An optimized semiclassical approximation for vibrational response functions

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The observables of multidimensional infrared spectroscopy may be calculated from nonlinear vibrational response functions. Fully quantum dynamical calculations of vibrational response functions are generally impractical, while completely classical calculations are qualitatively incorrect at long times. These challenges motivate the development of semiclassical approximations to quantum mechanics, which use classical mechanical information to reconstruct quantum effects. The mean-trajectory (MT) approximation is a semiclassical approach to quantum vibrational response functions employing classical trajectories linked by deterministic transitions representing the effects of the radiation-matter interaction. Previous application of the MT approximation to the third-order response function $R^{(3)}(t_3, t_2, t_1)$ demonstrated that the method quantitatively describes the coherence dynamics of the t_3 and t_1 evolution times, but is qualitatively incorrect for the waiting-time t_2 period. Here we develop an optimized version of the MT approximation by elucidating the connection between this semiclassical approach and the double-sided Feynman diagrams (2FD) that represent the quantum response. Establishing the direct connection between 2FD and semiclassical paths motivates a systematic derivation of an optimized MT approximation (OMT). The OMT uses classical mechanical inputs to accurately reproduce quantum dynamics associated with all three propagation times of the third-order vibrational response function. © 2013 American Institute of Physics. [<http://dx.doi.org/10.1063/1.4795941>]

I. INTRODUCTION

Multidimensional infrared spectroscopy is the analog in the domain of molecular vibrations of multidimensional magnetic resonance measurements.^{1–5} By probing the coupling among vibrational modes, these techniques provide both structural and dynamical information about systems as various as liquid water⁶ and biomolecules.^{7–10} Within the experimentally accessible weak-field limit, multidimensional vibrational spectra can be calculated from nonlinear response functions,¹¹ which describe the effects of radiation-matter interactions perturbatively. Interpreting multidimensional spectra at the molecular level, such as elucidating the effect of a mutation on protein dynamics,^{8,12} requires calculating nonlinear response functions from atomistic models. Fully quantum dynamical calculations for multiple degrees of freedom are impractical, and completely classical computations, while feasible, can be unphysical at long times as the perturbation theory on which they are based is only valid over a finite time window.^{13–25} These challenges motivate the use of semiclassical approximations to quantum mechanics, which hold the promise to approximate quantum effects with computational effort comparable to that of a classical mechanical calculation.

An alternative and widely applicable approach to calculating a quantum vibrational response function for many degrees of freedom is to employ a system-bath partitioning in

which the chromophore system is treated quantum mechanically and the influence of the remaining bath degrees of freedom is treated classically or semiclassically with dynamical input from classical simulations.^{26–32} Such models may be applied to electronic degrees of freedom or high-frequency vibrations interacting with lower-frequency motions. The response function of a model in which some degrees of freedom are constrained to be quantum mechanical^{33–39} lacks a classical mechanical limit as $\hbar \rightarrow 0$. The absence of a well-defined classical limit leads to ambiguities in treating bath dynamics associated with a system superposition state as in for example the use of classical bath dynamics to describe the dephasing of an electronic coherence. The motivation of the present work is to develop an approximation to quantum dynamics that in principle could be applied uniformly to all degrees of freedom. This approach may find application in situations where the classical mechanical limit is physically relevant so that a semiclassical treatment may be viewed as correcting the well-defined zeroth order case of a classical mechanical system.^{15–17,22}

Semiclassical approximations^{40–46} to the quantum propagator have been applied to time-dependent wavefunctions,^{47–50} to thermal time-correlation functions,^{51–57} and to linear and nonlinear response functions.^{21,22,58–61} It is useful to categorize qualitatively these time-dependent quantities according to the importance of the cancellation of quantum phases in determining time-dependence. A time-dependent wavefunction has no classical mechanical limit and hence represents a demanding application of

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semiclassical approximations. Time-correlation functions, which do in general have a classical limit, contain pairs of time-evolution operators with opposite time senses, leading to time-dependence controlled by cancellation of quantum phases.^{51–57} Response functions, which also in general have a classical limit, are expressible as sums of correlation functions¹¹ and hence involve phase cancellation both within and among correlation functions. Since the numerical challenges associated with semiclassical propagators arise in part from the highly oscillatory time-dependent phase factor,^{62–71} evaluation of response functions containing several such factors poses numerical difficulties. The existence of a classical limit associated with this high degree of phase cancellation nevertheless suggests that semiclassical dynamics are an appropriate description of nonlinear response functions, provided that the numerical challenges can be met.

The Herman-Kluk (HK) propagator is a frozen Gaussian approximation to the quantum time-evolution operator in the coherent states basis whose accuracy has been demonstrated in varying contexts.^{72–80} Noid, Ezra and Loring have evaluated linear and third-order spectroscopic response functions for a single anharmonic degree of freedom and have demonstrated the accuracy of the approximation for response functions.^{21,22} However, these calculations require the partial cancellation of time-dependent quantum phases to be carried out numerically through Monte Carlo integration of highly oscillatory integrands, rendering the approach impractical for large systems. The calculations are based on semiclassical propagators with time-dependence arising both from highly oscillatory phase factors and from classical monodromy matrix elements which grow without bound in time. Yet the eventual result of the calculation, the response function, is an experimental observable with well-behaved and bounded time-dependence. The HK response function calculation involves multiple integrations over classical states, associated with the ket and bra aspects of the quantum density operator. These integrations evidently remove pathological time dependence from both of these sources.

Gruenbaum and Loring^{81–84} analyzed the origin of the success of the HK approximation to vibrational response functions by investigating the fate of these time-dependences. It was established that if the integrations over classical phase space associated with the ket and bra aspects of the density matrix are rewritten in terms of mean and difference variables, then the integrations of the semiclassical phase factors over the difference variables approximately cancel the unbounded time dependences of the monodromy matrix elements. This realization motivated the construction of a mean-trajectory (MT) approximation, in which these integrals over difference coordinates and momenta are performed approximately analytically, leaving the better behaved integrations over mean coordinates and momenta to be performed numerically. The MT calculation of a nonlinear response function requires evaluating a sequence of classical trajectories linked by deterministic transitions. Performing these transitions requires carrying out a transformation between Cartesian momentum and coordinate variables and action and angle variables, as the transitions involve changing action variables at fixed angle variables. For this reason the method

is limited to quasiperiodic or approximately quasiperiodic dynamics in which these variables may be defined. The MT approximation was shown⁸² to perform as accurately as the HK approximation²² from which it was derived in calculations of the third-order response function $R^{(3)}(t_3, t_2, t_1)$ at the echo condition $t_1 = t_3$ and $t_2 = 0$ for thermal ensembles of noninteracting anharmonic oscillators. This time-dependence primarily reflects the dynamics of single quantum coherences. However, the dependence of $R^{(3)}(t_3, t_2, t_1)$ on the waiting time t_2 ,³¹ which can reflect two-quantum coherences in the models studied, is qualitatively incorrect even for a single degree of freedom. This incorrect time-dependence was identified⁸² as arising from a spurious process of deexcitation of the vibrational ground state, but a systematic improvement of the MT approximation that eliminated this artifact was not evident.

Here we develop a systematically improved version of the MT approximation that we denote the optimized mean trajectory (OMT) approximation. Rather than beginning with a semiclassical propagator as in Refs. 81–83, we start by establishing the connection between the semiclassical paths of linked classical trajectories in the MT approximation and the double-sided Feynman diagrams (2FD) that are conventionally used to represent phase-matched contributions to the quantum response function.^{5,11,85,86} We show that 2FD can be associated in pairs to yield semiclassical diagrams based on the paths of the MT approximation. The OMT approximation derived from analyzing the 2FD differs from the MT approximation in two respects. First, classical state information is collected at different points along the semiclassical paths, and second, semiclassical paths are weighted by a difference in classical distributions at different energies rather than by a single classical distribution. The first of these modifications removes the previously discussed artifact of the MT approximation so that the OMT provides an accurate calculation of quantum effects in the dependence of $R^{(3)}(t_3, t_2, t_1)$ on all three time variables. The second change improves the accuracy of the thermal amplitudes of different frequency contributions.

The MT approximation^{81–84} is briefly reviewed in Sec. II. In Sec. III we establish the connection between the 2FD that compose the quantum response function and semiclassical paths in the MT calculation. This connection motivates the construction of the OMT, which is presented there. The numerical procedure for calculating an OMT response function is described in Sec. IV, and numerical results for ensembles of noninteracting one-dimensional anharmonic oscillators are presented and discussed in Sec. V. Our conclusions are summarized in Sec. VI.

II. MEAN TRAJECTORY APPROXIMATION

We briefly summarize here the MT approximation for the vibrational response function, as developed by Gruenbaum and Loring.^{81–84} The amplitude of the coherent optical signal propagating with wavevector $\alpha \mathbf{k}_1 + \beta \mathbf{k}_2 + \gamma \mathbf{k}_3$ generated by successive interactions with electric fields with wavevectors $\mathbf{k}_1$, $\mathbf{k}_2$, and $\mathbf{k}_3$ may be calculated within perturbation theory

from the third-order response function

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

Interaction with the field is treated within the electric dipole approximation with the dipole operator taken to be proportional to a coordinate $\hat{q}$ and with the constant of proportionality between the dipole and $\hat{q}$ suppressed. The indices α , β , γ , and δ take on the values ± 1 , with the constraint that $\alpha + \beta + \gamma + \delta = 0$. This expression follows from writing the coordinate operator as $\hat{q} = \hat{q}_+ + \hat{q}_-$, with $\hat{q}_+ = \hat{a}^\dagger \sqrt{\hbar/2m\omega}$ and with $\hat{q}_- = \hat{a}^\dagger$. The boson creation operator, effective mass, and harmonic angular frequency are denoted $\hat{a}^\dagger$, m , and ω , respectively. The quantum propagator for the material system is denoted $\hat{K}(t)$ and the equilibrium density operator is $\hat{\rho}$.

The MT approximation is derived by representing $\hat{K}(t)$ with the Herman-Kluk propagator,^{72–80} a frozen Gaussian approximation in the coherent states basis. Each operation of $\hat{K}$ in Eq. (1) produces one integration over classical phase space, turning the trace in Eq. (1) into a 12-dimensional integral for a single degree of freedom. Each phase-space integration is associated with the semiclassical representation of either the bra or ket aspect of the density operator. The MT approximation follows from changing phase space integration variables to mean and difference variables, and approximately performing the integration^{81,82} over difference variables to yield for the phase-matched response function in Eq. (1):

$$R_{\gamma\beta\alpha}^{(3)}(t_3, t_2, t_1) = \frac{i\beta\omega}{2^4\hbar^4} \int dz_1 \int dz_2 \int dz_3 f_{\text{cl}}(z_1)\sigma(z_1) \\ \times \delta(\phi_2 - \phi_{1t_1})\delta(\phi_3 - \phi_{2t_2}) \\ \times Q_\alpha(z_1)(Q_\beta(z_2)D_1^+ - Q_\beta(z_{1t_1})D_1^-) \\ \times (Q_\gamma(z_3)D_2^+ - Q_\gamma(z_{2t_2})D_2^-)Q_\delta(z_{3t_3}). \quad (2)$$

Here z_j is a point in classical phase space, represented either by Cartesian coordinate and momentum (q , p) or by action and angle variables (J , ϕ), z_{jt} is the phase-space point resulting from classical propagation of z_j for time t , $f_{\text{cl}}(z)$ is the classical distribution, and

$$Q_\pm(z) \equiv q \mp ip/m\omega, \quad (3)$$

$$\sigma(z_1) \equiv \hbar \sum_{n=0}^{\infty} \delta(J_1 - n\hbar), \quad (4)$$

$$D_j^\pm \equiv \hbar \delta(J_{j+1} - (J_j \pm \hbar/2)). \quad (5)$$

The MT result in Eq. (2) is expressed in part in terms of action and angle variables, which presumes that such variables can be defined. The applicability of this method for multi-dimensional systems is therefore limited to regimes in which the motion is exactly or approximately quasiperiodic.^{87,88} The application of the MT approximation to multiple degrees of freedom is discussed in Ref. 83.

Multiplying the terms containing $D_j^\pm$ in Eq. (2) permits the expression to be written as the sum of four correlation functions, one of which is, for example,

$$\frac{i\beta\omega}{2^4\hbar^4} \left\langle \int dz_2 \int dz_3 \sigma(z_1)\delta(\phi_2 - \phi_{1t_1})\delta(\phi_3 - \phi_{2t_2}) \right. \\ \left. \times Q_\alpha(z_1)Q_\beta(z_2)Q_\gamma(z_3)Q_\delta(z_{3t_3})D_1^+D_2^+ \right\rangle, \quad (6)$$

where the angular brackets denote a classical phase space average over z_1 . This correlation function is evaluated by selecting an initial phase-space point z_1 , propagating a trajectory for t_1 , making a discontinuous transition to a phase-space point z_2 , propagating a second trajectory for t_2 , making a second transition to z_3 , and propagating for t_3 . At each transition, the angle variable ϕ is held constant and the action variable J is incremented by $\hbar/2$. Each of the other three correlation functions in Eq. (2) is similarly calculated from classical trajectories linked by transitions at fixed angle in which the action is increased or decreased by $\hbar/2$. The four possible combinations of transitions in action are shown schematically in Fig. 1 which plots action versus time. Each horizontal segment represents classical propagation, while each vertical segment denotes a transition in action at fixed angle. Each of the four correlation functions in Eq. (2) is determined from a sequence of classical trajectories represented by one of the four paths from left to right in Fig. 1. The correlation function in Eq. (6), for example, is calculated from trajectories depicted by the path in Fig. 1 with both vertical arrows pointing up. The factor $\sigma(z_1)$ in Eq. (4) restricts each classical path to begin with action quantized to an integer multiple of $\hbar$. Therefore, propagation during the t_1 and t_3 periods occurs with integer action and during the t_2 period occurs with half-odd-integer action.

The essential feature of the MT approximation is the calculation of a vibrational response function from a thermal average over classical trajectories linked by transitions in action at constant angle. According to Eq. (2), a linear combination of coordinate and momentum, $Q_\pm$ in Eq. (3), is calculated at the start and end of the sequence of three trajectories and at two intermediate points, either before or after each transition. The particular points at which coordinates and momenta are collected follow from the approximations made in Ref. 82. In Sec. III, we develop a MT approximation that preserves the essential feature of the original version, but varies where coordinates and momenta are collected so as to be more consistent

FIG. 1. The four paths associated with the mean-trajectory approximation for the third-order vibrational response function are shown. The action of the first trajectory is quantized to integer multiples of $\hbar$ and interactions with the electric field are represented by jumps of $\pm\hbar/2$ in the action at constant angle.

with quantum mechanics. This derivation follows from establishing a new connection between the semiclassical paths in Fig. 1 and the double-sided Feynman diagrams^{5,11,85,86} that represent contributions to quantum response functions.

III. OPTIMIZED MT APPROXIMATION

Phase-matched contributions to quantum mechanical spectroscopic response functions are conventionally expressed as sums of 2FD.^{5,11,85,86} Four examples are shown on the left side of Fig. 2, which contribute to the phase-matched response function $R_{++-}^{(3)}(t_3, t_2, t_1)$ in Eq. (1) associated with the signal at $-\mathbf{k}_1 + \mathbf{k}_2 + \mathbf{k}_3$. Time increases upwards and the left and right vertical lines represent, respectively, the ket and bra aspects of the density operator. The rotating wave approximation is applied so that arrows pointing towards or away from a vertical line can be interpreted, respectively, as excitation or deexcitation of the material system.⁵ Each 2FD can be associated with one of the four semiclassical paths in Fig. 1. This correspondence follows from identifying the value of the action, J , during a classical trajectory in Fig. 1 with the mean quantum number associated with the bra and ket sides of the 2FD. This identification is carried out in the harmonic limit, in which the quantum and classical energies are, respectively, $E_n = (n + 1/2)\hbar\omega$ and $E = J\omega$. During a particular propagation period in a Feynman diagram, the density operator is proportional to $|n_L\rangle\langle n_R|$. The average quantum number for this population ($n_L = n_R$) or coherence ($n_L \neq n_R$) is defined as $\bar{n} \equiv (n_L + n_R)/2$, so that the average quantum number is either an integer or half of an odd integer. The corresponding classical action for the semiclassical path is taken to be $J(\bar{n}) \equiv (\bar{n} + 1/2)\hbar$. In the correspondence between quantum and semiclassical diagrams, quantum time evolution of the density operator $|n_L\rangle\langle n_R|$ is replaced by a classical trajectory with action $J(\bar{n})$.

FIG. 2. Correspondence between double-sided Feynman diagrams and semiclassical paths from Fig. 1 is illustrated.

For example, the uppermost 2FD in Fig. 2 begins in a population $|n\rangle\langle n|$, with a sum over n weighted by the thermal density. This population corresponds to mean quantum number $\bar{n} = n$ and to a semiclassical action $J_0 = (n + 1/2)\hbar$. The first interaction produces the coherence $|n\rangle\langle n + 1|$, with $\bar{n} = n + 1/2$, corresponding to action of $J_1 = (n + 1)\hbar$. The second interaction yields the population $|n + 1\rangle\langle n + 1|$, with $\bar{n} = n + 1$ and corresponding action $J_2 = (n + 3/2)\hbar$. The third interaction produces the coherence $|n + 1\rangle\langle n|$, with $\bar{n} = n + 1/2$ and action $J_3 = J_1$. The final interaction returns the density operator to $|n\rangle\langle n|$, a population being required by the trace, corresponding to action $J_4 = J_0$. This 2FD maps onto the uppermost semiclassical path in Fig. 2, which begins with a vertical line representing the transition in action by $\hbar/2$ from J_0 to J_1 , followed by a horizontal solid line representing propagation at J_1 for time t_1 . The second dashed vertical line increments the action again by $\hbar/2$ to J_2 , followed by propagation for t_2 . The third dashed vertical line decreases the action by $\hbar/2$, to $J_3 = J_1$, and is followed by propagation for t_3 . The final dashed vertical line decreases the action by $\hbar/2$ to $J_4 = J_0$. This semiclassical path is equivalent to the MT contribution in Fig. 1 in which a vertical arrow upwards is followed by a vertical arrow downwards. The initial and final vertical lines in the path are included in Fig. 2 to emphasize the connection between semiclassical diagrams and 2FD. These do not appear in Fig. 1 and do not affect the value of the associated contribution to the response function. Applying this analysis to the other three 2FD in Fig. 2 illustrates the correspondence to the three remaining MT paths in Fig. 1.

The preceding analysis not only reveals the connection between semiclassical MT diagrams and 2FD, it also permits the systematic derivation of an optimized version of the MT approximation, the OMT, that follows directly from expressing the quantum response function in terms of 2FD, rather than from the more indirect derivation using semiclassical propagators in Refs. 81–83. According to Eq. (2), the response function is calculated by determining the value of $Q_{\pm}$ in Eq. (3) at four points along the semiclassical path. For example, in the correlation function of Eq. (6), momentum and coordinate information are collected at the start of the first (z_1), second (z_2), and third (z_3) trajectories, and at the conclusion (z_{3f}) of the third trajectory. All four MT correlation functions contain the factor $Q_{\alpha}(z_1)Q_{\delta}(z_{3f})$, but Q_{β} may be evaluated at z_{1f} or z_2 and Q_{γ} at z_{2f} or z_3 . The discontinuity of the trajectories at these transition points confers an ambiguity on the identity of the phase-space point that is chosen. The identification of semiclassical paths with 2FD clarifies the significance of the points at which $Q_{\pm}$ are evaluated, and provides a unique prescription for determining these classical states, as shown in Fig. 3.

The left side of Fig. 3(a) shows a 2FD drawn to emphasize the bra and ket aspects of the density operator. This 2FD contributes to $R_{++-}^{(3)}(t_3, t_2, t_1)$, associated with the wavevector $-\mathbf{k}_1 + \mathbf{k}_2 + \mathbf{k}_3$. The corresponding semiclassical diagram is shown on the right side of Fig. 3(a). According to Eq. (2), this path generates the factor $Q_{-}(z_1)Q_{+}(z_{1f})Q_{+}(z_3)Q_{-}(z_{3f})$, so that in the MT approximation, phase-space information is collected at the points indicated by red dots in Fig. 3(a). The dependence of this product of Q_{σ} factors on action can be

FIG. 3. Two double-sided Feynman diagrams (2FD) are shown with the corresponding optimized mean trajectory (OMT) diagrams. Both 2FD correspond to the same semiclassical path but classical states are collected at different points along the path in the OMT diagrams as indicated by red dots.

evaluated in a quasi-harmonic^{82,83} approximation,

$$Q_{\pm}(J, \phi) = \sqrt{2J/m\omega} \exp(\pm i\phi). \quad (7)$$

The form in Eq. (7) is exactly correct only for a harmonic potential, but we will use it approximately, allowing the time-dependence of the angle variable ϕ to depend on action J , as would be the case for an anharmonic system, effectively modeling an anharmonic oscillator as a harmonic one with an energy-dependent frequency. Within this approximation the product of Q_{σ} factors associated with the semiclassical diagram in Fig. 3(a) is proportional to $J_1 J_3$, which within the correspondence to 2FD may be converted into a dependence on quantum number of $(n+1)^2$. We can assess this choice of the placement of red dots on the semiclassical diagram in Fig. 3(a) by comparing this n -dependent factor to that generated by the action of harmonic creation and annihilation operators in the corresponding 2FD. Approximating the states $\{|n\rangle\}$ as harmonic indeed generates the same factor $(n+1)^2$ indicating that for this diagram the choice of phase-space points at which information is collected in the MT approximation is consistent with the value of the corresponding 2FD.

This consistency between a 2FD and the corresponding MT diagram in Fig. 3(a) does not however hold in Fig. 3(b), which shows a 2FD contributing to $R_{-++}^{(3)}(t_3, t_2, t_1)$ that maps onto the same semiclassical path as the 2FD in Fig. 3(a). In the MT approximation, the factor $J_1 J_3$ noted in connection with Fig. 3(a) corresponds to $(n+1)^2$, which differs from the factor $n(n+1)$ generated by creation and annihilation operators in the 2FD of Fig. 3(b). While these two factors approach the common limit n^2 for large quantum numbers, their discrepancy is significant at $n=0$. Here the quantum result vanishes, as it must, since it involves deexcitation of state n , but the MT result is nonzero. The result is a spurious frequency in the MT calculation associated with deexcitation of the ground state, which is manifest in the dependence of $R_{-++}^{(3)}(t_3, t_2, t_1)$ on t_2 . The origin of this artifact was correctly identified in Ref. 82 in the discussion of Fig. 6 of that work, but without the cor-

respondence between the MT approximation and 2FD, there was no evident way to correct this deficiency of the MT. The semiclassical diagram in Fig. 3(b) shows that this inconsistency between the MT approximation and quantum mechanics can be remedied by preserving the semiclassical path, but altering the choice of phase-space points at which information is collected, i.e., varying the placement of the red dots in Fig. 3(a). With the red dots placed as in Fig. 3(b) rather than as in Fig. 3(a), the trajectories calculated are unchanged, but, at the start and end of the second trajectory, the action is decremented by $\hbar/2$, and the resulting phase points are used to calculate factors of $Q_{\pm}$. The factor of $Q_{+}(z_{1\uparrow})Q_{-}(z_3)$ in the MT approximation is replaced in the OMT by $Q_{+}(z_{2\downarrow})Q_{-}(z_{2\downarrow})$, with $\downarrow$ representing a decrease in action by $\hbar/2$ at constant angle. Figures 3(a) and 3(b) show that in the OMT approximation more than one semiclassical diagram is associated with the same semiclassical path in Fig. 2. By contrast in the MT approximation the second semiclassical path in Fig. 2 is only associated with the diagram of Fig. 3(a). Figure 3 also demonstrates that processes in which the t_2 period reflects population dynamics are treated differently in the OMT approximation from processes in which this time period reflects dynamics of a two-quantum coherence. In the MT approximation these processes are treated with the same semiclassical diagram.

The complete OMT approximation is presented diagrammatically in Fig. 4, with $R_{++-}(t_3, t_2, t_1)$ for wavevector $-\mathbf{k}_1 + \mathbf{k}_2 + \mathbf{k}_3$ in panel (a) and $R_{-++}(t_3, t_2, t_1)$ for wavevector $\mathbf{k}_1 + \mathbf{k}_2 - \mathbf{k}_3$ in panel (b). Panel (c) shows the four semiclassical diagrams of the MT approximation representing the four paths in Fig. 1. Expanding the three commutators in Eq. (1) for any phase-matching condition yields eight terms, each of which is represented by a 2FD. As shown in Fig. 4, these eight 2FD associate in pairs to produce four OMT diagrams. We illustrate this correspondence by considering the sum of the 2FD in the first line of Fig. 4(a), which has the approximate value

$$2\text{FD} = \left(\frac{-i}{4m^2\omega^2\hbar} \right) \sum_{n=0}^{\infty} (\rho_{nn} - \rho_{n+1,n+1})(n+1)^2 \times \exp[i\omega_{n+1,n}(t_1 - t_3)]. \quad (8)$$

Here harmonic oscillator selection rules have been approximately applied, and $\omega_{jk} \equiv (E_j - E_k)/\hbar$. Evaluating the semiclassical diagram in the first row of Fig. 4(a) using the MT rules of Eq. (2) with the quasi-harmonic approximation of Eq. (7) gives

$$\text{SC} = \left(\frac{-i\beta\hbar}{4m^2\omega} \right) \sum_{n=0}^{\infty} f_{\text{cl}}(z_1)|_{J_1=(n+1)\hbar}(n+1)^2 \times \exp[i((\phi_{1t_1} - \phi_1) - (\phi_{3t_3} - \phi_3))]. \quad (9)$$

Neither expression in Eqs. (8) or (9) depends on t_2 , since this model does not include dynamics for a population $|n\rangle\langle n|$. The dependences on t_1 and t_3 reflect dephasing dynamics, and in the quantum and semiclassical expressions are equal in the event that the classical angle variable and quantum frequency are related by $\phi_t - \phi_0 = \omega_{n+1,n}t$. The time-dependence of the angle is given by

$$\phi_t = \phi_0 + \omega(J)t, \quad (10)$$

FIG. 4. The double-sided Feynman diagrams contributing to signal wavevectors (a) $-\mathbf{k}_1 + \mathbf{k}_2 + \mathbf{k}_3$ and (b) $\mathbf{k}_1 + \mathbf{k}_2 - \mathbf{k}_3$ are shown with their corresponding OMT diagrams. The MT diagrams corresponding to each row are shown in (c). Red dots on the semiclassical diagrams indicate the collection of phase-space information.

$$\omega(J) \equiv \frac{dE(J)}{dJ}. \quad (11)$$

With the substitution $\bar{n} = n + 1/2$, the time-dependences are identical if

$$\frac{E_{\bar{n}+1/2} - E_{\bar{n}-1/2}}{\hbar} = \frac{dE(J)}{dJ} \Big|_{J=(\bar{n}+1/2)\hbar}. \quad (12)$$

For an anharmonic oscillator, the quantum energy E_n can be expanded in a power series in $n + 1/2$ and the classical energy $E(J)$ can correspondingly be expanded in powers of J . The equality in Eq. (12) holds up to second order in these variables, and is an approximation for cubic and higher orders. The energy of a Morse oscillator is quadratic in J , so the time-dependences of the quantum expression in Eq. (8) and the semiclassical one in Eq. (9) are identical in this case.

The quantum expression in Eq. (8) and the semiclassical one in Eq. (9) differ in the nature of the thermal average, with the density matrix difference in Eq. (8) replaced in Eq. (9) by

$$\rho_{nn} - \rho_{n+1,n+1} \rightarrow \beta \hbar^2 \omega f_{\text{cl}}(z_1)|_{J_1=(n+1)\hbar}. \quad (13)$$

With the identification $(n + 1)\hbar \rightarrow J_1$, this density matrix difference may be expressed in terms of the classical phase space distribution as

$$\rho_{nn} - \rho_{n+1,n+1} = (f_{\text{cl}}(z)|_{J=J_1-\hbar/2} - f_{\text{cl}}(z)|_{J=J_1+\hbar/2})(Z_{\text{cl}}/Z_q), \quad (14)$$

with Z_{cl} and Z_q the classical and quantum partition functions. Linearizing the partition function ratio in $\hbar$ in the harmonic limit gives $Z_{\text{cl}}/Z_q = \hbar$. Similarly, linearizing the difference in classical distributions in Eq. (14) in action about $J = J_1$ in the harmonic limit gives the right-hand side of Eq. (13). This analysis fully establishes the connection between the MT approach and 2FD, and also suggests another modification to the MT approximation to be included in the OMT. We add to the rules for evaluating the OMT diagrams in Fig. 4

the replacement of $f_{\text{cl}}(z_1)$ in Eq. (2) with the result obtained by equating the right-hand sides of Eqs. (13) and (14), $f_{\text{cl}}(z_1) \rightarrow (\beta \hbar \omega)^{-1} (f_{\text{cl}}(z)|_{J=J_1-\hbar/2} - f_{\text{cl}}(z)|_{J=J_1+\hbar/2})$.

The OMT approximation thus uses the same semiclassical pathways as the MT approximation in Eq. (2), but the approximations differ in the points at which classical states are collected and in the thermal average over initial classical states. In only one case, the second semiclassical diagram in panels (a) and (c) of Fig. 4, also shown in Fig. 3(a), are classical states collected at the same points in the MT and OMT diagrams. In the OMT approximation to the phase-matched response function, the MT approximation in Eq. (2) is replaced by

$$\begin{aligned} R_{\gamma\beta\alpha}^{(3)}(t_3, t_2, t_1) &= \frac{i}{2^4 \hbar^5} \sum_{p=1}^4 \epsilon_p \int dz_1 \int dz_2 \int dz_3 \sigma(z_1) \\ &\times (f_{\text{cl}}(z)|_{J=J_1-\hbar/2} - f_{\text{cl}}(z)|_{J=J_1+\hbar/2}) \\ &\times \delta(\phi_2 - \phi_{1t_1}) \delta(\phi_3 - \phi_{2t_2}) D_{1p} D_{2p} \\ &\times Q_\alpha(z_1) Q_\beta(z'_p) Q_\gamma(z''_p) Q_\delta(z_{3t_3}). \end{aligned} \quad (15)$$

The index p labels the four semiclassical paths in Fig. 4. The overall sign ϵ_p is 1 for the first two rows of Fig. 4 and -1 for the last two rows, and results from the signs associated with expanding the three nested commutators in Eq. (1) to generate 2FD. One of each pair of 2FD contributing to an OMT diagram begins with an excitation. If an even number of interactions occur on the right-hand side of this 2FD, $\epsilon_p = 1$, and $\epsilon_p = -1$ if an odd number of interactions occur on the right-hand side. In all OMT diagrams, Q_α is evaluated at z_1 and Q_δ at z_{3t_3} , but the phase-space points at which Q_β and Q_γ are evaluated, z'_p and z''_p , respectively, vary according to diagram, as shown by the placement of red dots in Fig. 4. The factor D_{jp} denotes the delta function in action variables $D_j^\pm$ of Eq. (5) that is appropriate for path p . The computational

methods used to evaluate Eq. (15) numerically are discussed in Sec. IV.

IV. CALCULATING OMT RESPONSE FUNCTIONS

The OMT response function for a phase-matched component of the third-order signal is given by $R_{\gamma\beta\alpha}^{(3)}(t_3, t_2, t_1)$ in Eq. (15), which includes a summation over the paths illustrated in Fig. 4. This expression contains three phase-space integrations over the classical states z_1 , z_2 , and z_3 . With the initial action variable J_1 quantized to integer values of $\hbar$ by the factor $\sigma(z_1)$ in Eq. (4) and with delta functions fixing the values of z_2 and z_3 , the evaluation of one diagram in Fig. 4 reduces to a sum over J_1 and an integral over initial angle ϕ_1 . The number of terms required in the sum over J_1 is controlled by the difference of classical distributions in Eq. (15). At the temperatures considered here, five terms suffice, so that the maximum initial action is $J_1 = 5\hbar$. In the quasiharmonic approximation of Eq. (7), the integrand of Eq. (15) is independent of ϕ_1 . This can be seen, for example, from Eq. (9), in which the angle differences $\phi_{1t_1} - \phi_1$ and $\phi_{3t_3} - \phi_3$ are independent of initial angle ϕ_1 . For systems with the anharmonicities considered here, the dependence of this integrand on ϕ_1 is weak, allowing the angle integration to be approximated by a sum with about 20 equally spaced points.

Evaluating a response function diagram in Fig. 4 requires linking classical trajectories with transitions in action of $\pm\hbar/2$ at constant angle. To perform this calculation for a given potential we construct a set of trajectories with action variables quantized in steps of $\hbar/2$. Quantized trajectories are determined using a root-finding algorithm to find initial conditions that give the desired action value, as defined by

$$J = \frac{1}{2\pi} \oint p(t) \dot{q}(t) dt. \quad (16)$$

For each trajectory the period of oscillation, $T(J)$, is determined. The angle variable at any time ϕ_t is then determined from its initial value and Eq. (10) with $\omega(J) = 2\pi/T(J)$, with the angle given modulo 2π and the time given modulo $T(J)$.

The left side of Fig. 5 shows the OMT diagram listed last in Fig. 4(a). The evaluation of this diagram begins by propagating a trajectory at action J_1 for t_1 . Next, a trajectory at

FIG. 5. The phase-space path for a Morse oscillator corresponding to the OMT diagram on the left is shown. Solid lines show portions of classical trajectories used in the calculation, with the remainder of each period indicated with dotted curves. Red dots show classical states along the semiclassical path used to calculate the spectroscopic response.

action $J_1 + \hbar/2$ is propagated for t_2 beginning at angle ϕ_{1t_1} . Last, a trajectory at action $J_1 + \hbar$ is run for t_3 beginning at angle ϕ_{2t_2} . This series of linked classical trajectories is shown in phase space to the right of the OMT diagram in Fig. 5 for a Morse oscillator with initial state $J_1 = \hbar$ and $\phi_1 = 0.2$. Coordinate and momentum in Fig. 5 are made dimensionless as αq and $\alpha p/m\omega$, with the Morse potential given by $D(1 - e^{-\alpha q})^2$ and the corresponding harmonic angular frequency by ω . The evolution times are $\omega t_1 = 5$, $\omega t_2 = 5.5$, and $\omega t_3 = 5$. Solid curves show the classical trajectories used in the calculation, and the remainder of each period is shown in dotted curves. The red dots in the phase-space plot correspond to those in the OMT diagram, representing classical states used in the response function calculation. Numerical calculations in Sec. V are performed by averaging contributions from these linked classical trajectories with a weight determined by a difference of classical thermal distributions, as shown in Eq. (15).

V. NUMERICAL RESULTS

We now present OMT calculations from Eq. (15) of the third-order vibrational response function for two anharmonic potentials, the Morse oscillator, and a quartically perturbed harmonic oscillator, $V(q) = m\omega^2 q^2/2 + aq^4$. The dimensionless response function is expressed as $m^2\omega D R_{\gamma\beta\alpha}^{(3)}(t_3, t_2, t_1)$ for the Morse oscillator and as $m^4\omega^5 a^{-1} R_{\gamma\beta\alpha}^{(3)}(t_3, t_2, t_1)$ for the quartic potential. This dimensionless response function can then be written in terms of two dimensionless parameters, a quantum mechanical quantity $\beta\hbar\omega$ with $\beta \equiv 1/k_B T$ and a classical parameter quantifying the system anharmonicity, which is βD for the Morse potential and $a/(\beta m^2\omega^4)$ for the quartic case.

The MT approximation of Refs. 81–83 has been shown to reproduce well the coherence dynamics of an anharmonic potential at the vibrational echo condition $t_2 = 0$ and $t_1 = t_3 = t$. Figure 6 shows that the changes made to the MT procedure in Eq. (2) to produce the OMT approximation in Eq. (15) preserve this accuracy. The real parts of the response functions $R_{+++}^{(3)}(t, 0, t)$ and $R_{++-}^{(3)}(t, 0, t)$ are shown, respectively, in the left- and right-hand panels of Fig. 6 for a thermal ensemble of Morse oscillators with $\beta\hbar\omega = 2$ and $\beta D = 40$. Time is scaled by the harmonic frequency ω . The time-dependence of $R_{+++}^{(3)}(t, 0, t)$ is identical to that of $R_{++-}^{(3)}(t, 0, t)$ and so is not shown. All plots are shown for a single period given by $4\pi D/(\hbar\omega^2) = 251\omega^{-1}$. This period vanishes in the harmonic limit and diverges in the classical limit. $R_{++-}^{(3)}(t, 0, t)$ represents the vibrational echo signal, which for this model nearly filters out all system frequencies besides the anharmonic quantum frequency $\hbar\omega^2/2D$ as shown previously in Fig. 7 of Ref. 82. $R_{++-}^{(3)}(t, 0, t)$ displays both this low frequency as well as higher frequencies. The uppermost plots (a) and (b) in Fig. 6 show quantum mechanical results, the middle plots (c) and (d) are calculated with the OMT approximation of Eq. (15), and the lowest plots (e) and (f) are calculated with the MT approximation of Eq. (2). The OMT method reproduces well the quantum calculations of coherence dynamics, as was the case for the MT approximation.^{81–83}

FIG. 6. The real parts of $R_{++}^{(3)}(t, 0, t)$ (left-hand panel) and $R_{++}^{(3)}(t, 0, t)$ (right-hand panel) are shown for a thermal ensemble of Morse oscillators with $\beta\hbar\omega = 2$ and $\beta D = 40$. Quantum mechanical results are shown in plots (a) and (b), the OMT approximation is shown in plots (c) and (d), and the MT approximation is given in plots (e) and (f).

The development of the OMT result was motivated by the failure of the MT approximation to reproduce even qualitatively the t_2 dynamics of the response function. The real part of $R_{++}^{(3)}(5, t, 0)$ is shown in Fig. 7 for a thermal ensemble of Morse oscillators with the same parameters as in Fig. 6. This component was chosen because for a single anharmonic degree of freedom, it has nontrivial t_2 dependence arising from two-quantum coherences even in the limit of harmonic selection rules. The other phase-matched components considered here reflect population dynamics during the t_2 period

FIG. 7. The real part of $R_{++}^{(3)}(5, t, 0)$ for a thermal ensemble of Morse oscillators with $\beta\hbar\omega = 2$ and $\beta D = 40$ is shown. The quantum mechanical result is shown in (a), the OMT approximation in (b), and the MT approximation in (c).

FIG. 8. The frequency dependence of $|\tilde{R}_{++}^{(3)}(5, \omega', 0)|^2$ for a thermal ensemble of Morse oscillators with $\beta\hbar\omega = 2$ and $\beta D = 40$ is shown on a semilogarithmic plot. The quantum mechanical result is shown in (a), the OMT calculation in (b), and the MT result in (c). Gray dashed vertical lines indicate peaks present in the quantum mechanical response and the red dashed vertical line indicates the position of the spurious $\omega_{1,-1}$ peak in the MT response. Dots indicate the area associated with each peak relative to the peak at $\omega_{2,0}$. Peaks associated with n -quantum coherences are labeled nQ .

in the limit of harmonic selection rules allowing only one-quantum transitions. For a single degree of freedom without population dynamics, these components show only a weak t_2 dependence arising from multiple-quantum transitions not allowed in the harmonic limit. Panel (a) of Fig. 7 shows the quantum mechanical result, with the OMT in panel (b) and the MT in panel (c). Comparison of panels (a) and (c) confirms that the MT approximation is qualitatively incorrect in this case. The OMT result in panel (b) by contrast agrees well with the quantum result.

The comparison of waiting time dependences of quantum, OMT, and MT response functions can be made more effectively in the frequency domain. Figure 8 shows $|\tilde{R}_{++}^{(3)}(5, \omega', 0)|^2$ the absolute square of the Fourier transform of $R_{++}^{(3)}(5, t, 0)$ in Fig. 7 with respect to the waiting time t . The quantum mechanical result is shown in panel (a), the OMT result in panel (b), and the MT result in panel (c). The exact spectra of quantum and semiclassical response functions consist of Dirac delta function peaks for this model that includes no dynamical broadening mechanisms. Apparent peak widths in Fig. 8 are an artifact of taking the Fourier transform of the response function over a finite time period. To compare approximately the relative contributions of processes at different frequencies, we have computed peak areas, indicated by the relative heights of dots in Fig. 8. The dot heights are normalized so that the peak associated with frequency $\omega_{2,0}$ has unit area. In the approximation of harmonic selection rules permitting only one-quantum transitions, the only frequencies controlling the t_2 period are those of two-quantum coherences,

$$\omega_{n+2,n} = 2\omega - \left(\frac{\hbar\omega^2}{D}\right)\left(n + \frac{3}{2}\right). \quad (17)$$

Peaks at these frequencies are visible for $n = 0$ to $n = 4$ in panel (a) of Fig. 8, and are labeled 2Q to indicate their origin with two-quantum coherences. The other peaks shown in panel (a) from 1Q, 3Q, and 4Q coherences arise from deviations from harmonic selection rules. Gray dashed vertical lines running through all panels show the peak frequencies in the quantum spectrum in panel (a). The MT spectrum in panel (c) reproduces the 2Q peaks from panel (a) but shows a dominant peak at an incorrect frequency corresponding to the spurious 2Q coherence $\omega_{1,-1}$. The location of this frequency is marked by a vertical dashed red line. This frequency is largely responsible for the discrepancies between the time-domain plots in panels (a) and (c) in Fig. 7. The OMT calculation in panel (b) reproduces the 2Q frequencies of quantum mechanics but does not include the incorrect frequency of the MT result. The modification of the MT approximation that removes this spurious frequency is discussed in connection with Fig. 3(b).

In addition to reproducing the frequencies of 2Q coherences in Fig. 8, the OMT improves on the MT in predicting the areas of spectral lines. In the quantum calculation of Fig. 8(a), the integrated areas of the 2Q peaks at $\omega_{3,1}$ and $\omega_{4,2}$ are 18% and 1.6%, respectively, relative to the area of the dominant 2Q peak at $\omega_{2,0}$. In the MT calculation of Fig. 8(c), the importance of these peaks is underestimated, with relative areas of the peaks at $\omega_{3,1}$ and $\omega_{4,2}$ of 8% and 0.5%. In the OMT calculation of Fig. 8(b), these peaks have relative areas of 16% and 1.4% close to the quantum mechanical results.

The remaining peaks in Fig. 8(a) labeled 1Q, 3Q, and 4Q are associated with frequencies of one-, three-, and four-quantum coherences. None of these peaks are allowed within the quasiharmonic approximation of Eq. (7) and within harmonic selection rules. The peaks associated with 1Q and 3Q coherences are reproduced qualitatively by both MT and OMT approximations, which results from these calculations employing exact classical dynamics on anharmonic potentials. The 4Q frequencies are reproduced accurately in the OMT and MT calculations, because the 4Q frequencies $\omega_{n+3,n-1}$ have the same average quantum number as the 2Q frequencies $\omega_{n+2,n}$ and hence are represented in the semi-classical calculations by classical trajectories with the same action. The MT calculation in Fig. 8(c) shows two incorrect 4Q peaks corresponding to spurious frequencies $\omega_{3,-1}$ and $\omega_{2,-2}$. The OMT result in Fig. 8(b) contains only the incorrect frequency $\omega_{3,-1}$. This demonstrates that while using exact classical dynamics enhances the accuracy of the OMT and MT spectra by introducing frequencies from anharmonic transitions, it also introduces some spurious frequencies since all frequencies corresponding to the same average action are incorporated into the spectra. However, the intensities of these spurious frequencies in the OMT approximation are low enough in these calculations as not to cause noticeable discrepancies in the linear time-domain plots of Fig. 7.

The calculations in Figs. 6–8 demonstrate the accuracy of the OMT method for the Morse potential. As noted in connection with Eqs. (8) and (9), the OMT is expected to be particularly accurate for the Morse oscillator, because the classical energy is quadratic in action in that case. To assess the

FIG. 9. The real part of $R_{++}^{(3)}(5, t, 0)$ for a thermal ensemble of quartically perturbed harmonic oscillators with $\beta\hbar\omega = \sqrt{2}$ and $a/(\beta m^2 \omega^4) = 0.025$ is shown in the left-hand panel. The frequency spectrum $|R_{++}^{(3)}(5, \omega', 0)|^2$ is shown in the right-hand panel. Dots indicate the area of each peak relative to the peak at $\omega_{2,0}$. Dashed lines indicate the frequencies (vertical) and areas (horizontal) of quantum mechanical peaks in (b). The quantum mechanical system response is shown in plot (a) and the corresponding frequency spectrum in plot (b). The OMT results are shown in plots (c) and (d) and the MT calculations are shown in plots (e) and (f).

OMT for a more general anharmonic potential, we examine the t_2 dependence of the response function for a quartically perturbed harmonic oscillator in Fig. 9. Here the quantum parameter is $\beta\hbar\omega = \sqrt{2}$ and the classical anharmonicity parameter is $a/(\beta m^2 \omega^4) = 0.025$. The left-hand panel shows the real part of $R_{++}^{(3)}(5, t, 0)$ and the right-hand panel shows the series of 2Q peaks in the absolute square of $\tilde{R}_{++}^{(3)}(5, \omega', 0)$, the Fourier transform with respect to t_2 , defined as in Fig. 8. As in Fig. 8, dots indicate peak areas relative to the peak at $\omega_{2,0}$. Panels (a) and (b) are quantum mechanical results, panels (c) and (d) show OMT calculations, and panels (e) and (f) show MT results. For comparison among spectra, in each of the right-hand panels vertical dashed lines indicate the frequencies and horizontal dashed lines show the areas of the quantum mechanical peaks in panel (b). The principal features discussed in connection with the Morse oscillator calculations in Fig. 8 are present here as well. The dominant peak in the MT calculation in Fig. 9(f) occurs at the spurious frequency $\omega_{1,-1}$, and this peak is absent in the OMT calculation in Fig. 9(d). Outside of the 2Q region, so not shown in the right-hand panel of Fig. 9, the OMT and MT calculations qualitatively reproduce lines resulting from deviations from harmonic selection rules, but these are of low enough intensity to not visibly affect the time-dependence in the left-hand panels of Fig. 9. Unlike the case of the Morse oscillator, the frequencies of 2Q peaks are slightly shifted relative to the quantum result in both MT and OMT calculations, but this shift is less than 1% for the dominant $\omega_{2,0}$ peak. As for the Morse potential, the peak areas are more accurately reproduced by the OMT calculation than by the MT result. The relative area of the peak at $\omega_{3,1}$ is 35% in the quantum calculation, 33% in the OMT approximation, and 23% in the MT result. The relative area of

the peak at the next overtone frequency $\omega_{4,2}$ is 5% in quantum mechanics, 4% in OMT, and 2% in MT. The calculations in Fig. 9 demonstrate that while the OMT works particularly well for the Morse case in which the classical energy is rigorously quadratic in action, the OMT also shows quantitative accuracy for more general anharmonic potentials.

VI. CONCLUSIONS

We have demonstrated that quantum effects in nonlinear vibrational response functions for anharmonic potentials can be accurately reproduced using a semiclassical approach based on computing classical trajectories connected by deterministic transitions. For example, the slowest oscillation shown in Fig. 6 has a frequency proportional to $\hbar$, representing a quantum recurrence that is entirely absent in a fully classical mechanical calculation of the same response function for the same potential.²³ As shown in that figure, the semiclassical calculation quantitatively reproduces this quantum recurrence. The previously developed MT approximation^{81–84} has been shown to reproduce coherence dynamics associated with the initial and final time-evolution periods of the third-order response function, but not to replicate dynamics associated with the middle waiting-time period,³¹ even for a single degree of freedom. The MT approximation was derived starting with the semiclassical Herman-Kluk approximation to the quantum propagator, and resulted from a succession of motivated but uncontrolled approximations. The development of the MT approximation illustrates how and why the Herman-Kluk approximation is successful in this calculation, but does not suggest a route to systematic improvement of the method. Here we have developed an optimized version of the MT approximation by an entirely different strategy based on the correspondence between semiclassical MT paths and double-sided Feynman diagrams. The quantum diagrams are shown to associate in pairs to give one semiclassical diagram. The OMT employs the same semiclassical paths as the MT but differs from it in two respects. In both methods classical state information is collected at four points along the semiclassical path, represented by red dots in Figs. 3 and 4. The first difference between MT and OMT calculations is the identity of these classical states as indicated by the different placements of red dots in panels (a) and (b) versus panel (c) of Fig. 4. In the MT approximation, processes in which the waiting time reflects coherence dynamics are represented by the same semiclassical diagram as those in which the waiting time is associated with population dynamics. In the OMT approximation, these processes are represented by distinct diagrams based on the same semiclassical path, that is, the same pattern of solid lines but different placements of red dots in Fig. 4. The second difference between the MT and OMT calculations is the thermal weight assigned to each semiclassical path. In the MT approach, the trajectory is weighted by the classical phase-space distribution, while in the OMT method this weight is proportional to a difference of classical distributions at different energies. The thermal weight in the OMT calculation reflects the association of a pair of quantum diagrams with different thermal weights to give one semiclassical diagram.

As shown in Figs. 7 and 8 for a Morse potential and in Fig. 9 for a quartically perturbed harmonic potential, the OMT calculations quantitatively reproduce dynamics during each of the three time periods in the third-order response function. In addition to removing the artifacts associated with the MT calculation, the OMT approach provides more accurate predictions for the relative contributions from different frequencies, as shown by the intensities in the frequency spectra in Figs. 8 and 9. The simpler derivation of the OMT from quantum diagrams not only yields a qualitatively improved approximation, but also provides insight into the workings of a semiclassical approximation to a nonlinear response function. Semiclassical paths in the OMT approximation consist of classical trajectories linked by transitions representing the radiation-matter interaction. These trajectories are characterized by action variables corresponding to the average energy of the ket and bra aspects of the density matrix. While this correspondence is carried out in the harmonic limit, it is the good action variables of the system that are quantized to the prescribed integer and half-odd-integer values. Within the quasi-harmonic approximation of Eq. (7), accurate waiting-time dependence is then guaranteed when the energy is at most quadratic in action, as is the case for the Morse potential. The accuracy of the OMT method for the quartically perturbed harmonic potential in Fig. 9 demonstrates that the method can work well even when this condition is not satisfied.

Like the MT approach, the OMT method is based on a canonical transformation from Cartesian coordinates and momenta to action and angle variables. Both methods are therefore only applicable for dynamics that are rigorously or approximately quasiperiodic, so that action and angle variables can be defined. The calculations reported here demonstrate the validity of the method for a single anharmonic degree of freedom, for which this transformation must exist. We are currently generalizing the OMT approximation to treat interacting anharmonic oscillators using the relationship established here between the quantum mechanical 2FD and classical trajectories. For application to multiple degrees of freedom the primary challenge is constructing a suitable approximation to good action and angle variables. Previously, Gruenbaum and Loring demonstrated⁸³ that a transformation to action and angle variables based on low order perturbation theory⁸⁷ can work well in the MT calculation of response functions for coupled oscillators, suggesting that a similar approach may be applied to OMT calculations for multidimensional systems.

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