desired child diagrams generated from parent diagrams beginning with the chromophore modes in the ground state are included in the forward-backward implementation. Energy transfer can result in other possible states at time t_1 for diagrams with thermally excited chromophore modes prior to the first interaction with the field. Neglecting these excited state energy transfer diagrams does not affect results for the parameters used in Sec. V. Further technical aspects of the forward-backward implementation are outlined in the Appendix.

V. RESULTS

We calculate spectra for the Hamiltonian in Eq. (1), with the local modes a and b taken to be Morse oscillators. The well depths of modes a and b are specified by $\beta D_a = 391$ and $\beta D_b = 291$, with $\beta \equiv 1/k_B T$. We take $\omega_b = 0.96\omega_a$, the coupling between modes a and b to be $c_{ab} = 0.0096m_a\omega_a^2$ and $\beta\hbar\omega_a = 7.75$. The bath defined in Eq. (4) is specified by $N_B = 60$, $\Omega = 0.06\omega_a$, $\eta = 100m_a\omega_a$, and $\gamma = 0.004\omega_a$. All masses are taken to be equal.

All results were computed using the forward-backward implementation described in Sec. IV and the Appendix. The coupled chromophore normal modes were treated with first order perturbation theory⁴⁹ in cubic anharmonicity and the bath modes were treated to zeroth order as harmonic oscillators in carrying out the required canonical transformations between Cartesian coordinates and momenta and action-angle variables.^{44,45} Diagram initial conditions were generated from 2500 Metropolis sampled initial actions, $\mathbf{J}_0$, and random angles with $\mathbf{J}_1(t_1) = \mathbf{J}_0|_{J_0 \rightarrow J_0'}$. One set of initial conditions was used to compute all results. To reduce the number of initial conditions required to converge the response function at long times, a one-sided cosine-squared window function in t_1 and t_3 was applied to the response function prior to taking the Fourier transforms.^{23,45}

Figure 4 shows $R_{\text{abs}}^{(3)}(\omega_3, \omega_1; t_2)$ for various values of t_2 . Row (i) shows the full response function computed from Eq. (8). Row (ii) shows the contribution to (i) generated by trace-satisfying parent diagrams defined in Eq. (7) and row (iii) shows the remaining contribution to (i) resulting from non-

FIG. 3. Illustration of energy transfer during t_1 in the forward-backward implementation. (a) Child diagram with energy transfer during t_1 reproduced from Fig. 2(a). In the forward-backward implementation, the parent diagram for (a) is (b) which is a contribution to $\rho_{++}^{2,1,2,1}$. If energy transfer occurs, the identity of the first interacting mode is changed resulting in child (a).

FIG. 4. $R_{\text{abs}}^{(3)}(\omega_3, \omega_1; t_2)$ for a thermal ensemble of coupled Morse oscillators. OMT results from Eq. (8) are shown in row (i), while contributions from trace-satisfying parent diagrams are shown in row (ii) and from non-trace-satisfying parent diagrams in row (iii). Spectra are shown for $\omega_a t_2 = 0, 70, 140, 420$, and 1250 in columns (a)-(e), respectively. Six equally spaced positive and negative contours up to 50% of the maximum absolute value in panel (ai) are drawn in each plot, with positive contours in red and negative in blue.

trace-satisfying parent diagrams. Spectra are shown at $\omega_a t_2 = 0, 70, 140, 420$, and 1250 in columns (a)-(e), respectively. The spectra show bath-induced dephasing. At $t_2 = 0$, shown in column (a), all peaks are diagonally elongated, indicating inhomogeneous broadening.⁴⁻⁶ The peaks in each row become more rounded as the waiting time becomes long compared to dephasing times as seen in columns (d) and (e).

The spectrum at zero waiting time in Fig. 4(ai) shows four pairs of peaks. In the absence of energy transfer, the diagonal pairs are generated by OMT diagrams with all interactions occurring either with chromophore mode 1, with higher frequency, or with chromophore mode 2, with lower frequency. The off-diagonal pairs of peaks are generated from OMT diagrams with two interactions occurring with each mode. The negative (blue) peak in each pair corresponds to one mode being in a coherence during the t_3 time period and the other being in the ground state. In the absence of thermally excited chromophore states, these peaks are generated by OMT diagrams with one of the middle interactions increasing and the other decreasing the action, such as in Fig. 1(c). The positive (red) anharmonic peak corresponds to one mode being in a coherence and the other in the first excited state during the t_3 time period and is generated under these conditions from diagrams with both middle interactions increasing the system action, such as in Fig. 1(a). The association of OMT diagrams with specific peaks in the 2D spectra aids in the interpretation of the spectra, as demonstrated through the discussion below of Figs. 5 and 6.

Contributions from both trace-satisfying parent diagrams in row (ii) and non-trace-satisfying parent diagrams in row (iii) can include energy transfer events. In particular, contributions from OMT diagrams with one energy transfer event during the t_1 time period will contribute to row (ii), as t_1 coherence transfer does not alter the trace-satisfying nature of a diagram in the forward-backward implementation. The dominant contribution to this row, however, is from trace-satisfying parent diagrams that do not include energy transfer events. The non-trace-satisfying parent diagrams used to compute the results in row (iii) will not contribute in the absence of anharmonic processes such as energy transfer. Comparison of row (i) of Fig. 4 with rows (ii) and (iii) shows that the non-trace-satisfying diagrams have a small but non-negligible contribution to the 2D spectra. At $t_2 = 0$, all contributions from non-trace-satisfying parent diagrams in (a(iii)) are expected to result from child diagrams that have energy transfer during the t_3 or during both the t_1 and t_3 time periods. The effect of these diagrams on the complete spectrum in (ai) is to increase the relative contribution of the positive anharmonic off-diagonal peaks while decreasing the magnitude of the diagonal peaks, particularly the diagonal anharmonic peak. The ω_3 frequencies associated with anharmonic peaks occur during t_3 if both middle interactions increase the action. The larger relative amplitudes of the off-diagonal anharmonic peaks in column (a) of Fig. 4 therefore indicate that energy transfer is more likely to occur when higher energy states are accessed during t_3 than when lower energy states are propagated during t_1 or t_3 .

FIG. 5. Contribution to the rephasing response, $|\tilde{R}_1^{(3)}(\omega_3, -\omega_1; t_2)|$, from the non-trace-satisfying parent diagram with interaction order 1211 and the second and third interactions increasing the action is shown in (a) for $t_2 = 0$. Six equally spaced contours between 0% and 75% of the maximum height in peak B are shown. Relative integrated volumes of the peaks labeled A, B, and C in (a) are shown as a function of t_2 in panel (b). Volumes are normalized to the volume of peak B at $t_2 = 0$. The two trace-satisfying child 2FDs with one energy transfer event during t_3 are shown in (c) and the two trace-satisfying child diagrams with one energy transfer event during t_2 are shown in (d).

For two coupled chromophores, 2FDs indicate that the off-diagonal peaks will oscillate in t_2 with frequency $\omega_{10,01}$, the difference between the frequencies of the $|1\rangle\langle 0|$ coherences of modes 1 and 2. Spectra in column (b) of Fig. 4 are shown at $\omega_a t_2 = 70$, roughly half the period of this oscillation, and in column (c) are shown at $\omega_a t_2 = 140$, roughly one period. The trace-satisfying contribution in row (ii) shows the expected oscillation of the off-diagonal peaks. The non-trace-satisfying contribution to the off-diagonal peaks in row (iii) also shows an oscillation on this time scale. This results in an oscillation in the off-diagonal peaks in the full spectrum in Figs. 4(ai)–4(ci), although there is a non-negligible contribution to the off-diagonal peaks at $\omega_a t_2 = 70$. The diagonal peaks in row (iii) also exhibit an oscillation on this time scale. This phase oscillation is absent in row (ii) since trace-satisfying parent diagrams contributing to the diagonal peaks evolve in populations during t_2 .

The contributions from specific non-trace-satisfying parent diagrams are analyzed in Figs. 5 and 6. Figure 5(a) shows a contribution to $|\tilde{R}_1^{(3)}(\omega_3, -\omega_1; t_2)|$, the absolute value of the rephasing contribution to the purely absorptive spectrum in Eq. (6), at $t_2 = 0$. This figure shows the contribution from the non-trace-satisfying parent diagram with sequence of chromophore interactions 1211 and the second and third interactions increasing the action. The 2FD and the OMT diagram corre-

FIG. 6. Contribution to the nonrephasing response, $|\tilde{R}_2^{(3)}(\omega_3, \omega_1; t_2)|$, from the non-trace-satisfying parent diagram with the same sequence of interactions as in Fig. 5 is shown in (a) for $t_2 = 0$. Six equally spaced contours between 0% and 75% of the maximum height of peak B are shown. (b) Relative volumes of the peaks labeled A, B, and C in (a) are shown as a function of t_2 , normalized to the volume of peak B at $t_2 = 0$. (c) The two trace-satisfying child diagrams with one energy transfer event during t_3 with ordering 1211 and the second and third interactions increasing the quantum number are shown. (d) The two trace-satisfying child diagrams with one energy transfer event during t_2 .

sponding to this contribution are shown in Fig. 7(bi) in the Appendix. The three visible peaks in the spectrum are labeled A, B, and C. In the absence of anharmonicity, this non-trace-satisfying diagram would not contribute. The distinct peaks at $t_2 = 0$ can be attributed to energy transfer processes during the t_3 time period or during both the t_3 and t_1 time periods. Figure 5(c) shows the two trace-satisfying child 2FDs of the parent diagram in Fig. 7(bi) with one energy transfer event during the t_3 time period. The positions of the peaks in Fig. 5(a) can be directly related to the 2FDs in (c). Specifically, the applied frequency ω_1 for peaks A and B is associated with material frequency $\omega_{00,10}$, from the evolution of a single quantum coherence for the higher frequency normal mode 1. This is the expected t_1 frequency without energy transfer. Peak A is an off-diagonal peak with frequency ω_3 corresponding to $\omega_{11,10}$, that is, the evolution of a single quantum coherence for the lower frequency mode 2 and a population in mode 1. This is the frequency expected without energy transfer during the t_3 time period and is the first frequency accessed during t_3 in the 2FDs in Fig. 5(c). The ω_3 frequency of peak B is expected to include contributions from both $\omega_{11,01}$ and $\omega_{20,10}$, which are similar in magnitude. These frequencies are not reached in the parent diagram in Fig. 7(bi) but are accessed in the child diagrams shown in Fig. 5(c) due to energy transfer during the t_3 time period. In contrast to peaks A and B, peak C reflects the

frequency $\omega_{00,01}$ during t_1 , a coherence in the lower frequency mode 2. This frequency may be reached if energy transfer occurs during back propagation of $|00\rangle\langle 10|$ during the t_1 time period. This transfer alone would not make the diagram in Fig. 7(bi) trace-satisfying, consistent with no visible peak in the unlabeled quadrant of Fig. 5(a). To satisfy the trace, energy transfer must additionally occur during t_3 , as reflected by the ω_3 frequency associated with peak C being $\omega_{11,01}$ or $\omega_{20,10}$.

Dynamics of the integrated volumes of the peaks labeled A, B, and C in Figure 5(a) are shown in Figure 5(b) relative to the volume of peak B at $t_2 = 0$. We define each peak as being located in the gray shaded regions in panel (a). Energy transfer events may occur during t_2 for nonzero propagation times. Therefore, the 2FDs in panel (d) may contribute to Fig. 5(b) both without and with t_1 energy transfer. In Fig. 5(b), all three peak volumes show an oscillation in t_2 that corresponds to the difference in the frequencies of the two single quantum coherences, $\omega_{01,10}$. This is the expected frequency during this time period as indicated in the 2FDs in (c) and (d). In addition to this oscillation, there is an overall bath-induced decay in the rephasing signal.

Figure 6(a) shows the contribution to the nonrephasing response, $|\tilde{R}_{\text{II}}^{(3)}(\omega_3, \omega_1; t_2)|$ at $t_2 = 0$ from the non-trace-satisfying parent diagram with the same sequence of interactions as Fig. 5. The three peaks labeled A, B, and C can be related to the trace-satisfying child diagrams in Fig. 6(c). The ω_1 and ω_3 frequencies of peak A are approximately $\omega_{10,00}$ and $\omega_{20,01}$, which correspond to the frequencies present during t_1 and t_3 in the absence of energy transfer. The relatively high ω_3 frequency of this peak was not present in the diagrams contributing to the rephasing signal in Fig. 5(c) and had negligible peak volume in 5(a) (result not shown), consistent with the 2FDs shown in both figures. The ω_1 frequency of peak B of Fig. 6, $\omega_1 = \omega_{10,00}$, corresponds to no energy transfer occurring during t_1 , while its ω_3 frequency corresponds to energy transfer during t_3 . It is expected that both $\omega_{20,10}$ and $\omega_{11,01}$ can be reached during t_3 via energy transfer as shown in the 2FDs in Fig. 6(c), so that both ω_3 frequencies may contribute to peak B. Peak C corresponds to energy transfer during both the t_1 and the t_3 time periods. Integrated peak volumes normalized to the volume of peak B at $t_2 = 0$ are shown in panel (b). With nonzero t_2 , the trace-satisfying child diagrams with one energy transfer event during t_2 shown in panel (d) may also contribute to the signal in (b). The volumes of peaks A, B, and C oscillate in Fig. 6(b) at a single dominant frequency, $\omega_{10,01}$, as predicted by the 2FDs in (c) and (d). The oscillations in Fig. 6(b) are out of phase with the oscillations in Fig. 5(b). The peak volumes in Fig. 6(b) increase as a function of time, as expected^{45,58} for the nonrephasing signal, and begin at a lower absolute amplitude than the rephasing signal in Fig. 5(a). An increase in the nonrephasing signal, as in Fig. 6(b), together with a decay in the rephasing signal, as in Fig. 5(b), results in the rounding of peaks in the 2D spectrum as a function of t_2 , as shown in Fig. 4.

VI. CONCLUSIONS

The OMT approximation is a semiclassical method for computing nonlinear vibrational response functions from action-quantized classical trajectories linked by transitions in

action at fixed angle values representing radiation-matter interactions. The reliance of this approach on the action-angle representation of classical mechanics restricts its application to regimes in which these variables can be defined, at least approximately. In previous numerical applications of the OMT method,^{43–45} we employed low-order perturbation theory in potential anharmonicity⁴⁹ to determine expressions for the Cartesian coordinates and momenta in which trajectories are propagated as a function of the action and angle variables in which quantization rules are applied. We have demonstrated that this approach has the capacity to reproduce several anharmonic effects, such as generating vibrational coherences that are inaccessible under harmonic selection rules.⁴⁴

The original formulation of the OMT presumes that trajectories are propagated at action values that well approximate constants of the motion. Approximate good action variables derived as perturbative corrections to harmonic action variables of normal modes will display significant time dependence for sufficiently strong anharmonic couplings, representing energy transfer. Here, we extended the OMT to include these energy transfer processes. The OMT approximation to a response function is expressed as a sum of semiclassical diagrams. Each diagram is constructed by a direct mapping from two quantum mechanical 2FDs. To include coherence and energy transfer among modes, we enlarged the set of 2FDs representing the third-order response function, thereby expanding the corresponding set of OMT diagrams. In these new diagrams, energy transfer processes among classical coupled oscillators represent either coherence or population transfer processes among quantum oscillators, depending on the values of the classical actions and the phases of the interactions. We ensure that these additional diagrams are correctly included by relating “child” diagrams that include energy transfer to “parent” diagrams that nominally do not. If significant energy transfer occurs during the propagation of classical trajectories, the parent generates the child. Parent diagrams are of two types; some would satisfy the trace condition if evaluated for a harmonic system and others would not. Trace-satisfying parent diagrams were included in previous implementations of the OMT, while non-trace-satisfying terms are added in the generalization here to allow for all energy transfer contributions to the response function. If the parameters of the classical Hamiltonian are not conducive to energy transfer processes among interacting oscillators, trace-satisfying parent diagrams represent legitimate contributions to the response function, while the non-trace-satisfying terms are expected to make a negligible numerical contribution. In the presence of energy transfer, however, both types of parent diagrams can generate trace-satisfying child diagrams that may contribute significantly.

An OMT diagram is defined independently of any method for its numerical evaluation; however, the association of a parent diagram with its children is inherently dependent on the procedure for evaluating parent diagrams. In a naive forward-only implementation of the OMT, the assignment of a parent diagram to its children is clear, and all child diagrams are naturally generated, as described in Sec. III. In Ref. 45, we introduced an efficient forward-backward procedure for numerically calculating OMT diagrams. This forward-backward implementation must be modified to ensure that the required child

diagrams can be generated from the directly computed parent diagrams, as described in Sec. IV and the Appendix.

In Sec. V, we present purely absorptive 2D spectra for a model of resonantly coupled anharmonic chromophore local modes coupled to a harmonic bath. The waiting time dependence shows the evolution from static to dynamic broadening. The full spectrum in Fig. 4(i) is decomposed into the contribution from trace-satisfying parent diagrams that would individually generate significant signal in the absence of anharmonic effects (Fig. 4(ii)) and non-trace-satisfying parent diagrams that would be expected to be negligible in this case (Fig. 4(iii)). The non-trace-satisfying terms are shown to contribute for the couplings studied. We relate these contributions to physical processes in Figs. 5 and 6 by examining contributions from individual OMT parent diagrams and interpreting them in terms of 2FDs that explicitly include coherence transfer processes among normal modes. The semiclassical calculation is shown to reproduce the spectral peaks and waiting-time dependences expected from the quantum diagrams. This analysis demonstrates that the generalization of the OMT described here has the capacity to treat a regime in which approximate classical action variables show significant time dependence over the simulation time scale.

The 2D spectra in Sec. V were computed for a model of two chromophore degrees of freedom and a bath of 60 oscillators. While harmonic bath models can lead to analytical simplifications, we treat the bath as discrete degrees of freedom and propagate numerical classical trajectories for all degrees of freedom. This calculation shows that the efficient forward-backward implementation of the OMT may be combined with relatively simple approximations to action-angle variables and demonstrates the practical promise of the OMT method in computing nonlinear response functions for large systems with significant resonant interactions.

The further application of the OMT to an atomistic model of, for example, a solvated biomolecule²⁴ or a neat liquid⁵⁹ will require the following steps. First, two sets of phase space variables must be identified: the variables used to propagate trajectories and those in terms of which OMT diagrams are expressed. In principle, the same set of variables could serve both purposes, but in general may not. Here, these sets of phase space variables are, respectively, the local modes with coordinates q_j in Eq. (1) and the normal modes with coordinates x_j in Eq. (14). The canonical transformations between these sets of variables must be determined, as must transformations between the phase space variables used in the OMT diagrams and the action-angle variables in which the quantization conditions are imposed. Here, the normal mode coordinates and momenta were obtained in terms of action and angle variables with perturbative corrections to the harmonic solutions. Second, chromophore modes must be identified and expressed in terms of the phase space variables used in the OMT diagrams. Here, the dipole was taken to be proportional to the sum of normal mode coordinates $x_1 + x_2$, so that only normal modes 1 and 2 directly interact with radiation. In a treatment that excludes non-trace-satisfying parent diagrams as in Eq. (7), OMT diagrams involve jumps in the actions of at most two chromophore modes. For n_c chromophore modes, this results in a total of $8n_c^2 - 4n_c$ OMT diagrams in each phase

matched direction.⁴⁴ In general, non-trace-satisfying parent diagrams may involve up to four chromophore modes, resulting in $4n_c^4$ OMT diagrams. Because of this additional complexity, the OMT approximation should be extended as in Eq. (8) only if calculations of trajectories or individual non-trace-satisfying diagrams indicate that coherence and energy transfer processes are significant. It should be emphasized that some of these processes can be incorporated without increasing the number of OMT diagrams and that specific processes of interest can be investigated without computing the full vibrational response, as in Figs. 5 and 6. Third, the calculation will require a potential energy surface including quantitative treatment of anharmonicity of chromophore modes.²³ The OMT approach presumes the existence of an accurate electronic ground state potential energy surface and approximates quantum nuclear dynamics on this surface from a calculation based on classical trajectories.

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APPENDIX: FORWARD-BACKWARD IMPLEMENTATION

In Sec. IV, we adapted the forward-backward implementation of the OMT approximation⁴⁵ to include contributions to the response function from coherence and energy transfer processes. As described in connection with Fig. 3, forward-backward evaluation of an OMT diagram with energy transfer during the t_1 period requires switching the identity of the first interacting chromophore mode in the parent diagram, r'_0 , to the other chromophore, r_0 , interacting first in the child diagram. This switch of identity affects the evaluation of the statistical weight ΔF^{r_0} in Eq. (11). Here, we describe evaluation of this statistical weight. Additionally, procedures for executing jumps in action at fixed angle values and for choosing the arguments of Q_σ in Eq. (14), corresponding to the placement of red and blue dots in OMT diagrams, are presented.

Metropolis sampling from the equilibrium distribution F in Eq. (12) is used to compute a set of half-odd-integer quantized actions $\mathbf{J}_0$. This sampling weights a diagram initialized with actions $\mathbf{J}_1(t_1) = \mathbf{J}_0|_{J_0^{r'_0 \rightarrow J_0^{r'_0 + \hbar/2}}}$ by $F(\mathbf{z}|\mathbf{J}_0)$. To approximately correct the weight of a diagram to $\Delta F^{r_0}(\mathbf{z}_1)$, its contribution is multiplied by the factor $1 - F(\mathbf{z}|\mathbf{J}_0, J_0^{r_0 \rightarrow J_0^{r_0 + \hbar}})/F(\mathbf{z}|\mathbf{J}_0)$ with r_0 determined according to the procedure described in Sec. IV so that r_0 is not necessarily equal to r'_0 . This will result in the correct statistical weight in the absence of energy transfer. If energy transfer occurs during the t_1 time period, this correction will be approximate in the forward-backward implementation. The effect of this approximation on the calculated response function is expected to be small, especially when the chromophore modes have similar frequencies.

FIG. 7. Example contributions to $\rho_{++-}^{1,1,1,1}$ in column (a) and $\rho_{+-+}^{1,2,1,1}$ in column (b). Red and blue dots correspond to points in the diagrams where factors of Q_{σ}^r are evaluated in Eq. (9). If a different point is chosen at time t using the approximate method described in text, it is indicated by an x.

To include energy transfer processes in the OMT method, it is essential that action jumps are executed so that the interacting mode's current action is altered by $\pm\hbar/2$, even if it changed during the trajectory. We will approximate an action jump at constant angle values within a harmonic limit by scaling the coordinate and momentum of the interacting chromophore r in trajectory i by $(1 \pm \hbar/2J_i^r)^{1/2}$, which is correct for a harmonic oscillator. The actions prior to the jump, $\mathbf{J}_i(t)$, can be determined approximately by using the perturbative expression for the Hamiltonian as described in Sec. IV. This allows for interactions with the field to change the interacting mode's action by $\pm\hbar/2$ without assuming the actions are fixed as a function of time. In the forward-backward implementation, the action is assumed to be known explicitly at t_1 so that harmonic scaling is not necessary for this jump. We nevertheless include it to ensure that the same energy is propagated during the t_1 and t_3 time periods upon an increasing and decreasing jump when $t_2 = 0$.

A final approximation will be applied to determine the arguments of Q_{σ}^r in Eq. (9). In general, the arguments of the factors Q_{σ}^r should vary if energy transfer occurs in a diagram. Figure 7 gives example contributions to $\rho_{++-}^{1,1,1,1}$ in column (a) and to $\rho_{+-+}^{1,2,1,1}$ in column (b). In each diagram, the correct points for evaluating Q_{σ}^r are shown as colored dots on the OMT diagram, determined according to the procedure described in Ref. 44. In Fig. 7(ai), a trace-satisfying parent diagram is given and two possible child diagrams are shown in (aii) and (aiii). As can be seen by comparing the third interaction with mode 1 in panels (ai) and (aii), energy transfer can change both the magnitude of the action at which Q_{σ}^r is evaluated and its value relative to the action prior to the jump. Furthermore, it is not always possible to uniquely determine the correct arguments of Q_{σ}^r based on the diagram since distinct information about the bra and ket aspects of the density operator is not maintained throughout the trajectory, only the average action. An example is shown in column (a) of Fig. 7. The distinct 2FDs in (aii) and (aiii) give rise to their respective OMT diagrams which differ only in the action value at which $Q_{+}^1(\mathbf{z}_{p_2}(t_{p_2}))$ is evaluated. When propagating the parent diagram in (ai), it is not possible to distinguish between the two sequences of energy transfer events in the 2FDs shown in (aii) and (aiii) since both correspond to the same sequence of changes in the average action of the trajectories. This figure therefore demonstrates that for some sequences of energy transfer events determining the arguments of Q_{σ}^r is inherently ambiguous.

To deal with this ambiguity and simplify the evaluation of OMT diagrams, we will make the following choices for the arguments of Q_{σ}^r evaluated in Eq. (9). The first factor in a trace-satisfying diagram is always given by $Q_{+}^{r_0}(\mathbf{z}_1)$, with r_0 determined appropriately for each evaluation time. The points at t_1 are sampled directly in the forward-backward implementation and therefore can be chosen so that $Q_{+}^{r_1}(\mathbf{z}_{p_1}(t_{p_1}))$ is evaluated at the integer quantized action value involved in the transition. This choice will be correct unless a two quantum coherence is involved in the t_1 interaction. This condition is satisfied by all parent diagrams in the $\mathbf{k}_I$ and $\mathbf{k}_{II}$ phase-matched directions. We choose to evaluate $Q_{+}^{r_2}$ at time $t_1 + t_2$ at the action of the oscillator either before or after the jump, whichever is an integer multiple of $\hbar$ in the parent diagram without energy transfer. For example, in Fig. 7(bi), a non-trace-satisfying parent diagram is shown and (bii) and (biii) show example trace-satisfying child diagrams with energy transfer during the t_3 and t_2 time period, respectively. In the parent diagram, mode 1 transitions to a half-odd-integer action in the third interaction with the field. Therefore for all child diagrams, including those in (bii) and (biii), the point prior to the third interaction with the field, $\mathbf{z}_2(t_2)$, is taken as the argument of $Q_{+}^{r_2}$. This will be the correct evaluation point if no energy transfer occurred during the t_2 time interval and if this interaction does not cause a transition to or from a two-quantum coherence, as in (bii). For $\mathbf{k}_I$ and $\mathbf{k}_{II}$, trace-satisfying parent diagrams will not be in a two-quantum coherence during t_2 or t_3 although some trace-satisfying child diagrams may be. We take the final evaluation point at time $t_1 + t_2 + t_3$ to be $Q_{-}^{r_3}(\mathbf{z}_3(t_3))$, which is correct for any trace-satisfying diagram. If a factor of Q_{σ}^r is not evaluated at the correct argument according to these rules, the approximate selected point is shown as an x in Fig. 7. This simplifying approximation may select an action that is too high (x higher than dot), as in (aii), or an action that is too low (x lower than dot), as in (aiii) or (biii). We expect the effect of this approximation to be small since factors of Q_{σ}^r are correctly chosen for all trace-satisfying parent diagrams.

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