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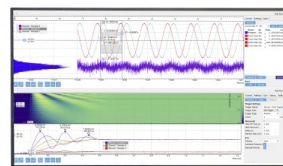
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Decoherence in an anharmonic oscillator coupled to a thermal environment: A semiclassical forward-backward approach

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The decoherence of an anharmonic oscillator in a thermal harmonic bath is examined via a semiclassical approach. A computational strategy is presented and exploited to calculate the time dependence of the purity and the decay of individual matrix elements in the energy representation for a variety of initial states. The time dependence of the decoherence is found to depend on the temperature of the bath, the coupling strength, the initial state of the oscillator, and the choice of quantity measuring the decoherence. Recurrences in the purity and in the off-diagonal matrix elements are observed, as well as the collapse of these matrix elements to the diagonal, providing evidence for the retention of quantum coherence for time scales longer than that indicated by the purity. The results are used to analyze the utility of the Caldeira-Leggett and Redfield models of decoherence and to assess the dependence of dephasing rates on the degree of structure in phase space. In several cases we find that the dephasing dynamics can be described as an initial Zeno-effect regime, followed by a Caldeira-Leggett region, followed by recurrences. © 2004 American Institute of Physics. [DOI: 10.1063/1.1766009]

I. INTRODUCTION

A great deal of current research is dedicated to understanding decoherence, i.e., the loss of quantum phase information when a quantum system is coupled to an environment. Quantifying decoherence is important since it plays a crucial role in the transition between quantum and classical behavior¹ and is a negative influence on any area relying upon quantum coherence effects, such as quantum computation² and the quantum control of atomic and molecular processes.^{3–5} Decoherence is also central to the chemistry of reactions in solution and plays an important role in the generic vibrational relaxation process of a molecule in the condensed phase.

Until recently, most of the related research, both theoretical and experimental, has focused on obtaining vibrational relaxation rates (see, e.g., Refs. 6–9). With the availability of ultrafast spectroscopic techniques, more detailed information can be obtained for these dynamical processes, as well as for the loss of quantum coherence.¹⁰

The theoretical approach to decoherence considers time evolution of the density matrix,¹¹

$$\frac{d\hat{\rho}_T}{dt} = i\hbar[\hat{H}, \hat{\rho}_T], \quad (1)$$

where $\hat{\rho}_T$ is the density operator for the system plus the environment and $\hat{H}$ is the total Hamiltonian. The evolution of $\hat{\rho}_T$ is unitary. However, we are often not interested in the dynamics of the environment. Hence, we trace over the environmental degrees of freedom. The dynamics of the resulting reduced density operator $\hat{\rho}$, which obeys a generalized master equation, is no longer unitary.

In this paper we focus on a number of measures of the time evolution of the decoherence, including the purity of the

state $\text{Tr}(\hat{\rho}^2)$ (Refs. 12–14) and the time evolution of the off-diagonal matrix elements of $\hat{\rho}$ in the energy representation. The former is basis set independent and provides an overall view of the loss of phase information as a system decoheres.¹⁴ Specifically, it is unity for a pure state and is $1/N$ for a totally incoherent mixture $\hat{\rho} = N^{-1} \sum_{i=1,N} |i\rangle\langle i|$ of N states. The latter provides a measure of loss of phase information in precisely that representation responsible for the time evolution of $\hat{\rho}$. That is, in this representation, the reduced density matrix is diagonal when all the coherences have completely decayed and the populations are constant in time. Further, comparing the rates of decay of these off-diagonal elements, which provides T_2 , with the decoherence rate obtained from $\text{Tr}(\hat{\rho}^2)$ provides important insights into the relative magnitude of these rates.

In this paper, we consider decoherence in a system comprising an anharmonic oscillator that is linearly coupled to a thermal bath of harmonic modes. We study the dependence of the decoherence on the initial state of the system, where the initial states include coherent states, cat states, and superposition states, the temperature of the environment and the system-bath coupling. The results are also used to assess the utility of models, such as those due to Redfield,¹⁵ and various quantum-master-equation-based models (for a review, see Refs. 13 and 14).

In this paper we compute decoherence rates by using a correlation function approach in conjunction with a FB-IVR (Forward-Backward Initial Value Representation) semiclassical propagation method.^{16,17} The introduction of this approach is motivated by noting the limitations associated with currently available approaches to computational studies of relaxation and dephasing. For example, the reduced density matrix can be obtained by propagating the full density op-

erator and then tracing out the bath degrees of freedom. In this case, it is convenient to use Feynman¹⁸ path integrals to formulate the expression for the reduced density matrix (for a review see Ref. 19). However, although these methodologies are, in general, both accurate and efficient for short time dynamics, they are not applicable for long times due to the well-known “sign problem.”²⁰ Alternatively, the influence functional approach^{21,22} is both accurate and efficient even for long times, but this method cannot at present accurately describe anharmonic interactions in the liquid phase without introducing additional approximations. By contrast, the method that we introduce works for both large and small systems for time scales over which the semiclassical mechanics is reliable.

Another approach studied here replaces the quantum mechanical operators with their Wigner representation²³ and introduces semiclassical approximations. The resulting expression,²⁴ also known as the linearized IVR,^{25,26} is easier to employ than the FB-IVR, and we compare the results of the two methods.

In addition to quantifying decoherence we compare model theories based on master equations for the reduced density matrix to our results and find that the predictions of the Redfield theory^{15,27} and of the Caldeira-Leggett equation²⁸ are unable to properly describe, either quantitatively or qualitatively, the results obtained numerically. However, we do identify a range over which exponential decay is observed. The origins of these differences, in the approximations inherent in these master equation models, are discussed below.

This paper is organized as follows: Section II introduces the correlation function approach and Sec. III summarizes the theory for the calculation of density matrix elements. In Sec. IV we discuss the computational application of the formulas to a system-bath model. In Sec. V, we discuss the results and finally, in Sec. VI, we summarize. For convenience, the phrase “density matrix” refers to the reduced density matrix for the remainder of this paper.

II. CORRELATION FUNCTIONS AND THE DENSITY MATRIX

Consider the time correlation function between two operators $\hat{A}$ and $\hat{B}$,

$$C_{AB}(t) = \text{Tr}[\hat{A}e^{i\hat{H}t/\hbar}\hat{B}e^{-i\hat{H}t/\hbar}], \quad (2)$$

where $e^{i\hat{H}t/\hbar}$ is the time evolution operator of the system plus bath and the trace is performed over both the bath and the system degrees of freedom. We can obtain a formally exact expression for the time-dependent reduced density matrix element in the energy representation $\rho_{ij}(t)$, where the bath is in thermal equilibrium, by choosing $\hat{A}$ as

$$\hat{A} = \frac{e^{-\beta\hat{H}_B}}{Q_B} |\Phi_0\rangle\langle\Phi_0| \quad (3)$$

and $\hat{B}$ as the projection operator

$$\hat{B} = |\psi_i\rangle\langle\psi_j|, \quad (4)$$

so that

$$\rho_{ij}(t) = \text{Tr} \left[\frac{e^{-\beta\hat{H}_B}}{Q_B} |\Phi_0\rangle\langle\Phi_0| e^{i\hat{H}t/\hbar} |\psi_i\rangle\langle\psi_j| e^{-i\hat{H}t/\hbar} \right]. \quad (5)$$

Here, $|\psi_k\rangle$ are eigenkets of the system Hamiltonian, $\hat{H}_B$ is the Hamiltonian for the thermal bath with partition function Q_B , $|\Phi_0\rangle$ is the initial state for the vibrational coordinate, $\beta \equiv 1/k_B T$, and T is the temperature of the bath. In principle, we may choose any propagation scheme to evolve $\hat{B}$, however, since the environment is multidimensional and the initial state of the system can be rather complicated (for example, a coherent state studied in this paper is described by sixty-one vibrational levels), a natural choice is to use semiclassical techniques. Such methods are able to describe quantum effects accurately while maintaining the advantage of computational simplicity characteristic of purely classical methods. Below we use the FB-IVR variant of the semiclassical initial value representation techniques which have proven to be accurate in a wide variety of studies.^{16,17,25,29–37} In particular, we adapt the forward-backward version of the semiclassical IVR (Refs. 16 and 17) to this study. We also examine the utility of the linearized IVR method.

III. THE DENSITY MATRIX

Consider first the FB-IVR expression for a system coupled to a bath. The semiclassical IVR procedure [whether full Herman-Kluk (HK) or forward-backward] replaces the unitary quantum time evolution operator,

$$\hat{U} = e^{i\hat{H}t/\hbar} |\psi_i\rangle\langle\psi_j| e^{-i\hat{H}t/\hbar}, \quad (6)$$

in Eq. (5) with an integral expression over initial phase space variables. The full HK-IVR procedure²⁹ requires replacing each of the operators $e^{i\hat{H}t/\hbar}$, $e^{-i\hat{H}t/\hbar}$ with such an integral expression, resulting in a double phase space IVR expression of dimensionality $2f$, where f is the number of degrees of freedom in the system.

Unfortunately, this high-dimensional expression also has a highly oscillatory integrand with large complex amplitudes and cannot be accurately computed for systems with many degrees of freedom. A more practical expression can be obtained by using the FB-IVR expression for the evolution operator in Eq. (6) since it does not have these numerical problems. This procedure has been used before for problems with local operators.^{16,17} In our case, however, the operator $|\psi_i\rangle\langle\psi_j|$ can, in general, be nonlocal, and applying the FB-IVR requires that we rewrite it in terms of exponential operators. This can be done by expressing $|\psi_i\rangle\langle\psi_j|$ in terms of the Weyl ordered product,^{17,38}

$$|\psi_i\rangle\langle\psi_j| = \int d\mathbf{p} \int d\mathbf{q} \tilde{B}_{ij}(\mathbf{p}, \mathbf{q}) e^{(i/\hbar)\mathbf{p}\cdot\hat{\mathbf{q}}} e^{-(i/\hbar)\mathbf{q}\cdot\hat{\mathbf{p}}}, \quad (7)$$

where

$$\tilde{B}_{ij}(\mathbf{p}, \mathbf{q}) = \left(\frac{1}{2\pi\hbar} \right)^N \int d\bar{\mathbf{q}} e^{-(i/\hbar)\mathbf{p}\cdot\bar{\mathbf{q}}} \langle \bar{\mathbf{q}} | \psi_i \rangle \langle \psi_j | \bar{\mathbf{q}} - \mathbf{q} \rangle \quad (8)$$

and $\{\mathbf{p}, \mathbf{q}\}$ are the N degree of freedom system phase space variables that provide a representation of $|\psi_i\rangle\langle\psi_j|$. Inserting Eq. (7) into Eq. (6) gives the evolution operator as

$$\hat{U} = \int d\mathbf{p} \int d\mathbf{q} \tilde{B}_{ij}(\mathbf{p}, \mathbf{q}) e^{i\hat{H}t/\hbar} e^{(i/\hbar)\mathbf{p}\hat{\mathbf{q}}} e^{-(i/\hbar)\mathbf{q}\hat{\mathbf{p}}} e^{-i\hat{H}t/\hbar}. \quad (9)$$

We now replace $\hat{U}$ with the FB-IVR approximation so that

$$\begin{aligned} \hat{U} \sim & \left(\frac{1}{2\pi\hbar} \right)^f \int d\mathbf{p} \int d\mathbf{q} \tilde{B}_{ij}(\mathbf{p}, \mathbf{q}) \int d\mathbf{q}_0 \int d\mathbf{p}_0 \\ & \times C(\mathbf{q}_0, \mathbf{p}_0, \mathbf{q}, \mathbf{p}, t) \times e^{i\hat{H}S(\mathbf{q}_0, \mathbf{p}_0, \mathbf{q}, \mathbf{p}, t)} |\mathbf{q}'_0 \mathbf{p}'_0\rangle \langle \mathbf{q}_0 \mathbf{p}_0|, \end{aligned} \quad (10)$$

where f is the number of degrees of freedom in the system and $\{\mathbf{q}_0, \mathbf{p}_0\}$ is a set of coordinates and momenta describing initial conditions (at time zero) for a classical trajectory. The quantities $\{\mathbf{q}'_0, \mathbf{p}'_0\}$ are phase space points that are obtained by integrating the classical equations of motion for $\{\mathbf{q}_0, \mathbf{p}_0\}$ until time t , making a “phase space jump” at time t in the system variables according to the equations

$$\mathbf{q}_t \rightarrow \mathbf{q}_t + \mathbf{q}, \quad (11)$$

$$\mathbf{p}_t \rightarrow \mathbf{p}_t + \mathbf{p} \quad (12)$$

and then propagating the point $\{\mathbf{q}_t + \mathbf{q}, \mathbf{p}_t + \mathbf{p}\}$ back to time $t=0$. The quantity $S(\mathbf{q}_0, \mathbf{p}_0, \mathbf{q}, \mathbf{p}, t)$ is the FB action integral for the trajectory,

$$\begin{aligned} S(\mathbf{q}_0, \mathbf{p}_0, \mathbf{q}, \mathbf{p}, t) = & \int_0^t d\tau [\mathbf{p}_\tau \cdot \dot{\mathbf{q}}_\tau - H(\mathbf{p}_\tau, \mathbf{q}_\tau)] + \mathbf{p} \cdot (\mathbf{q}_t + \mathbf{q}) \\ & + \int_t^0 d\tau [\mathbf{p}_\tau \cdot \dot{\mathbf{q}}_\tau - H(\mathbf{p}_\tau, \mathbf{q}_\tau)]. \end{aligned} \quad (13)$$

The complex preexponential factor $C(\mathbf{q}_0, \mathbf{p}_0, t)$, the monodromy matrix, is defined as

$$\begin{aligned} C(\mathbf{q}_0, \mathbf{p}_0, \mathbf{q}, \mathbf{p}, t) = & \det \left[\frac{1}{2} \left(\gamma^{-1/2} \frac{\partial \mathbf{p}'_0}{\partial \mathbf{p}_0} \gamma^{1/2} + \gamma^{1/2} \frac{\partial \mathbf{q}'_0}{\partial \mathbf{q}_0} \gamma^{-1/2} \right. \right. \\ & \left. \left. - i\hbar \gamma^{1/2} \frac{\partial \mathbf{q}'_0}{\partial \mathbf{p}_0} \gamma^{1/2} + \frac{i}{\hbar} \gamma^{1/2} \frac{\partial \mathbf{p}'_0}{\partial \mathbf{q}_0} \gamma^{1/2} \right) \right]^{1/2}, \end{aligned} \quad (14)$$

where γ denotes an f -dimensional diagonal matrix. The real, positive, arbitrary elements γ_i of this matrix are the width parameters in the coordinate space representation of the i th degree of freedom Gaussian wave packet

$$\langle x_i | q_i, p_i \rangle = \left(\frac{\gamma_i}{\pi} \right)^{1/4} \exp \left[-\frac{\gamma_i}{2} |x_i - q_i|^2 + \frac{i}{\hbar} p_i \cdot (x_i - q_i) \right]. \quad (15)$$

The dependence of $C(\mathbf{q}_0, \mathbf{p}_0, \mathbf{q}, \mathbf{p}, t)$ on $\{\mathbf{q}, \mathbf{p}\}$ arises from the fact that the phase space jump at time t affects the backward evolution of the derivatives in $C(\mathbf{q}_0, \mathbf{p}_0, \mathbf{q}, \mathbf{p}, t)$.

Finally, when Eq. (10) is inserted into Eq. (5), the semiclassical FB-IVR expression for the (i, j) element of the density matrix is obtained,

$$\begin{aligned} \rho_{ij}(t) = & \left(\frac{1}{2\pi\hbar} \right)^{-f} \int d\mathbf{p} \int d\mathbf{q} \tilde{B}_{ij}(\mathbf{p}, \mathbf{q}) \int d\mathbf{q}_0 \\ & \times \int d\mathbf{p}_0 C(\mathbf{q}_0, \mathbf{p}_0, \mathbf{q}, \mathbf{p}, t) e^{(i/\hbar)S(\mathbf{q}_0, \mathbf{p}_0, \mathbf{q}, \mathbf{p}, t)} \\ & \times \langle \mathbf{q}_0 \mathbf{p}_0 | \frac{e^{-\beta \hat{H}_B}}{Q_B} | \Phi_0 \rangle \langle \Phi_0 | \mathbf{q}'_0 \mathbf{p}'_0 \rangle, \end{aligned} \quad (16)$$

where $\langle \mathbf{q}_0 \mathbf{p}_0 | e^{-\beta \hat{H}_B} / Q_B | \Phi_0 \rangle \langle \Phi_0 | \mathbf{q}'_0 \mathbf{p}'_0 \rangle$ is the coherent state representation of the thermal density operator $(e^{-\beta \hat{H}_B} / Q_B) | \Phi_0 \rangle \langle \Phi_0 |$, whose explicit form is described in the following section.

IV. APPLICATION TO A SYSTEM-BATH MODEL

In this section this treatment is applied to a Morse oscillator coupled to a bath of harmonic oscillators. This model was previously used by Wang *et al.*¹⁶ to study quantum effects in the coordinate space probability distribution in the vibrational coordinate. The total Hamiltonian for this case, where the bath has $(f-1)$ oscillators, is

$$\begin{aligned} H = & \frac{p^2}{2\mu} + D[1 - e^{-a(q-q_e)}]^2 \\ & + \sum_{j=1}^{f-1} \left[\frac{P_j^2}{2} + \frac{\omega_j^2}{2} \left(Q_j + \frac{c_j}{\omega_j^2} (q - q_e) \right)^2 \right], \end{aligned} \quad (17)$$

where $\{p, q\}$ are the system phase space variables and $\{P_j, Q_j\}$ are the mass-scaled momenta and coordinates of the bath. The Morse potential parameters used for the system correspond to the ground state potential of molecular iodine: $D = 1.2547 \times 10^4 \text{ cm}^{-1}$, $q_e = 2.6663 \text{ \AA}$, and $a = 1.8576 \text{ \AA}^{-1}$. The quantity μ is the reduced mass of I_2 . The harmonic bath was chosen to have an Ohmic spectral density,

$$J(\omega) = \eta_{sb} \omega \exp \left(-\frac{\omega}{\omega_c} \right), \quad (18)$$

where η_{sb} is the system-bath coupling coefficient and $\omega_c = 20 \text{ cm}^{-1}$ is the characteristic bath frequency. The discrete bath frequencies ω_j and the coupling constants c_j are related to $J(\omega)$ via¹⁶

$$c_j = \omega_j \sqrt{\frac{2\eta_{sb}\omega_c}{\pi(f-1)}} (1 - e^{-5}) \quad (19)$$

and

$$\omega_j = -\omega_c \ln \left[1 - \frac{j}{(f-1)} (1 - e^{-5}) \right]. \quad (20)$$

In this work, we examine decoherence associated with different initial states of the diatomic. Specifically, we first consider decoherence from coherent states given by

$$\langle q | \Phi_0 \rangle = \left(\frac{\gamma}{\pi} \right)^{1/4} \exp \left[-\frac{\gamma}{2} (q - q_i)^2 + \frac{i}{\hbar} p_i (q - q_i) \right], \quad (21)$$

where (q_i, p_i) are the average position and momentum of the initial wave packet and γ is the width of the coherent state.

Second, we consider a superposition of two different coherent states (Schrödinger “cat” states) given by

$$\langle q|\Phi_0\rangle = \sum_{j=a,b} \left(\frac{\gamma}{4\pi} \right)^{1/4} \exp \left[-\frac{\gamma}{2}(q-q_j)^2 + \frac{i}{\hbar} p_j(q-q_j) \right]. \quad (22)$$

Finally, we consider superposition states given by

$$\langle q|\Phi_0\rangle = \sum_n C_n \psi_n(z), \quad (23)$$

where $\psi_n(z)$ is the n th bound state eigenfunction of the I_2 Morse oscillator,

$$\psi_n(z) = N_n \exp \left(-\frac{z}{2} \right) \times z^{(\sqrt{2\mu D}/a) - n - (1/2)} L_n^{(2\sqrt{2\mu D}/a) - 2n - 1}(z). \quad (24)$$

In this expression, N_n is a normalization constant, $L_n^x(z)$ are the Laguerre polynomials as defined in Abramowitz and Stegun,³⁹ and $z \equiv 2\sqrt{2\mu D}/a \exp[-a(q-q_e)]$.

To calculate the density matrix from Eq. (16) note that the “jump” phase space variables (q,p) are one dimensional, the action $S(\mathbf{q}_0, \mathbf{p}_0, q, p, t)$ and prefactor $C(\mathbf{q}_0, \mathbf{p}_0, q, p, t)$ are given by Eqs. (13) and (14), and $\tilde{B}_{ij}(p, q)$ is given in Eq. (8). Finally, the explicit form of the coherent state representation of the thermal density operator is (hereafter, we set $\hbar=1$)

$$\begin{aligned} \langle \mathbf{q}_0 \mathbf{p}_0 | \frac{e^{-\beta \hat{H}_B}}{Q_B} | \Phi_0 \rangle \langle \Phi_0 | \mathbf{q}'_0 \mathbf{p}'_0 \rangle \\ = \langle q_0 p_0 | \Phi_0 \rangle \langle \Phi_0 | q'_0 p'_0 \rangle \prod_{j=1}^{f-1} \langle Q_{j0} P_{j0} | \frac{e^{-\beta \hat{H}_B}}{Q_B} | Q'_{j0} P'_{j0} \rangle, \end{aligned} \quad (25)$$

where¹⁶

$$\begin{aligned} \langle Q_{j0} P_{j0} | \frac{e^{-\beta \hat{H}_B}}{Q_B} | Q'_{j0} P'_{j0} \rangle \\ = (1 - e^{-\beta \omega_j}) \times \exp \left[-\frac{\Gamma_j}{4} (Q_{j0}^2 + Q_{j0}'^2) \right. \\ \left. - \frac{1}{4\Gamma_j} (P_{j0}^2 + P_{j0}'^2) + \frac{i}{2} (P_{j0} Q_{j0} - P_{j0}' Q_{j0}') \right] \\ \times \exp \left\{ \frac{1}{2} e^{-\beta \omega_j} \left[\Gamma_j Q_{j0} Q_{j0}' + \frac{1}{\Gamma_j} P_{j0} P_{j0}' \right. \right. \\ \left. \left. + i(P_{j0}' Q_{j0} - P_{j0} Q_{j0}') \right] \right\}. \end{aligned} \quad (26)$$

Here the width parameters of the bath coherent states and the Morse oscillator are chosen as $\Gamma_j = \omega_j$ and $\gamma = \sqrt{2D\mu a^2} \equiv \mu \Omega_s$, respectively, where $\Omega_s = 213.7 \text{ cm}^{-1}$ is the harmonic frequency of the Morse oscillator. The coherent state representation of the system wave functions, $\langle q_0 p_0 | \Phi_0 \rangle$ and

$\langle \Phi_0 | q'_0 p'_0 \rangle$, differs for each initial state of the diatomic. An analytic formula for these wave functions can be obtained from

$$\langle q_0 p_0 | \Phi_0 \rangle = \int dq \langle q_0 p_0 | q \rangle \langle q | \Phi_0 \rangle, \quad (27)$$

where

$$\langle q_0 p_0 | q \rangle = \left(\frac{\gamma}{\pi} \right)^{1/4} e^{-(\gamma/2)(q-q_0)^2 - i p_0(q-q_0)}. \quad (28)$$

Using this, we obtain for an initial coherent state,

$$\langle q_0 p_0 | \Phi_0 \rangle = e^{-(\gamma/4)(q_0-q_i)^2 - (1/4\gamma)(p_0-p_i)^2 + (i/2)(p_0+p_i)(q_0-q_i)}, \quad (29)$$

and for a superposition of coherent states (cat state),

$$\begin{aligned} \langle q_0 p_0 | \Phi_0 \rangle \\ = \frac{1}{\sqrt{2}} \left[e^{-(\gamma/4)(q_0-q_a)^2 - (1/4\gamma)(p_0-p_a)^2 + (i/2)(p_0+p_a)(q_0-q_a)} \right. \\ \left. + e^{-(\gamma/4)(q_0-q_b)^2 - (1/4\gamma)(p_0-p_b)^2 + (i/2)(p_0+p_b)(q_0-q_b)} \right]. \end{aligned} \quad (30)$$

Obtaining an analytical formula for $\langle q_0 p_0 | \Phi_0 \rangle$ when $|\Phi_0\rangle$ is a superposition of Morse oscillator eigenfunctions is a tedious task (if possible at all). However, for $\langle q_0 p_0 | \Psi_n \rangle$, where $\langle q | \Psi_n \rangle \equiv \Psi_n(q - q_e)$ is a harmonic oscillator eigenfunction corresponding to the n th (harmonic) energy level, an analytical expression is straightforward,

$$\begin{aligned} \langle q_0 p_0 | \Psi_n \rangle = \frac{2^{-n/2}}{\sqrt{n!}} \left[\frac{\gamma(q_0 - q_e) - i p_0}{\sqrt{\gamma}} \right]^n \\ \times e^{-(\gamma/4)(q_0 - q_e)^2 - (p_0^2/4\gamma) + (i p_0/2)(q_0 - q_e)}. \end{aligned} \quad (31)$$

We can therefore expand the superposition of Morse oscillator eigenfunctions in Harmonic oscillator eigenfunctions and then calculate $\langle q_0 p_0 | \Phi_0 \rangle$ using

$$\begin{aligned} \langle q_0 p_0 | \Phi_0 \rangle &\equiv \left\langle q_0 p_0 \left| \sum_m c_m \psi_m \right. \right\rangle \\ &= \left\langle q_0 p_0 \left| \sum_n d_n \Psi_n \right. \right\rangle \\ &= \sum_n d_n \langle q_0 p_0 | \Psi_n \rangle. \end{aligned} \quad (32)$$

One of Eqs. (29), (30), or (32), depending on the initial conditions, is inserted into Eq. (16) and the density matrix can be calculated. The computational effort in calculating the density matrix elements [Eq. (16)] is formidable. We therefore implement the following strategy to minimize this effort. Equation (16) can be rewritten as

$$\rho(t) = \left(\frac{1}{2\pi\hbar} \right)^{-f} \int dp \int dq \tilde{\mathbf{B}}(p, q) I(q, p, t), \quad (33)$$

where

$$I(q,p,t) \equiv \int d\mathbf{q}_0 \int d\mathbf{p}_0 C(\mathbf{q}_0, \mathbf{p}_0, q, p, t) e^{(i/\hbar)S(\mathbf{q}_0, \mathbf{p}_0, q, p, t)} \\ \times \langle \mathbf{q}_0 \mathbf{p}_0 | \frac{e^{-\beta \hat{H}_B}}{Q_B} | \Phi_0 \rangle \langle \Phi_0 | \mathbf{q}'_0 \mathbf{p}'_0 \rangle, \quad (34)$$

and $\underline{p}$ and $\tilde{\mathbf{B}}$ are $n \times n$ matrices, with n the number of significantly populated levels of the diatomic. Note that $\mathbf{q}_0, \mathbf{p}_0$ in Eq. (34) includes *all* system+bath coordinates and momenta, whereas p, q corresponds only to the system and provides independent system phase-space jumps. It is computationally advantageous to calculate these equations in three stages: First, the calculation and storage of $\tilde{\mathbf{B}}(p, q)$ on a grid. Second, the evaluation of Eq. (34), and finally the calculation of the product $\tilde{\mathbf{B}}(p, q) \times I(q, p, t)$ followed by the integration in Eq. (33). The code for the second step can be executed separately from the first and third stages and hence can be very efficiently parallelized, without the need to include the extremely large (and computationally expensive) matrix $\tilde{\mathbf{B}}(p, q)$ in the code.

In the first stage, the matrix element $\tilde{B}_{ij}(p, q)$ is calculated numerically using Morse wave functions for levels i and j [Eq. (24)] via Eq. (8) using the trapezoidal rule. The range of the (p, q) grid on which $\tilde{\mathbf{B}}(p, q)$ is calculated is determined by the spatial spread of the n th level wave function. For the highest level considered ($n=60$) a typical range for the wave function coordinate is 2–4 Å. Convergence of $\tilde{B}_{ij}(p, q)$ required 264 grid points in each dimension. Since $\tilde{B}_{ij}(p, q)$ is the only function in the calculation that is dependent on i and j , we iterate over all possible i, j levels to create the matrix $\tilde{\mathbf{B}}(p, q)$, which is stored for the third step.

To compute the integrals, Eq. (33) is evaluated using uniform Monte Carlo sampling and Eq. (34) is evaluated using importance sampling Monte Carlo for the bath variables using the Husimi distribution $\langle \mathbf{Q}_0 \mathbf{P}_0 | e^{-\beta \hat{H}_B} | \mathbf{Q}_0 \mathbf{P}_0 \rangle$, see [Eq. (25)] as the sampling function. The system variables are sampled with importance Monte Carlo when the diatomic is initially in a coherent state, using $|\langle q_0 p_0 | \Phi_0 \rangle|$ as the sampling function, and sampled with uniform Monte Carlo for the initial superposition states. A typical trajectory for this calculation involves the following algorithm: First, the randomly generated “phase space jump” variables p and q are interpolated to the “nearest-neighbor” values p_j and q_j used for the $\tilde{\mathbf{B}}(p, q)$ grid. If $\tilde{\mathbf{B}}(p_j, q_j) < k \approx 0$, where k is a cutoff orders of magnitude smaller than a typical minimum value of $I(q, p, t)$ (chosen in this work to be 0.001), $\tilde{\mathbf{B}}(p, q) \times I(q, p, t)$ will have negligible contribution to the integral and there is no need to run the dynamics. When $\tilde{\mathbf{B}}(p_j, q_j) > k$, $I(q, p, t)$ must be evaluated. A 2f-dimensional initial phase space point $(\mathbf{q}_0, \mathbf{p}_0)$ is chosen, and Newton’s equations, together with the action and the derivatives that appear in the prefactor, are integrated until time t . At time t , a phase space jump in the system variables is performed according to Eqs. (11) and (12) and the integration is reversed until time $t=0$, culminating at the phase space point $(\mathbf{q}'_0, \mathbf{p}'_0)$. The integrand is now calculated and stored for the third step. In this final step, the product of the stored functions: $\tilde{\mathbf{B}}(p, q)$

$\times I(q, p, t)$, is calculated and integrated to complete the calculation of the density matrix.

A total of 4×10^6 trajectories were needed for convergence for the coherent initial states and 16×10^6 trajectories were needed for the superposition initial states. These numbers can be reduced by a factor of ≈ 4 if only averaged quantities (such as the purity) are required (as distinct from individual density matrix elements). This appears to be a rather large number of trajectories compared to the modest number (50 000–100 000) reported by Wang *et al.*¹⁶ in their semiclassical calculations. However, in their propagation scheme, each of the 50 000 trajectories branches off into ~ 80 additional trajectories at time t , resulting in an effective number of trajectories comparable to the number that we use. In addition, the quantity investigated in their work required the propagation of a local operator and hence the integration over system jump variables was one-dimensional and could be performed using numerical quadrature, as opposed to the Monte Carlo integration required here. The larger number of trajectories needed for the superpositions states results from the fact that the integrand is less localized in the system variables and the initial conditions for the diatomic are selected via uniform sampling.

The results presented in the following section are also convergent with respect to the number of bath oscillators, which was taken to be twenty for all the cases studied. This is the lowest number of oscillators found to be required to reproduce the spectral density given in Eq. (18) and was found sufficient to provide accurate results for the decoherence measures, as discussed below.

V. RESULTS AND DISCUSSION

A. Semiclassical results

We have done numerous computations on systems with varying temperatures, system-bath coupling parameters (given in terms of $\eta \equiv \eta_{sb}/\mu\Omega_s$) and initial vibrational states. To present these results we first consider a specific case that typifies the general behavior observed (for this case, results were obtained at time intervals of 16 fs until time $t=288$ fs, and time intervals of 64 fs from $t=320$ fs to $t=640$ fs). We then examine how different conditions effect decoherence (using for this analysis time intervals of 64 fs).

We note at the outset, as observed in a set of representative cases, that both the dynamics of $\text{Tr}(\rho^2)$ and of individual ρ_{ij} depend upon the *product* ηT . Figure 1 shows the purity $\text{Tr}(\rho^2)$ as a function of time for an initial coherent state placed at $q_i=2.4$, $p_i=0.0$. This coherent state, termed the multilevel coherent state, populates the first 61 vibrational levels of the Morse oscillator peaked around the 24th state. The temperature of the bath was taken as 300 K and the coupling coefficient $\eta=0.25$. Figure 1 shows that the purity of the system falls off very slowly until ≈ 100 fs, when it abruptly decays, showing short recurrences at ≈ 250 and ≈ 450 fs. The decay between $t \approx 100$ and 250 fs, can be fitted to an exponential decay with excellent agreement. The recurrence frequency is slightly larger than the harmonic vibrational period of the Morse oscillator ~ 156 fs for the present parameter set, suggesting a correlation between the vibra-

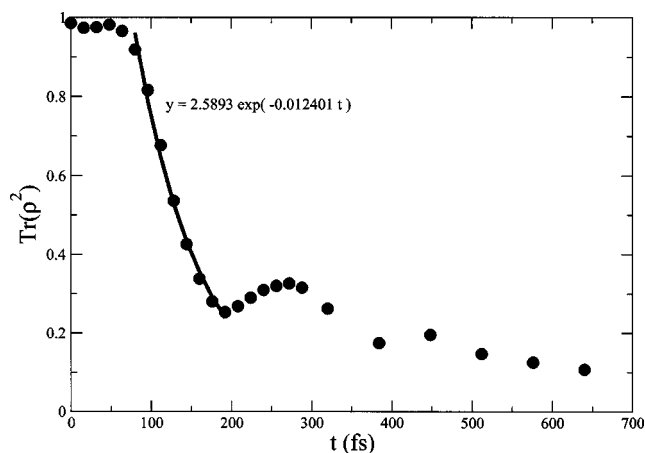


FIG. 1. Purity as a function of time for the multilevel coherent state. $T = 300$ K, $\eta = 0.25$. The group of points corresponding to the first abrupt decay of this function have been fitted to an exponential curve described by the given equation.

tional motion and the quantum coherences. The value of $\text{Tr}(\rho^2)$ at the largest time computed is ≈ 0.1 . If, at this time, ρ were a statistically mixed state with equal probabilities, it would imply that the total number of states in the system were $N = 10$. Clearly this is inconsistent with the actual number of states that are in the wave packet, and with Fig. 3, discussed below, which shows the involvement of far more states. Nonetheless, this “effective number of levels” provides us with some idea as to how far the system is from complete relaxation. The time scale of these coherences is shown in greater detail in Fig. 2, which plots the real and imaginary parts of a sample matrix element near the diagonal: $\rho_{23,27}$ and $\rho_{27,23}$. Here the overall decay of this matrix element is evident, but on a far longer time scale than projected by the purity measure.

A more general view of the time evolution of the off-diagonal density matrix elements (in the energy representation) is given in Fig. 3. Here, each point depicts a density matrix element whose absolute value is larger than the cutoff of 0.02. Results are shown at three different times. The collapse of these matrix elements towards the diagonal is visibly

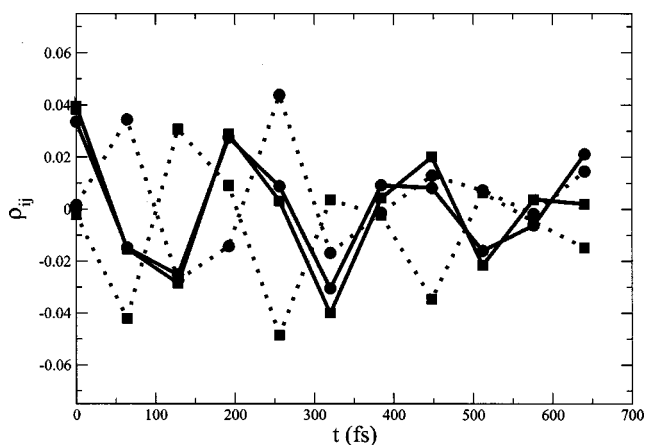


FIG. 2. Sample $\rho_{i,j}$ as a function of time. Solid lines: $\text{Re}(\rho_{i,j})$; dotted lines: $\text{Im}(\rho_{i,j})$. Circles: $i = 27, j = 23$; squares: $i = 23, j = 27$.

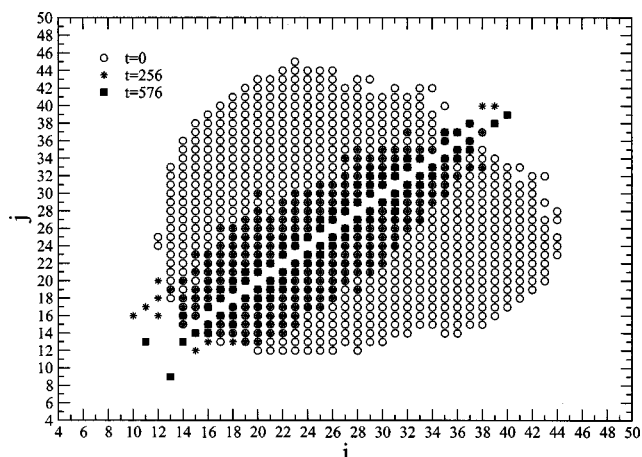


FIG. 3. Map of the off-diagonal density matrix elements that obey $|\rho_{ij}| > 0.02$ at three different times. For clarity note that those elements $|\rho_{ij}| > 0.02$ at time t also satisfy this condition at earlier times. Note the collapse of the density to the diagonal with increasing time.

impressive. Generally speaking, the higher frequency coherences arising from levels that are widely separated decay much faster than levels that are close to each other. This behavior is qualitatively consistent with predictions²⁷ of Redfield theory, but are quantitatively different, as discussed below. These results illustrate the persistence of quantum coherence for longer times than predicted by the purity.

The combination of Figs. 1, 2, and 3 plus auxiliary studies of the matrix elements make clear that the primary decoherence process that we are seeing in Fig. 1 is the disappearance of the extreme high frequency off-diagonal components of the density matrix. Since

$$\begin{aligned} \text{Tr}(\rho^2) &= \sum_{i,j} \langle i|\rho|j\rangle \langle j|\rho|i\rangle \\ &= \sum_i |\langle i|\rho|i\rangle|^2 + \sum_{i \neq j} \langle i|\rho|j\rangle \langle j|\rho|i\rangle, \end{aligned} \quad (35)$$

the decrease of the high frequency components reduces the second term in Eq. (35), leading to a reduction in the size of $\text{Tr}(\rho^2)$.

Despite the fact that exponential decay is observed over a small time region, the total falloff in Fig. 1 is distinctly nonexponential. Nevertheless, we can extract some sort of dephasing time by noting that $\text{Tr}(\rho^2)$ has fallen below $1/e$ by $t \approx 200$ fs. By contrast, the off-diagonal matrix element in Fig. 2 appears to be falling off, with oscillations, over a much longer timescale. Specifically, we would very crudely estimate that the peaks of the oscillations would reach $1/e$ of their initial value by ≈ 700 fs, a considerably longer time.

One note regarding computational accuracy is in order. Formally, the map in Fig. 3 should be completely symmetric, as a result of microreversibility. Similarly, complex conjugate matrix elements in Fig. 2, computed independently, should be equal. In general, we do observe good agreement with the expectation that $[\text{Re}(\rho_{i,j}) = \text{Re}(\rho_{j,i}), \text{Im}(\rho_{i,j}) = -\text{Im}(\rho_{j,i})]$, for most of the time studied, but with small deviations from complete symmetry due to errors in the Monte Carlo evaluation of the integrals.

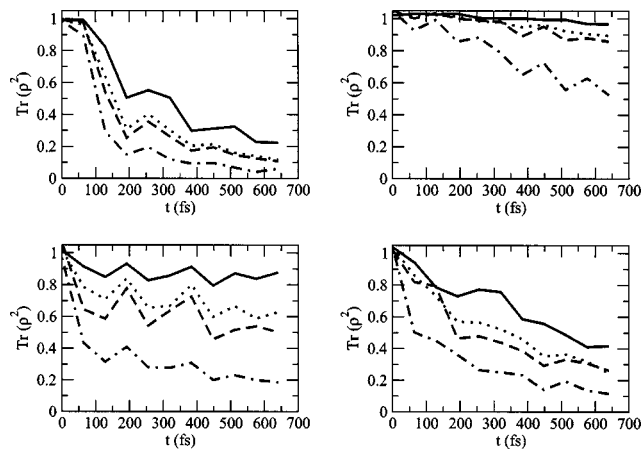


FIG. 4. Purity as a function of time for: upper left pane: multilevel initial coherent state; upper right pane: six-level coherent state; lower left pane: superposition state; lower right pane: cat state. Solid lines: $T=100$ K, $\eta=0.15$; dotted lines: $T=300$ K, $\eta=0.15$; dashed lines: $T=300$ K, $\eta=0.25$; dot-dashed lines: $T=400$ K, $\eta=0.9$.

The general behavior seen in Figs. 1–3, in both the purity as well as the off-diagonal density matrix elements, was observed for all the cases that we studied. These cases, analyzed in greater detail below, differ primarily in the time scale and magnitude of the behavior.

Consider now the effects of different conditions, including the initial state, on the rates of decoherence. In Fig. 4 we observe the dependence of the decoherence on the temperature of the bath and on the coupling as portrayed by the purity. Results are shown for the multilevel coherent state (described above), as well as an initial coherent state placed at $q_i=2.75$, $p_i=2.5$ that populates the first six levels (hereafter termed the six-level coherent state), for a superposition of two states, given by Eq. (32) with

$$D_n = \begin{cases} \frac{1}{\sqrt{2}} & \text{if } n=9,10 \\ 0 & \text{otherwise,} \end{cases} \quad (36)$$

and for cat states, defined as a superposition of localized Gaussians Eq. (30), here with $q_a=2.6$, $p_a=0.0$, $q_b=3.0$, $p_b=0.0$. In all cases and consistent with expectation, the system decoheres much faster when the temperature is higher and when the coupling is more substantial. We also observe the same qualitative behavior for all cases: an abrupt initial exponential decay, often following an initial flat region, followed by a series of recurrences (although the exponential decay region is hardly observable in the six-level coherent state). These recurrences occur, in all cases, and at the same times for each initial state, regardless of the temperature and the coupling. However, the magnitude of the recurrences decreases as the product ηT increases (the significance of this product will be discussed below).

Figure 5 compares the decoherence rate of the four different initial states at the same bath and coupling conditions ($T=300$ K and $\eta=0.25$). The order of the overall observed decoherence rates is that the multilevel state decoheres faster than the cat state, which is faster than the superposition state, which is faster than the six level state. A comparison with

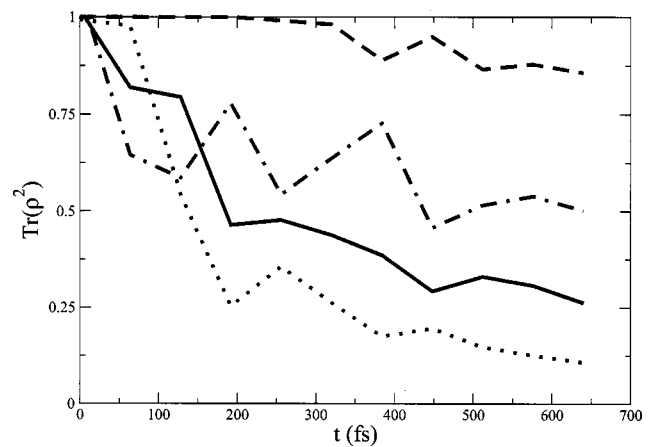


FIG. 5. Purity as a function of time for different initial states at $T=300$ K, $\eta=0.25$; solid line: cat state; dotted line: multilevel coherent state; dashed line: six-level coherent state; dot-dashed line: superposition state.

Fig. 6, which shows the distribution of the populations of the initial states among the eigenstates of the oscillator, shows that the larger the quantum number of the maximal level populated, the faster the decoherence rate. We discuss, later below, a more general phase space method for quantifying this dependence.

B. Model master equation approaches

Numerous model master equations exist, incorporating various approximations. It is of importance, in order to assess the utility of these models, to compare the results of some simple theories to the exact semiclassical results in this paper, which do not invoke approximations other than the use of semiclassical mechanics. Before making specific comparisons to two well-known models, we first note that the appearance of recurrences in the decay of $\text{Tr}(\rho^2)$, as we have observed, calls into question the utility of many Markovian master equation treatments that predict exponential decay (e.g., Ref. 40). These observed recurrences are important and provide evidence that although initial decoherence may be

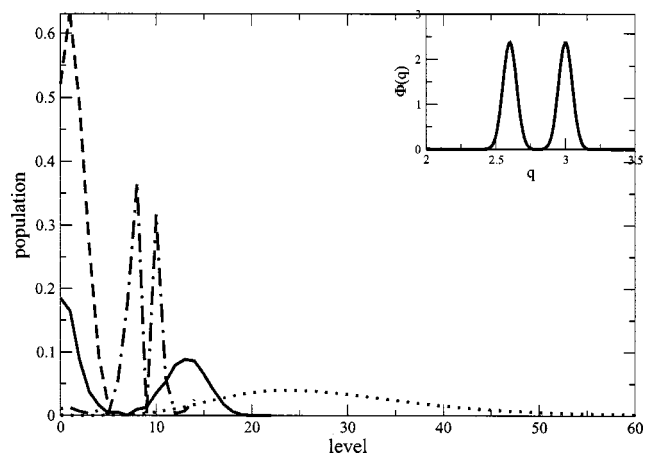


FIG. 6. Relative population of the initial superposition state (dot-dashed line), the initial multilevel coherent state (dotted line), the initial six-level coherent state (dashed line) and the initial cat state (solid line). The initial cat state wave function appears in the inset.

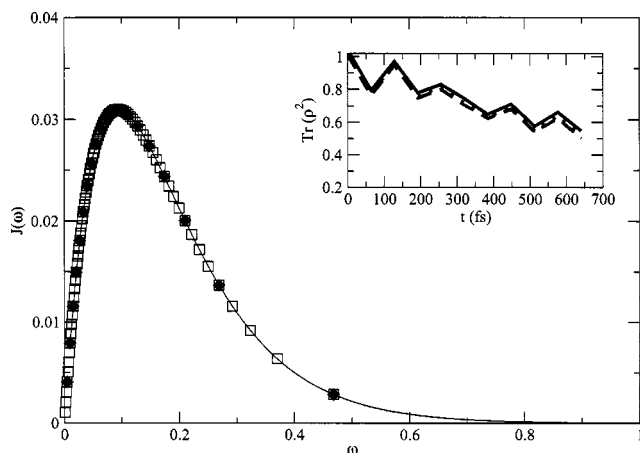


FIG. 7. Bath spectral density; solid line: exact; diamonds: 20 oscillators; squares: 80 oscillators. In the inset: convergence of the linearized IVR with respect to the number of bath oscillator for an initial six-level coherent state at $T=300$ K, $\eta=0.25$; solid line: 20 oscillators; dotted line: 40 oscillators; dashed line: 80 oscillators.

rapid, some coherence is retained for much longer periods of time. One may be tempted to dismiss these recoherences as a nonphysical result of the finite number of oscillators used in the calculation. However, as previously noted, our results converge with an increasing number of oscillators, so even with 80 bath oscillators these recoherences are observed. For example, Fig. 7 compares the discrete spectral density using two different numbers of bath oscillators to the exact result and also shows the convergence of $\text{Tr}(\rho^2)$ for a bath with 20, 40, and 80 oscillators using an initial coherent state placed at $q_i=2.75$, $p_i=2.5$, and the linearized IVR that is described later below. Calculations at a few specific times using the full FB-IVR for these numbers of bath oscillators suggest similar convergence. Hence, the absence of recurrences in Markovian models is an artifact of the assumptions upon which they are based. In particular, memory and backreaction that can play an important role in the dynamics of decoherence is often missed by conventional models.⁴¹

We now consider, in more detail, a comparison with some aspects of two common approaches, the Caldeira-Leggett master equation²⁸ and the Redfield theory.^{15,27}

1. Caldeira-Leggett model

The Caldeira-Leggett model arises upon considering a Hamiltonian system coupled to a bath of harmonic oscilla-

tors via linear coupling, i.e., the case considered here. They then adopt the Markovian approximation and consider the high temperature, low coupling limit. The resultant equation of motion for the density matrix (with coupling through the position operator), in the Wigner approximation, is given by

$$\begin{aligned} \frac{\partial \rho^w}{\partial t} = & \{H, \rho^w\} + \sum_{n \geq 1} \frac{\hbar^{2n} (-1)^n}{2^{2n} (2n+1)!} \frac{\partial^{2n+1}}{\partial q^{2n+1}} V(q) \\ & \times \frac{\partial^{2n+1}}{\partial p^{2n+1}} \rho^w + D \frac{\partial^2 \rho^w}{\partial p^2}. \end{aligned} \quad (37)$$

The first term on the RHS of this equation is the Poisson bracket, which generates the classical evolution for the Wigner representation of the density matrix ρ^w ; the terms in $\hbar$ add the quantal evolution, with the expansion being formally valid for a system potential $V(q)$ analytic in q (in our case the Morse potential). The last term describes the decoherence. The parameter D depends monotonically on the coupling and temperature of the environment. The standard form for D for coordinate coupling is $D=2\gamma M k_B T$, where T is the temperature of the bath, γ is an unknown measure of the system-environment coupling, k_B is the Boltzmann constant, and M is the system mass.

Pattanayak and Brumer⁴² showed that the rate of decay of the Renyi entropy, $S = \ln[\text{Tr}[(\rho^w)^2]]$, which is evidently related to the purity, is given for the Caldeira-Leggett model by

$$\frac{dS}{dt} = 2D \frac{\text{Tr} \left[\rho^w \frac{\partial^2 \rho^w}{\partial p^2} \right]}{\text{Tr}[(\rho^w)^2]} \equiv -2D\chi^2, \quad (38)$$

where χ^2 is implicitly defined in Eq. (38). (Note that here, unlike Ref. 42, we use the second derivative with respect to the momentum, rather than derivatives with respect to both coordinates and momenta, since the system-bath coupling adopted here depends on the coordinate only.) The physical interpretation of χ^2 can be understood by Fourier analyzing the Wigner density $\rho^w(p, q)$ as $\rho^w(p, q) = \int d\mu \tilde{\rho}^w(\mu, q) e^{2\pi i \mu p}$. Inserting this into the definition of χ^2 as given by Eq. (38),

$$\begin{aligned} \chi^2 = & - \frac{\text{Tr} \left[\rho^w \frac{\partial^2 \rho^w}{\partial p^2} \right]}{\text{Tr}[(\rho^w)^2]} = - \frac{\int dp \int dq \int d\mu \int d\mu' (-4\pi^2 \mu^2) \tilde{\rho}^w(\mu, q) \tilde{\rho}^w(\mu', q) e^{2\pi i (\mu + \mu') p}}{\text{Tr}[(\rho^w)^2]} \\ & = \frac{4\pi^2 \int dq \int d\mu \mu^2 |\tilde{\rho}^w(\mu, q)|^2}{\text{Tr}[(\rho^w)^2]}. \end{aligned} \quad (39)$$

Hence, in this case χ^2 is a measure of the structure in momentum space, averaged over coordinate space. Note that since χ^2 is a positive real number, dS/dt is negative definite in the Caldeira-Leggett model. Thus, at the outset, the Caldeira-Leggett result is inconsistent with the exact semiclassical dynamics that show recurrences in $\text{Tr}(\rho^2)$, i.e., that show both negative and positive values of dS/dt . In particular, for the multidimensional coherent state in Fig. 1, the Caldeira-Leggett prediction that exponential decay occurs is only valid for the first abrupt decay between the times: $t \approx 100$ and 250 fs, where there is excellent agreement with an exponential fit. However, the Caldeira-Leggett model does not predict the first plateau ($t \approx 0-100$ fs), that is related to the Zeno effect,⁴³ or the recurrences at times later than 250 fs. This discrepancy appears in all the cases studied.

The quantity χ^2 provides a measure of phase space structure embodied in ρ^w . Further, the Caldeira-Leggett model implies, via Eq. (38), that the larger the χ^2 , i.e., the higher the phase space structure, the faster the decay of S . Our semiclassical results provide us with the opportunity to test the validity of the latter Caldeira-Leggett-based association. Consider first the relationship between χ^2 and phase space structure (in our case, averaged over the coordinate). The Wigner density ρ^w can be calculated from the reduced density matrix elements obtained using the FB-IVR method described here, since

$$\begin{aligned} \rho^w(p, q, t) &= \frac{1}{2\pi} \int_{-\infty}^{\infty} dy e^{ipy} \left\langle q - \frac{y}{2} \left| \hat{\rho}(t) \right| q + \frac{y}{2} \right\rangle \\ &= \frac{1}{2\pi} \sum_{i,j} \int_{-\infty}^{\infty} dy e^{ipy} \left\langle q - \frac{y}{2} \left| \psi_i \right\rangle \rho_{ij}(t) \right. \\ &\quad \times \left. \left\langle \psi_j \left| q + \frac{y}{2} \right\rangle \right. \right. \end{aligned} \quad (40)$$

where the wave functions $\langle q - y/2 | \psi_i \rangle$ and $\langle \psi_j | q + y/2 \rangle$ are the (numerically exact) Morse oscillator wave functions and $\rho_{ij}(t)$ are the time-dependent reduced density matrix elements in the energy representation. An expression for χ^2 can be derived by inserting Eq. (40) and its second derivative into Eq. (39) and performing the integrations over p and y to give

$$\begin{aligned} \chi^2(t) &= \frac{-1}{2\pi} \sum_{i,j,k,l} \int_{-\infty}^{\infty} dq dy y^2 \left\langle q - \frac{y}{2} \left| \psi_i \right\rangle \rho_{ij}(t) \right. \\ &\quad \times \left. \left\langle \psi_j \left| q + \frac{y}{2} \right\rangle \left\langle q + \frac{y}{2} \right| \psi_k \right\rangle \rho_{kl}(t) \left\langle \psi_l \left| q - \frac{y}{2} \right\rangle \right. \end{aligned} \quad (41)$$

Figure 8 compares $\chi^2(t)$ for three different initial states: the six-level coherent state, the cat state and the superposition state, all at the same temperature ($T = 300$ K) and coupling ($\eta = 0.25$). Figure 9 shows $\rho^w(p, q)$ at initial time $t = 0$ and a relatively long time $t = 384$ for these same cases. Qualitatively, we expect decoherence to reduce the amount of phase space structure, and this is indeed what we see, quantified by comparing Figs. 5, 8, and 9. That is, Fig. 8 suggests that the cat state has lost considerable phase structure by 400 fs that the six-level state remains similar at long

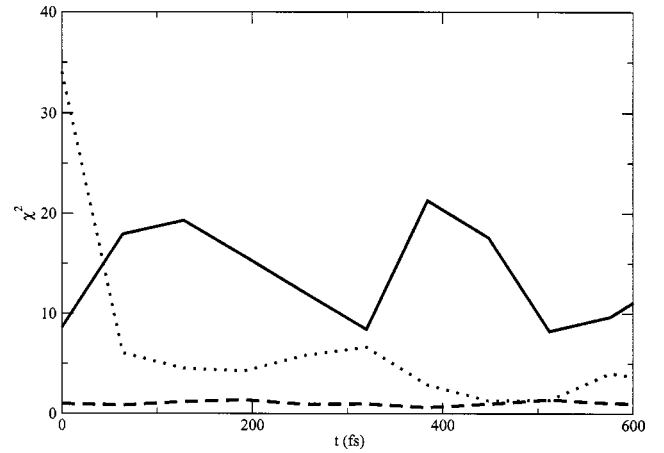


FIG. 8. $\chi^2(t)$ as a function of time at $T = 300$ K, $\eta = 0.25$ for different initial phase space structures. Solid line: superposition state; dotted line: cat state; dashed line: six-level coherent state. Note that straight lines are used to connect computed points. Multiply χ^2 by 2.219×10^{45} to obtain the result in units of $\text{J}^{-1} \text{Kg}^{-1}$.

times to when it started, and the superposition state loses and recovers its structure, at various times. This is indeed consistent with Fig. 9 (with structure visualized as averaged over coordinate space). However, things are only very weakly correlated with the loss of decoherence shown in Fig. 5. More specifically, there is absolutely no manifestation of the Caldeira-Leggett prediction [Eq. (38)] of a proportionality between dS/dt and χ^2 .

We can, nonetheless, attempt to obtain an estimate of D from the relationship $D = -(dS/dt)/(2\chi^2)$, by inserting the values of χ^2 from the exponential region of our dynamical calculations [Eq. (41)]. Using the finite differences value of dS/dt , for the eight points in the exponential region of the initial superposition state at $T = 300$ K and $\eta = 0.95$ (Fig. 10), gives us a range of $D = 2.56 \times 10^{-34}$ to $6.44 \times 10^{-35} \text{ kg Js}^{-1}$. Despite the limited range of applicability of the

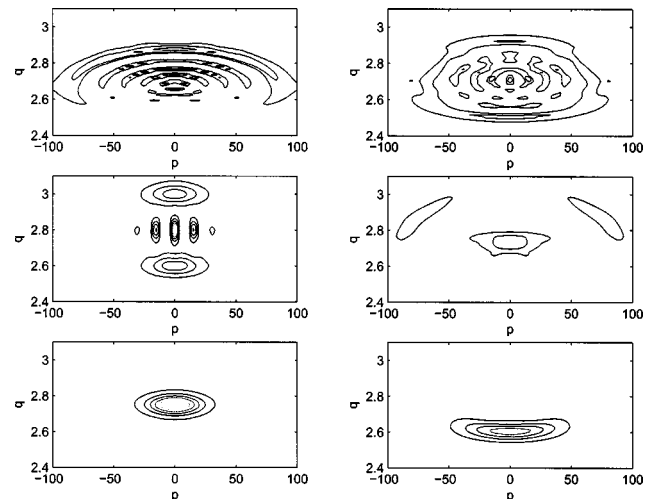


FIG. 9. $\rho^w(t)$ at time $t = 0$ (left column) and $t = 384$ (right column) with $T = 300$ K, $\eta = 0.25$ for different initial phase space structures. Upper panels: superposition state; middle panels: cat state; lower panels: six-level coherent state.

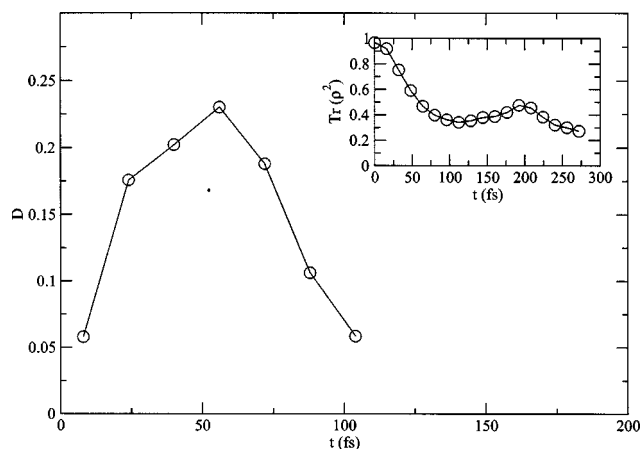


FIG. 10. Plot of D as a function of time for an initial superposition state with $T=300$ K, $\eta=0.95$. In the inset is the purity corresponding to these parameters. Multiply D by 1.112×10^{-33} to obtain the result in units of J Kg s^{-1} .

Caldeira-Leggett model, we have observed that our results do show a dependence on ηT , consistent with this model.

2. Redfield theory

Kohen and Tannor²⁷ considered the dynamics of a displaced Gaussian phase space distribution evolving on a harmonic oscillator potential using Redfield theory. They found a simple, linear relationship between the rate of decay of individual off-diagonal density matrix elements ρ_{ij} and the difference in quantum levels $|i-j|$. To test this we show, in Fig. 11, the time decay of off-diagonal density matrix levels with $|i-j|=1, 2$, respectively. In both cases, only two matrix elements are seen to decay in a similar fashion and at approximately the same rate, while the other matrix elements behave quite differently. The off-diagonal density matrix element that exhibit similar behavior correspond to the ρ_{ij} between highly populated quantum levels. This behavior is consistent for all the cases studied here. This disagreement with Redfield theory is not attributable to the fact that the Redfield theory predictions are based on a simple, one-

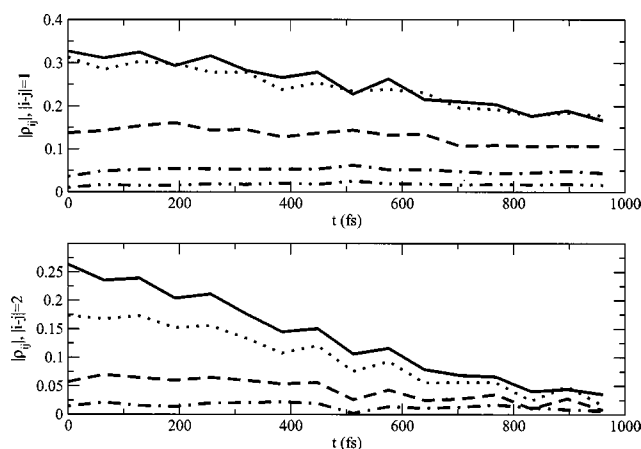


FIG. 11. Time dependence of off-diagonal matrix elements ρ_{ij} with $|i-j|=1$ (upper pane) and $|i-j|=2$ (lower pane) for the initial six-level coherent state at $T=400$ K and $\eta=0.9$. Each line represents a different ρ_{ij} element.

dimensional, harmonic model. Specifically, we observed the same behavior even when the anharmonic potential is replaced by an harmonic potential.

C. Linearized IVR

The computations described above are time consuming, due to the large number of trajectories needed to fully converge the results. In an effort to simplify the computations we also performed the same calculations using a classical analog approach.²⁴ In this approach, also termed the linearized IVR (Refs. 17, 25, 26, and 44) we replace the quantum operators in Eq. (5) by their Wigner representation and then perform the required dynamics classically. The density matrix is then given by

$$\rho_{ij}(t) = \left(\frac{1}{2\pi\hbar} \right)^{-f} \int d\mathbf{q}_0 \int d\mathbf{p}_0 A_w(\mathbf{q}_0, \mathbf{p}_0) B_w^{ij}(\mathbf{q}_t, \mathbf{p}_t), \quad (42)$$

where A_w and B_w^{ij} are the Wigner representations of the operators defined by Eqs. (3) and (4). An attempt to relate this approximation to the FB-IVR results by using the exact relationship between $\tilde{B}_{ij}(\mathbf{p}, \mathbf{q})$ and $B_w^{ij}(\mathbf{q}_t, \mathbf{p}_t)$,¹⁷

$$B_w^{ij}(\mathbf{q}_t, \mathbf{p}_t) = \int d\mathbf{p} \int d\mathbf{q} \tilde{B}_{ij}(\mathbf{p}, \mathbf{q}) e^{(i/\hbar)(\mathbf{p} \cdot \mathbf{q}/2 + \mathbf{q}_t \cdot \mathbf{p} - \mathbf{p}_t \cdot \mathbf{q})}, \quad (43)$$

giving, for Eq. (42),

$$\rho_{ij}(t) = \left(\frac{1}{2\pi\hbar} \right)^{-f} \int d\mathbf{p} \int d\mathbf{q} \int d\mathbf{q}_0 \times \int d\mathbf{p}_0 A_w(\mathbf{q}_0, \mathbf{p}_0) \tilde{B}_{ij}(\mathbf{p}, \mathbf{q}) e^{(i/\hbar)(\mathbf{p} \cdot \mathbf{q}/2 + \mathbf{q}_t \cdot \mathbf{p} - \mathbf{p}_t \cdot \mathbf{q})}. \quad (44)$$

This expression should be compared to Eq. (16), i.e., the FB-IVR result. However, we have not been able to derive Eq. (44) from Eq. (16), even by using the linearization scheme proposed in Ref. 17, since the approximation

$$\langle \mathbf{q}_0 \mathbf{p}_0 | \frac{e^{-\beta \hat{H}_B}}{Q_B} | \Phi_0 \rangle \langle \Phi_0 | \mathbf{q}_0 \mathbf{p}_0 \rangle \approx A_w(\mathbf{q}_0, \mathbf{p}_0) \quad (45)$$

is not valid in this case. To show this, note that $\langle \mathbf{q}_0 \mathbf{p}_0 | e^{-\beta \hat{H}_B} / Q_B | \Phi_0 \rangle \langle \Phi_0 | \mathbf{q}_0 \mathbf{p}_0 \rangle$ is the Husimi distribution^{16,45} which differs from the Wigner distribution as noted by the same authors in Appendix B of Ref. 46. In addition, the phase factor $\mathbf{p} \cdot \mathbf{q}/2$ in Eq. (44) is important and cannot simply be discarded. Hence we prefer to “derive” Eq. (42) by the more direct approach described above, which follows the “classical analog” philosophy developed elsewhere²⁴ and which provides Eq. (44) directly.

The computational advantage of Eq. (44) is that there is no need to evaluate the time-consuming monodromy matrix, making the linearized IVR computation ≈ 30 times faster. Hence, it would be advantageous to ascertain the extent to which this approach reproduces results of the FB-IVR. Further, this comparison should provide insight into quantum classical correspondence in this model.

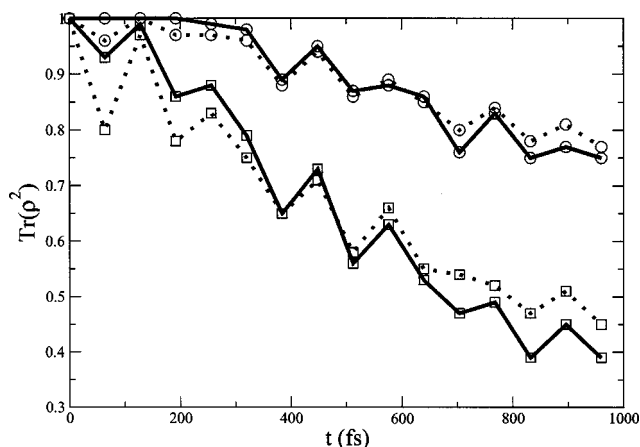


FIG. 12. Comparison of purity for the linearized IVR (dotted line) and the FB-IVR (solid line) using the initial six-level coherent state: circles: $T = 300$ K, $\eta = 0.25$; Squares: $T = 400$ K, $\eta = 0.9$.

Figure 12 shows a comparison between the two methods for the six-level coherent state with $T = 300$ K, $\eta = 0.25$, and for $T = 400$ K, $\eta = 0.90$. In most cases the linearized version agrees with the FB-IVR, however, there are some discrepancies that cannot be attributed to Monte Carlo-based errors. Specifically, at the early time: $t = 64$ fs, the two methods disagree somewhat, especially for the higher temperature and larger coupling. Figure 13 shows the comparison in terms of some density matrix elements. Interestingly, the major discrepancy at $t \approx 64$ fs relates to a slight, but nonetheless significant, shift in the value of the off-diagonal matrix elements.

Wang *et al.*,¹⁶ who compared the linearized IVR with the FB-IVR for a similar system, also found differences between the two methods in their calculations of the time-dependent probability distribution function. In contrast to the results presented here, the differences were dominant at lower temperatures and shorter times. The agreement at longer times was attributed to the fact that effectively complete decoher-

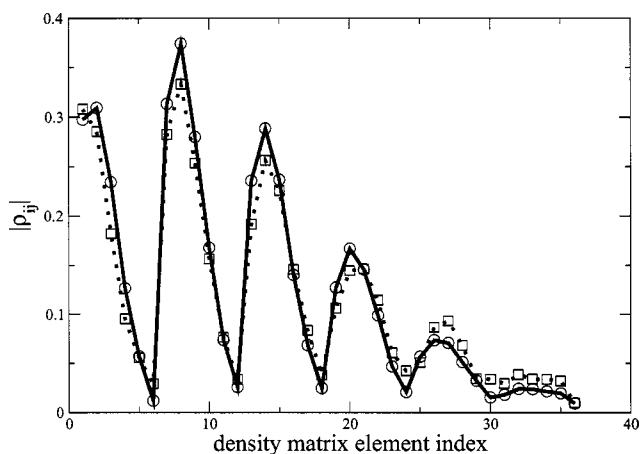


FIG. 13. Comparison of linearized IVR (dotted line and squares) and FB-IVR (solid line and circles) for the initial six-level coherent state at $T = 400$ K, $\eta = 0.9$. In order to show the values of all the density matrix elements in one 2D plot, the x axis was chosen such as each (discrete) x_i labels a different density matrix element ρ_{jk} according to $x_i = \sum_{j,k=0,5} 6j + k + 1$.

ence had occurred and hence, classical mechanics is adequate in describing the dynamics. An additional study of the linearized approximation is therefore necessary to further explore the deviations from the FB-IVR seen in Fig. 12.

VI. SUMMARY

In this paper, we have studied the decoherence of an anharmonic oscillator coupled to a bath of harmonic oscillators. In contrast with the common approach, master equations for the reduced density matrix were not used. Rather, we implemented a dynamics approach using a semiclassical formulation of density matrix evolution. We investigated the effects of the temperature and coupling strength of the environment, and the initial state of the system, on the decoherence, through the time dependence of the purity, and the off-diagonal density matrix elements in the energy representation. It was found that the decoherence is faster at higher temperatures T and stronger system-bath couplings η , with the dependence being on ηT . In general, decoherence is slower if the system's low energy states are initially populated. However, decoherence occurs rapidly for Schrödinger cat states, due to interference between the spatially separated coherent states. It was found that the off-diagonal matrix elements "collapse" to the diagonal as the system loses its coherences, with decoherence occurring faster for coherences between levels that are more energetically separated.

In the context of quantum computing, one usually wishes to reduce decoherence effects as much as possible. The results of this study suggest that the best way to achieve this is to create a coherent wave packet of low lying states, isolated from an environment which is kept at a low temperature. These strict conditions may be relaxed, if only a certain degree of coherence need be retained, since energy levels that are close retain their coherence for longer times. This may be the case for coherent control.

It is important to emphasize two specific dynamic features that are absent in many models of decoherence: First, both the purity and the off-diagonal matrix elements recur on a time scale that corresponds approximately to the vibrational period of the oscillator. Second, individual off-diagonal density matrix elements decohere with different rates, although similar rates were observed for coherences between highly populated quantum levels with the same energy difference between the quantum levels. These features, which have important consequences with respect to the time scale and mechanism of decoherence, are absent in treatments based on master equations such as the Caldeira-Leggett approach. A measure of phase-space structure, previously derived for chaotic systems, was shown to provide useful information for the system studied here, and agreed completely with the phase-space picture of the Wigner density. Additionally, this expression can be used together with our dynamical procedure as an independent method of obtaining values for the Caldeira-Leggett D parameter.

In this study, we formulated a FB-IVR expression for the density matrix, and introduced a new, efficient, computational strategy that allows us to perform this multidimensional complex calculation with relative ease and accuracy. This IVR calculation reproduces individual density matrix

elements. Both the FB-IVR and linearized IVR produce qualitatively accurate results, however, these methods are still semiclassical and improvements might be sought. For example, it would, perhaps, be preferable to use the generalized FB-IVR method,⁴⁷ which treats the system with the full (double phase space integral) HK treatment, while the bath is treated with the FB-IVR. However, there seems to be no advantage to this approach for the operator considered in this work, since $\tilde{B}_{ij}(\mathbf{p}, \mathbf{q})$ is, generally, delocalized in phase space. In addition, the generalized FB-IVR method introduces a further approximation in the form of a Filinov transformation to enhance convergence of the method. If full HK parameters are used for the system, it is questionable whether convergence could be achieved, given the large computational effort in this work when the system is treated with the faster converging FB-IVR.

There are several extensions of this study that should be investigated. An effort should be made to enhance the computational efficiency of the FB-IVR technique, especially for initial states that are not coherent states, perhaps by using importance sampling Monte Carlo. It would be interesting to apply the methodology developed here to other models, particularly to models with nonlinear coupling. Further, the results obtained here encourage a review of the applicability of coherent control to large scale systems, previously thought to be impossible due to decoherence. Quantum-classical correspondence also needs to be considered more carefully. In particular, it would be nice to compare the accuracy of the methods used in this work to other methods such as quantum-classical methods⁴⁸ and purely classical calculations.^{24,49} These methods may provide more insight into the origin of the discrepancies between the FB-IVR and the linearized IVR. Work along these lines is in progress.

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