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Generalized dephasing relation for fidelity and application as an efficient propagator

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The dephasing relation (DR), a linearization of semiclassical fidelity, is generalized to include the overlap of "off-diagonal" elements. The accuracy of the formulation is tested in integrable and chaotic systems and its scaling with dimensionality is studied in a Caldeira-Leggett model with many degrees of freedom. It is shown that the DR is often in very good agreement with numerically analytic quantum results and frequently outperforms an alternative semiclassical treatment. Most importantly, since there is no computationally expensive prefactor, and Monte Carlo Metropolis sampling is used to facilitate the calculation, the DR is found to scale remarkably well with increasing dimension. We further demonstrate that a propagator based on the DR can include more quantum coherence and outperform other popular linearized semiclassical methods, such as forward-backward semiclassical dynamics (FBSD) and the linearized semiclassical initial value representation (LSC-IVR). © *2013 AIP Publishing LLC*. [http://dx.doi.org/10.1063/1.4820880]

I. INTRODUCTION

In this work, a general notion of fidelity is defined as

$$F^{AB}(t) = |O^{AB}(t)|^2 = |\langle\Psi_B|e^{iH^\epsilon t/\hbar}e^{-iH^0 t/\hbar}|\Psi_A\rangle|^2, \quad (1)$$

where $H^\epsilon = H^0 + \epsilon V$. This can be described from the Loschmidt echo perspective as an initial state Ψ_A that is propagated forward for some time t obeying the Hamiltonian H^0 and then propagated back for the same time obeying the perturbed Hamiltonian H^ϵ. After this forward-backward propagation, the inner product with a state Ψ_B is considered. An equivalent description is as the overlap between states Ψ_A and Ψ_B both of which have been forward-propagated for time t but obeying different Hamiltonians, H^0 and H^ϵ, respectively. In either case, fidelity will range from being equal to 1 when the time-propagated Ψ_A and Ψ_B wavefunctions are the same, to 0 when they are fully orthogonal.

Over the years, a linearized Wigner transform of this expression has been defined in one form or another.[1–10] Most recently, Vaníček and co-workers derived a prefactorless form that they have called the "dephasing" relation (DR).[11,12] They have shown that the DR possesses many promising features, the most notable that the expression scales independently of dimension when sampled appropriately.[13] Furthermore, they report that in general, the more complex H^0 and H^ϵ are, the better the DR works.[14]

Many efforts have been made to develop an accurate semiclassical propagator that does not contain a prefactor dependent on the computationally costly propagation of stability (monodromy) matrices. Much of this work has been focused on the linearization of existing semiclassical methods. Perhaps the most successful are those pioneered by Makri and co-workers[15,16] and Miller and co-workers.[17,18] In their work, an additional stationary phase approximation (SPA) is made to combine the forward and backward propagators that are present in many correlation functions. This produces the prefactorless simplified expressions called forward-backward semiclassical dynamics (FBSD) and the linearized semiclassical initial value representation (LSC-IVR), respectively. Unfortunately, the SPA takes away quantum dynamical effects (quantum correlations) which leaves these methods with short applicable timescales in many systems.[15] There have been many suggestions made on how to improve these expressions[19,20] but this is often found to be difficult without the inclusion of stability matrix elements.

Here, we propose a very different approach for linearization based around fidelity and its efficient calculation by the DR. The main result we present is a semiclassical propagator that contains quantum dynamical effects, unlike its predecessors, and is computationally cheap because it remains free of any dependance on stability matrices.

This paper is organized as follows: The expression that results from extending the DR to include "off-diagonal" elements (where $\Psi_A \neq \Psi_B$) is presented in Sec. II along with an alternate semiclassical result to be used as a comparison. Section III A compares the performance of these two expressions when applied to two-dimensional test systems that are integrable and chaotic. Section III B further compares their performance with a Caldeira-Leggett model involving many more degrees of freedom. Section IV shows how the DR can be used as a semiclassical propagator and demonstrates its promising ability to include quantum coherence for longer times. Section V concludes the discussion and offers some potential applications for the DR-based propagator.

II. GENERALIZED DEPHASING RELATION

Fidelity has traditionally been defined and explored in Eq. (1) with $\Psi_A = \Psi_B \equiv \Psi$. This "diagonal" version has been

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found to be well approximated by a clever first-order perturbative expansion of its semiclassical Wigner transform.[14,21] Neglecting a prefactor, the resultant simplified expression consists of an integral over the Wigner function of $\Psi(t=0)$ multiplied by a time-dependent phase term. The form of this compact expression led Vaníček and co-workers[11,12] to call it the "dephasing relation".

Extending the DR to handle cases where $\Psi_A \neq \Psi_B$ produces a generalized form of fidelity capable of handling the "off-diagonal" elements that are necessary in any applications as a meaningful propagator. A thorough derivation for "diagonal" elements has been presented in the literature[14,21] and can be extended to "off-diagonal" elements simply by setting $\Psi_A \neq \Psi_B$. The main results are reprinted here.

Consider the Hamiltonians H^0 and $H^\epsilon \equiv H^0 + \epsilon V$. Taking the primitive semiclassical expression for Eq. (1) up to zeroth order in ϵ for the prefactor (i.e., neglecting it) and up to first order in ϵ for the phase, where the perturbation is taken around the trajectory obeying the mean Hamiltonian $((H^\epsilon + H^0)/2)$,

$$O^{AB}(t) = O^{AB}_{\mathrm{DR}}(t) \equiv h^{-d}\int d\boldsymbol{q}^0 d\boldsymbol{p}^0 \rho_W^{AB}(\boldsymbol{q}^0, \boldsymbol{p}^0) e^{iS_{\mathrm{DR}}(\boldsymbol{q}^0,\boldsymbol{p}^0;t)/\hbar} \quad (2)$$

in a d-dimensional system where

$$\rho_W^{AB}(\boldsymbol{q}^0, \boldsymbol{p}^0) \equiv (2\pi\hbar)^{-d}\int d\boldsymbol{s}\langle \boldsymbol{q}^0 - \boldsymbol{s}/2|\Psi_A\rangle \times \langle \Psi_B|\boldsymbol{q}^0 + \boldsymbol{s}/2\rangle e^{i\boldsymbol{s}\cdot\boldsymbol{p}^0/\hbar} \quad (3)$$

is the Wigner transform of $|\Psi_A\rangle\langle\Psi_B|$ and

$$S_{\mathrm{DR}}(\boldsymbol{q}^0, \boldsymbol{p}^0; t) \equiv -\epsilon\int_0^t d\tau\, V(\boldsymbol{q}_\tau, \boldsymbol{p}_\tau, \tau), \quad (4)$$

with $(\boldsymbol{q}_\tau, \boldsymbol{p}_\tau)$ following the classical trajectory of the average Hamiltonian $(H^0 + H^\epsilon)/2$.

The Wigner transform differs from that presented in the traditional DR solely in that ρ_W consists of the operator $|\Psi_A\rangle\langle\Psi_B|$ instead of $|\Psi\rangle\langle\Psi|$.

A. Position states

If we consider position states in Eq. (1) such that $\Psi_A(\boldsymbol{q}) = \delta(\boldsymbol{q} - \boldsymbol{q}_A)$ and $\Psi_B(\boldsymbol{q}) = \delta(\boldsymbol{q} - \boldsymbol{q}_B)$, then the expression in Eq. (2) simplifies to

$$O^{AB}_{\mathrm{DR}}(t) = \frac{1}{(2\pi\hbar)^d} \times \int d\boldsymbol{p}\, \exp\left[\frac{i}{\hbar}(\boldsymbol{q}_A - \boldsymbol{q}_B)\cdot\boldsymbol{p} + \frac{i}{\hbar}S_{\mathrm{DR}}\left(\frac{\boldsymbol{q}_A + \boldsymbol{q}_B}{2}, \boldsymbol{p}; t\right)\right]. \quad (5)$$

B. Momentum states

Similarly, for $\Psi_A(\boldsymbol{p}) = \delta(\boldsymbol{p} - \boldsymbol{p}_A)$ and $\Psi_B(\boldsymbol{p}) = \delta(\boldsymbol{p} - \boldsymbol{p}_B)$,

$$O^{AB}_{\mathrm{DR}}(t) = \frac{1}{(2\pi\hbar)^d} \times \int d\boldsymbol{q}\, \exp\left[\frac{i}{\hbar}(\boldsymbol{p}_A - \boldsymbol{p}_B)\cdot\boldsymbol{q} + \frac{i}{\hbar}S_{\mathrm{DR}}\left(\boldsymbol{q}, \frac{\boldsymbol{p}_A + \boldsymbol{p}_B}{2}; t\right)\right]. \quad (6)$$

C. Gaussian states

For $\Psi_A(\boldsymbol{q}) = (\pi\sigma^2)^{-\frac{d}{4}}\exp[-\frac{(\boldsymbol{q}-\boldsymbol{q}_A)^2}{2\sigma^2} + \frac{i\boldsymbol{p}_A\cdot(\boldsymbol{q}-\boldsymbol{q}_A)}{\hbar}]$ and $\Psi_B(\boldsymbol{q}) = (\pi\sigma^2)^{-\frac{d}{4}}\exp[-\frac{(\boldsymbol{q}-\boldsymbol{q}_B)^2}{2\sigma^2} + \frac{i\boldsymbol{p}_B\cdot(\boldsymbol{q}-\boldsymbol{q}_B)}{\hbar}]$,

$$O^{AB}_{\mathrm{DR}}(t) = \frac{1}{(\pi\hbar)^d}\int d\boldsymbol{q}\int d\boldsymbol{p} \times \exp\left\{-\left[\frac{(\boldsymbol{q}_A + \boldsymbol{q}_B - 2q)^2}{4\sigma^2} + \frac{(\boldsymbol{p}_A + \boldsymbol{p}_B - 2\boldsymbol{p})^2\sigma^2}{4\hbar^2} - i\left(\frac{(\boldsymbol{p}_A - \boldsymbol{p}_B)\cdot(\boldsymbol{q}_A + \boldsymbol{q}_B - 2\boldsymbol{q})}{2\hbar} + \frac{\boldsymbol{p}\cdot(\boldsymbol{q}_A - \boldsymbol{q}_B)}{\hbar}\right)\right] + \frac{i}{\hbar}S_{\mathrm{DR}}(\boldsymbol{q}, \boldsymbol{p}; t)\right\}. \quad (7)$$

These three examples illustrate how calculating "off-diagonal" elements of the DR introduces an additional phase into the traditional formula for "diagonal" elements as well as a slightly different phase integral in Eqs. (5) and (6) but does not make evaluation any more difficult.

D. Forward-backward semiclassical expression

Substituting the Heller-Herman-Kluk-Kay coherent state version of the semiclassical propagator for the quantum propagators in Eq. (1) yields

$$O(t)_{\mathrm{HK}} = \frac{1}{(2\pi\hbar)^{2d}}\int d\boldsymbol{q}_0^0\int d\boldsymbol{p}_0^0\int d\boldsymbol{q}_0^\epsilon\int d\boldsymbol{p}_0^\epsilon \times C_t(\boldsymbol{q}_0^0, \boldsymbol{p}_0^0)C_t(\boldsymbol{q}_0^\epsilon, \boldsymbol{p}_0^\epsilon)^*\langle \boldsymbol{q}_0^0, \boldsymbol{p}_0^0|\Psi_A\rangle \times \langle\Psi_B|\boldsymbol{q}_0^\epsilon, \boldsymbol{p}_0^\epsilon\rangle e^{i(S_t^0 - S_t^\epsilon)\hbar}\langle \boldsymbol{q}_t^\epsilon, \boldsymbol{p}_t^\epsilon|\boldsymbol{q}_t^0, \boldsymbol{p}_t^0\rangle, \quad (8)$$

where $C_t(\boldsymbol{q}_0, \boldsymbol{p}_0) = \sqrt{\det[\frac{1}{2}(\frac{\partial \boldsymbol{q}_t}{\partial \boldsymbol{q}_0} + \frac{\partial \boldsymbol{p}_t}{\partial \boldsymbol{p}_0} - i\gamma\hbar\frac{\partial \boldsymbol{q}_t}{\partial \boldsymbol{p}_0} + \frac{i}{\gamma\hbar}\frac{\partial \boldsymbol{p}_t}{\partial \boldsymbol{q}_0})]}$.

This integral is difficult to evaluate numerically due to the oscillating double phase. Taking a SPA of the final term in Eq. (8) simplifies matters. The details are presented in the Appendix, wherein taking the SPA is shown to be equivalent to assuming $\langle \boldsymbol{q}_t^\epsilon, \boldsymbol{p}_t^\epsilon|\boldsymbol{q}_t^0, \boldsymbol{p}_t^0\rangle = \delta(\boldsymbol{q}_t^\epsilon - \boldsymbol{q}_t^0)\delta(\boldsymbol{p}_t^\epsilon - \boldsymbol{p}_t^0)$. This allows the double-phase space integral to be replaced by a single one over a new set of coordinates $(\boldsymbol{q}, \boldsymbol{p})$ that are defined to start out at $(\boldsymbol{q}_0^0, \boldsymbol{p}_0^0)$, forward-propagate under H^0 to $(\boldsymbol{q}_t^0, \boldsymbol{p}_t^0) = (\boldsymbol{q}_t^\epsilon, \boldsymbol{p}_t^\epsilon)$, and finally return via back-propagation under H^ϵ to $(\boldsymbol{q}_0^\epsilon, \boldsymbol{p}_0^\epsilon)$. The final result is

$$O(t)_{\text{FB-HKR}} = \frac{1}{(2\pi\hbar)^{2d}} \int d\boldsymbol{q}_0 \int d\boldsymbol{p}_0 \times C_t(\boldsymbol{q}_0, \boldsymbol{p}_0)\langle \boldsymbol{q}_0, \boldsymbol{p}_0|\Psi_A\rangle\langle\Psi_B|\boldsymbol{q}_0^\epsilon, \boldsymbol{p}_0^\epsilon\rangle e^{i\left(S_t^0 - S_t^\epsilon\right)\hbar}. \quad (9)$$

This expression will be referred to as the "Forward-Backward Heller-Herman-Kluk-Kay relation" (FB-HKR). It is quite different from the DR; FB-HKR is accurate up to the assumption $\langle \boldsymbol{q}_t^\epsilon, \boldsymbol{p}_t^\epsilon|\boldsymbol{q}_t^0, \boldsymbol{p}_t^0\rangle = \delta(\boldsymbol{q}_t^\epsilon - \boldsymbol{q}_t^0)\delta(\boldsymbol{p}_t^\epsilon - \boldsymbol{p}_t^0)$, while the DR is accurate up to first order in ϵ in phase and zeroth order in the prefactor. Also, due to the prefactor containing monodromy matrix elements, the FB-HKR is more computationally expensive than the generalized DR. Nevertheless, the FB-HKR is introduced to serve, at the very least, as a qualitative semiclassical benchmark against which the accuracy of the DR can be compared, especially in higher dimensional systems where a full numerically analytic solution proves too costly.

III. NUMERICAL TESTS

Perhaps the most attractive feature of the DR is its excellent scaling with dimension, while the most important limitation is its dependence on small perturbations ϵ for accurate performance. This suggests that it has a natural application in the time-propagation of many-dimensional systems that are weakly coupled to each other. To study the DRs performance in such applications, a number of numerical tests were performed on weakly coupled systems with two degrees of freedom (Figures 1–3) as well as many more degrees of freedom (Figure 5) which propagated freely of each other forward in time but were coupled when returning backward in time. What follows is a short summary of their behavior according to the DR.

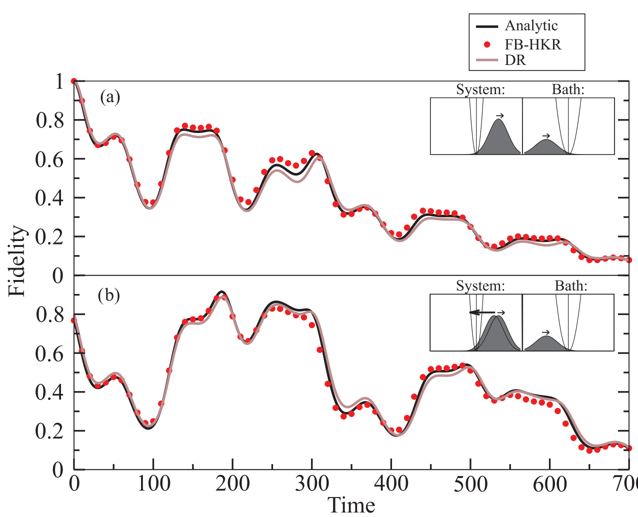

FIG. 1. The initial states for the system and bath harmonic oscillators are Gaussian wave packets propagating under a bilinear coupling ($\epsilon q_{\text{sys}} q_{\text{bath}}$) with parameters $\epsilon = 10$, $\hbar = 1$, $\Delta t = 0.01$, $t = 700\Delta t$, $m_{\text{sys}} = 10$, $m_{\text{bath}} = 2$, $\omega_{\text{sys}} = 5$, $\omega_{\text{bath}} = 3$, $\sigma_{\text{sys}} = 0.3$, and $\sigma_{\text{bath}} = 0.7$ where (a) shows "diagonal fidelity" ($q_{\text{sys}}^{\text{init}} = p_{\text{sys}}^{\text{init}} = 0.5$, $q_{\text{bath}}^{\text{init}} = -1$ and $p_{\text{bath}}^{\text{init}} = 0.5$) and (b) shows "off-diagonal fidelity" ($q_{\text{sys 'B'}}^{\text{init}} = 0.4$ and $p_{\text{sys 'B'}}^{\text{init}} = -1.5$). (Inset) A cartoon of initial system and bath states.

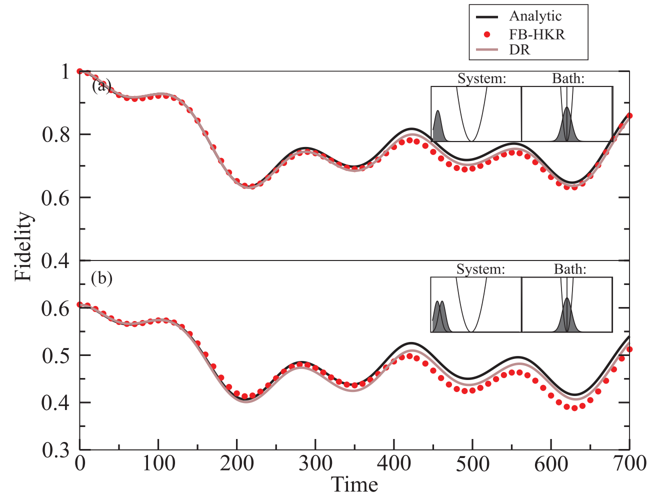

FIG. 2. Initial states for the system Morse oscillator ($D(1 - e^{-\alpha(q_{\text{bath}} - q_e)})^2$) and bath harmonic oscillator are Gaussians coupled bilinearly ($\epsilon q_{\text{sys}} q_{\text{bath}}$) with parameters $\epsilon = 10$, $\hbar = 1$, $\Delta t = 0.001$, $t = 700\Delta t$, $m_{\text{sys}} = 10$, $m_{\text{bath}} = 8$, $D = 10\,000$, $\alpha = 0.1$, $qe = 3$, $\omega_{\text{bath}} = 3$, $\sigma_{\text{sys}} = 0.1$, and $\sigma_{\text{bath}} = 0.3$ where (a) shows "diagonal fidelity" ($q_{\text{sys}}^{\text{init}} = 2.3$ and $p_{\text{sys}}^{\text{init}} = q_{\text{bath}}^{\text{init}} = p_{\text{bath}}^{\text{init}} = 0$) and (b) shows "off-diagonal fidelity" ($q_{\text{sys 'B'}}^{\text{init}} = 2.4$ and $p_{\text{sys 'B'}}^{\text{init}} = 0.0$). (Inset) A cartoon of initial system and bath states.

A. Two-dimensional systems

Figure 1 compares the fidelity of two rather different harmonic oscillators that are coupled bilinearly together. The DR agrees with the numerically analytic results very well. It is important to differentiate the set-up that produced this result from those in prior studies where the DR was found to break down in harmonic oscillators with significantly different force constants.[22] Whereas Figure 1 shows two harmonic oscillators with different force constants which were propagated independently of each other forward in time but were coupled together backward in time, these previous studies dealt with

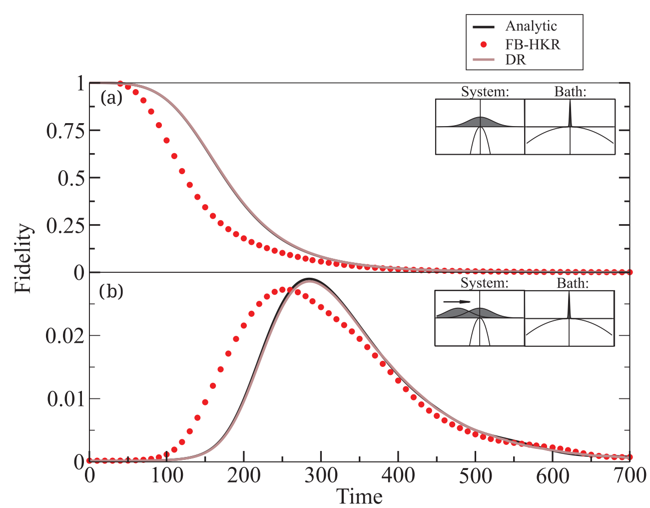

FIG. 3. Initial states for the system and bath obeying the hyperbolic Hamiltonian are Gaussians coupled bilinearly ($\epsilon q_{\text{sys}} q_{\text{bath}}$) with parameters $\epsilon = 3$, $\hbar = 1$, $\Delta t = 0.001$, $t = 700\Delta t$, $m_{\text{sys}} = 2$, $m_{\text{bath}} = 0.1$, $\omega_{\text{sys}} = 3$, $\omega_{\text{bath}} = 0.6$, $\sigma_{\text{sys}} = 0.8$, and $\sigma_{\text{bath}} = 0.2$ where (a) shows "diagonal fidelity ($q_{\text{sys}}^{\text{init}} = p_{\text{sys}}^{\text{init}} = q_{\text{bath}}^{\text{init}} = p_{\text{bath}}^{\text{init}} = 0$) and (b) shows "off-diagonal fidelity" ($q_{\text{sys 'B'}}^{\text{init}} = -1$ and $p_{\text{sys 'B'}}^{\text{init}} = 5$). (Inset) A cartoon of initial system and bath states.

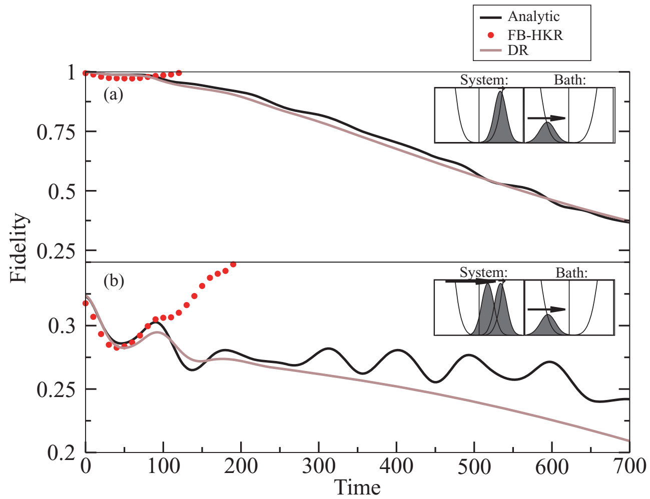

FIG. 4. Initial states for the system and bath quartic oscillators are Gaussians coupled biquadratically ($\epsilon q_{\mathrm{sys}}^2 q_{\mathrm{bath}}^2$) with parameters $\epsilon = 2, \hbar = 1, \Delta t = 0.01$, $t = 700\Delta t$, $m_{\mathrm{sys}} = 3$, $m_{\mathrm{bath}} = 1$, $\omega_{\mathrm{sys}} = 4.5$, $\omega_{\mathrm{bath}} = 1.4$, $\sigma_{\mathrm{sys}} = 0.2$, and $\sigma_{\mathrm{bath}} = 0.5$ where (a) shows "diagonal fidelity" ($q_{\mathrm{sys}}^{\mathrm{init}} = 0.5$, $p_{\mathrm{sys}}^{\mathrm{init}} = 0.1$, $q_{\mathrm{bath}}^{\mathrm{init}} = -1$, and $p_{\mathrm{bath}}^{\mathrm{init}} = 0.5$) and (b) shows "off-diagonal fidelity" ($q_{\mathrm{sys}\,\text{`B'}}^{\mathrm{init}} = 0.2$ and $p_{\mathrm{sys}\,\text{`B'}}^{\mathrm{init}} = 0.6$). (Inset) A cartoon of initial system and bath states.

cases where each harmonic oscillator had a different force constant going forward in time compared to backward in time. The situation presented here seems to be much more accurately reproduced by the DR, even for harmonic oscillators with very different force constants.

Figure 2 and the inset of Figure 5 also show good agreement between the DR and numerically analytic results for the fidelity of a Morse oscillator coupled bilinearly to a significantly different harmonic oscillator.

A very similar expression to the DR has been derived somewhat heuristically using the Shadowing theorem[12] which relies on the accuracy of trajectories that "shadow" exact trajectories. Only hyperbolic Hamiltonians have been shown to be capable of such shadowing for infinite time. It is perhaps for this reason that, in Figure 3, the DR shows great accuracy at reproducing the analytic fidelity of two bilinearly coupled hyperbolic systems.

Figure 4 shows good short-time agreement but poor long-time agreement with the numerically analytic results for the fidelity of two different quartic oscillators that are coupled together biquadratically. This is an interesting example because this system is integrable going forward in time, when the oscillators are uncoupled, but chaotic backward in time when they are coupled. The FB-HKR results become poor after a short-time due to monodromy matrix divergence, a common occurrence in chaotic systems. There are methods to deal with this, some as simple as throwing away divergent trajectories.[23]

In general, it is found that the DR results for "diagonal" and "off-diagonal" cases of fidelity agree with analytic results for the same amount of time in any system studied. In each case, calculations were shown for only a single value of ϵ that produced interesting fidelity decay. Larger values of ϵ and DR calculations at longer times generally produce poorer agreement with analytic calculations if the fidelity decay is slow or rephases. In particular, similar to the findings reported in many studies of the FBSD[24] and LSC-IVR,[19] the DR performs well when the overall decay in fidelity is faster than its ability to include effects such as quantum coherence, and poor when this overall decay is slower. This is especially true in systems with many degrees of freedom where the prevalence and importance of rephasing is small.

B. Many dimensional system: Caldeira-Leggett

To study the DRs scaling with dimensionality, the fidelity of a Caldeira-Leggett Hamiltonian[25] for I_2[26–28] was studied. This involved modelling one degree of freedom of the molecule, anharmonic stretching, through a Morse potential coupled to a harmonic oscillator (HO) bath. The Hamiltonian was

$$H = \frac{p^2}{2\mu} + D[1 - e^{-\alpha(q-q_e)}]^2 + \sum_{j=1}^{f-1}\left[\frac{P_j^2}{2} + \frac{\omega_j^2}{2}\left(Q_j + \frac{c_j}{\omega_j^2}(q - q_e)\right)^2\right] \quad (10)$$

with $D = 1.2547 \times 10^4\ \mathrm{cm}^{-1}$, $q_e = 2.6663$ Å, $\alpha = 1.8576$ Å^{-1}, and μ equal to the reduced mass of I_2. The sum runs over the $(f-1)$ HOs in the bath.

Coupling to the bath was chosen to be dictated by the Ohmic spectrum (hereafter $\hbar = 1$),

$$J(\omega) = \eta_{\mathrm{sb}}\omega e^{-\frac{\omega}{\omega_c}}, \quad (11)$$

where

$$\omega_j = -\omega_c \ln\left[1 - \frac{j}{f-1}\left(1 - e^{-5}\right)\right] \quad (12)$$

are the individual HO frequencies and

$$c_j = \omega_j\sqrt{\frac{2\eta_{\mathrm{sb}}\omega_c}{\pi(f-1)}(1 - e^{-5})} \quad (13)$$

are their corresponding coupling constants (otherwise equal to zero during forward time evolution). $\eta_{\mathrm{sb}} = 0.25 \times 213.7\ \mu\mathrm{cm}^{-1}$ is the system-bath coupling coefficient and $\omega_c = 20\ \mathrm{cm}^{-1}$ is the characteristic bath frequency. Expressed in terms of the coherent state basis used in the FB-HKR,

$$\langle q|q_i, p_i\rangle = \left(\frac{\gamma}{\pi}\right)^{\frac{1}{4}} \exp\left[-\frac{\gamma}{2}(q - q_i)^2 + ip_i(q - q_i)\right] \quad (14)$$

(where γ is the width of the coherent state basis), the initial state of the Morse oscillator was selected to be in its ground state,

$$\Psi_{\mathrm{sys}}(q, p) = \exp\left[-\frac{\gamma}{4}(q - q_i)^2 - \frac{1}{4\gamma}(p - p_i)^2 + \frac{i}{2}(p + p_i)(q - q_i)\right] \quad (15)$$

with $q_i = 2.4$ Å (just to the left of the potential minimum), $p_i = 0.0$, and $\gamma = \sqrt{2D\mu a^2} \equiv \mu\Omega_s$, where $\Omega_s = 213.7\ \mathrm{cm}^{-1}$ is the harmonic frequency of the Morse oscillator. The HO bath

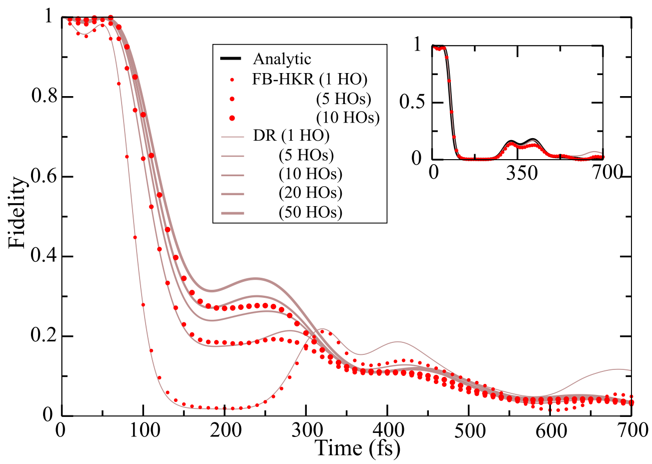

FIG. 5. Calculation of the fidelity of a Morse oscillator (parametrized to fit a diiodide bond) coupled to a thermalized bath of various numbers of harmonic oscillators at 300 K via Ohmic coupling performed using the DR and FB-HKR. (Inset) The same set-up but with only 1 HO in the bath in an excited pure state allowing for the calculation of an analytic numerical solution. It is likely that the analytic solution is similar in the case of the thermalized bath and so is in comparable agreement with the DR and FB-HKR.

began as a thermalized state $\frac{e^{-\beta \hat{H}_B}}{Q_B}$ at 300 K,[27]

$$\begin{aligned}\Psi_{\text{bath}}(Q_j, P_j, Q'_j, P'_j) &= (1 - e^{-\beta\omega_j}) \\ &\times \exp\left\{ -\frac{\Gamma_j}{4}(Q_j^2 + Q_j'^2) - \frac{1}{4\Gamma_j}(P_j^2 + P_j'^2) \right. \\ &+ \frac{i}{2}(P_j Q_j - P'_j Q'_j) + \frac{1}{2}e^{-\beta\omega_j}\Big[\Gamma_j Q_j Q'_j \\ &\left. + \frac{1}{\Gamma_j} P_j P'_j + i(P'_j Q_j - P_j Q'_j)\Big]\right\} \qquad (16)\end{aligned}$$

with $\gamma = \Gamma_j = \omega_j$ (where j is the HO bath index).

Figure 5 shows how the DR fares compared to FB-HKR with 1–50 HOs in the bath, though the latter method was only calculated with up to ten HOs. It has been shown that a minimum of 20 HOs are necessary to reproduce the Ohmic spectrum.[27] The DR-calculated fidelity shows convergence at a similar number of HOs. Impressively, the DR exhibited superior computational scaling compared to the prefactor-laden FB-HKR.

IV. DEPHASING RELATION PROPAGATOR

The DR can be implemented in the semiclassical propagation of any quantum state Ψ under the Hamiltonian H in the following general manner:

$$\langle \boldsymbol{q}|\Psi(t)\rangle = \langle \boldsymbol{q}|e^{-iHt/\hbar}|\Psi(0)\rangle \qquad (17)$$

$$= \int d\boldsymbol{q}' \langle \boldsymbol{q}|e^{-iHt/\hbar} e^{iH^0 t/\hbar}|\boldsymbol{q}'\rangle \times \langle \boldsymbol{q}'|e^{-iH^0 t/\hbar}|\Psi(0)\rangle \qquad (18)$$

$$\approx \int d\boldsymbol{q}' \left(O_{\text{DR}}^{H^0,H}(\boldsymbol{q},\boldsymbol{q}',t)\right)^* \langle \boldsymbol{q}'|e^{-iH^0 t/\hbar}|\Psi(0)\rangle. \qquad (19)$$

The quantum propagator is split into two terms by the introduction of another Hamiltonian, H^0: a fidelity term and another term governed by free evolution under H^0. In Eq. (17), an identity operator is inserted producing a fidelity term in Eq. (18) that is subsequently simplified by substituting in the generalized DR. In particular, the left term in Eq. (19) is the complex conjugate of the position state representation of the DR for the forward Hamiltonian H and the backward Hamiltonian H^0. Without loss of generality, it is helpful as before to let

$$H \equiv H^0 + \epsilon V. \qquad (20)$$

Expressed this way, it is clear that H^0 must be chosen wisely so that the DR term can be accurate. Furthermore, it is preferable to choose an H^0 such that the free evolution term can be calculated as easily as the DR-containing term. This can often be accomplished in weakly interacting many-body systems by letting H^0 be the Hamiltonian including only free-particle terms while ϵ governs the strength of V, the interparticle interactions. In such applications, the splitting introduced in Eq. (18) is similar, though not the same, as that introduced by the "interaction" representation.

This idea can be illustrated by considering the Hamiltonian,

$$H = \frac{1}{2}p^2 + \frac{1}{2}\omega^2 q^2 - aq^3 + bq^4 \qquad (21)$$

with $\omega = \sqrt{2}$ and $a = b = 0.1$. This is a strongly anharmonic oscillator system that has often been used before to test the limitations of other Wigner-type linearized approximations.[15,19,20,24,29,30]

Figure 6 shows the average position of an initially shifted ground state with time. Most Wigner-type linearized approximations and FBSD decay to small oscillations by the 300

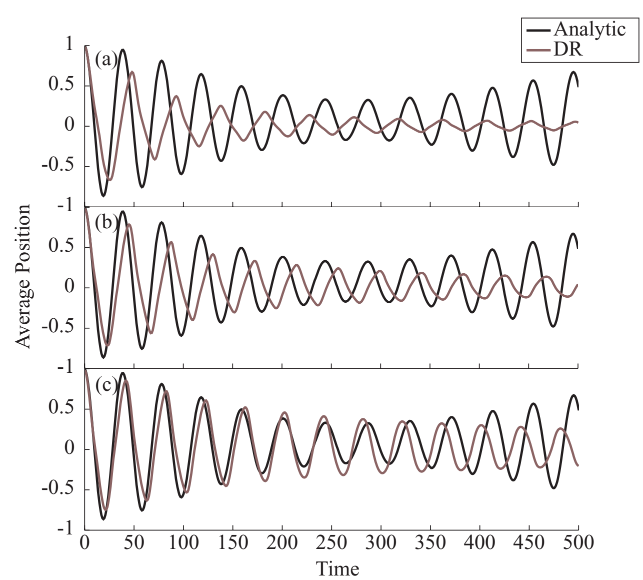

FIG. 6. Average position plotted versus time of a displaced wavepacket oscillating under the highly anharmonic Hamiltonian $H = \frac{1}{2}p^2 + \frac{1}{2}\omega^2 q^2 - 0.1q^3 + 0.1q^4$ with $\omega = \sqrt{2}$. The DR curves were calculated from the expression $\int d\boldsymbol{x}'(O_{\text{DR}}^{H^0,H}(\boldsymbol{q},\boldsymbol{q}',t))^* \langle \boldsymbol{q}'|e^{-iH^0 t/\hbar}|\Psi(0)\rangle$ where $H^0 = \frac{1}{2}p^2 + \frac{1}{2}\omega'^2 q^2$ with (a) $\omega' = \omega$, (b) $\omega' = 1.05\omega$, and (c) $\omega' = 1.1\omega$.

timestep mark.[15] Setting H^0 from Eq. (19) to be equal to $\frac{1}{2}p^2 + \frac{1}{2}\omega'^2 q^2$ simplified the free-evolution term to the analytically solvable Feynman propagator for a HO. When $\omega' = \omega$ the DR-calculated average position is relatively poor in Fig. 6(a) compared to the analytic result. This is because the anharmonic terms in the potential produce an initial effective frequency of oscillation that is faster than the harmonic frequency ω for the initial state. In other words, the free evolution term of Eq. (19) produces a curve with frequency ω that the DR term of the equation is unable to "dephase" effectively enough into the proper frequency. Increasing ω' to 1.05ω and 1.1ω reduces the work that the DR must do to "dephase" the free evolution term and produces better results, as demonstrated in Figs. 6(b) and 6(c). Notice that even in the worst example of the DR's performance shown in Fig. 6(a), the DR propagator far outperforms other prefactorless semiclassical propagators since it is still oscillating after 300 timesteps (although the frequency of this oscillation is incorrect).

Using Eq. (20) as a building block, it is possible to generate DR-based propagation schemes for many general expressions of interest. For instance, the expression for the purity of a system, a measure of decoherence from system-bath interaction, can be expressed as

$$\begin{aligned}
\mathrm{Tr}\left(\rho_s^2\right) \\
&= \int d\boldsymbol{q}_s d\boldsymbol{q}'_s d\boldsymbol{q}_b d\boldsymbol{q}'_b \\
&\quad \times d\boldsymbol{q}_{os} d\boldsymbol{q}'_{os} d\boldsymbol{q}_{ob} d\boldsymbol{q}'_{ob} \\
&\quad \times d\boldsymbol{q}''_{os} d\boldsymbol{q}'''_{os} d\boldsymbol{q}''_{ob} d\boldsymbol{q}'''_{ob} \\
&\quad \times \langle \boldsymbol{q}_s \boldsymbol{q}_b | e^{-iHt/\hbar} e^{iH^0 t/\hbar} | \boldsymbol{q}_{os} \boldsymbol{q}_{ob} \rangle \\
&\quad \times \langle \boldsymbol{q}'_{os} \boldsymbol{q}'_{ob} | e^{-iH^0 t/\hbar} e^{iHt/\hbar} | \boldsymbol{q}'_s \boldsymbol{q}_b \rangle \\
&\quad \times \langle \boldsymbol{q}'_s \boldsymbol{q}'_b | e^{-iHt/\hbar} e^{iH^0 t/\hbar} | \boldsymbol{q}''_{os} \boldsymbol{q}''_{ob} \rangle \\
&\quad \times \langle \boldsymbol{q}'''_{os} \boldsymbol{q}'''_{ob} | e^{-iH^0 t/\hbar} e^{iHt/\hbar} | \boldsymbol{q}_s \boldsymbol{q}'_b \rangle \\
&\quad \times \rho^0(\boldsymbol{q}_{os}, \boldsymbol{q}_{ob}, \boldsymbol{q}'_{os}, \boldsymbol{q}'_{ob}, t) \\
&\quad \times \rho^0(\boldsymbol{q}''_{os}, \boldsymbol{q}''_{ob}, \boldsymbol{q}'''_{os}, \boldsymbol{q}'''_{ob}, t),
\end{aligned} \tag{22}$$

where $\boldsymbol{q}_s$, $\boldsymbol{q}'_s$, $\boldsymbol{q}_{os}$, $\boldsymbol{q}'_{os}$, $\boldsymbol{q}''_{os}$, and $\boldsymbol{q}'''_{os}$ are system phase space coordinates, $\boldsymbol{q}_b$, $\boldsymbol{q}'_b$, $\boldsymbol{q}_{ob}$, $\boldsymbol{q}'_{ob}$, $\boldsymbol{q}''_{ob}$, and $\boldsymbol{q}'''_{ob}$ are bath phase space coordinates, H is the full Hamiltonian, H^0 is the same Hamiltonian with the system-bath interactions turned off, and ρ^0 is the full time-dependent density matrix with interactions turned off (usually this is simple to calculate).

Applying such a splitting scheme using an ancillary Hamiltonian H^0 will always result in an integral with a "kernel," such as the terms with ρ^0 above, alongside expressions of fidelity that can be approximated with the DR. Again, this means that it is prudent to choose H^0 such that this procedure produces an easily computed and accurate kernel while allowing for the smallest effective perturbation for the DR to deal with.

V. CONCLUSION

In this paper, the DR for fidelity was extended to treat "off-diagonal" elements. Its performance was examined with integrable and chaotic systems that were perturbatively coupled to a bath with few to many degrees of freedom. In general, the DR was found to be surprisingly accurate and efficient.

Subsequently, a particular approach to using the DR as a semiclassical propagator for quantum states was introduced. By exploiting the DR's unique efficiency and accuracy, this methodology demonstrated the potential to be superior to many previous linearization methods, such as FBSD and LSC-IVR, granted that perturbative splitting with an ancillary Hamiltonian is possible. Particularly attractive is the DR propagator's ability to include quantum correlation effects. A simple calculation of the evolution of the average position of a wavepacket in a heavily anharmonic potential using the DR-based propagator was shown to produce better results.

The DR-based propagator has many promising applications, including serving as a more physically intuitive approach for calculating the purity of many-dimensional system-baths compared to the traditional master equation approach. Its derivation is vastly different from other linearized methods and its effectiveness as a quick and cheap tool for semiclassical propagation deserves evaluation.

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APPENDIX: FORWARD-BACKWARD FIDELITY

Consider the two exponential operators in Eq. (1) as the single unitary operator $\hat{U} \equiv e^{\frac{i H^\epsilon t}{\hbar}} e^{-\frac{i H^0 t}{\hbar}}$, which is the time evolution via the time-dependent Hamiltonian,

$$\hat{H}(t) = \begin{cases} \hat{H}^0 & 0 \to t \\ \hat{H}^\epsilon & t \to 0. \end{cases} \tag{A1}$$

A position basis representation for $\hat{U}(\boldsymbol{q}, \boldsymbol{q}')$,

$$\begin{aligned}
\langle \boldsymbol{q}' | \hat{U} | \boldsymbol{q} \rangle \\
&= \int d\boldsymbol{q}'' \langle \boldsymbol{q}' | e^{i\hat{H}^\epsilon t/\hbar} | \boldsymbol{q}'' \rangle \langle \boldsymbol{q}'' | e^{-i\hat{H}^0 t/\hbar} | \boldsymbol{q} \rangle && \text{(A2)} \\
&\approx \int d\boldsymbol{q}'' e^{iS(\boldsymbol{q}', \boldsymbol{q}''; 0 \to t)/\hbar} e^{iS(\boldsymbol{q}'', \boldsymbol{q}; t \to 0)/\hbar}, && \text{(A3)}
\end{aligned}$$

where the integral over $\boldsymbol{q}''$ was evaluated by the SPA in Eq. (A3) and pre-exponential factors in this "primitive" semiclassical propagator were disregarded. The SPA condition for this integral is

$$\frac{\partial S(\boldsymbol{q}', \boldsymbol{q}''; 0 \to t)}{\partial \boldsymbol{q}''} = \frac{\partial S(\boldsymbol{q}'', \boldsymbol{q}; t \to 0)}{\partial \boldsymbol{q}''}, \tag{A4}$$

$$\boldsymbol{p}_t(\boldsymbol{q}', \boldsymbol{q}'') = \boldsymbol{p}_t(\boldsymbol{q}'', \boldsymbol{q}), \tag{A5}$$

where the left hand side of the final expression is the momentum at time t after going forward in time and the right hand side is the momentum at time t before going backward in time from the Loschmidt echo perspective. The same is manifestly true in this representation for the position at time t after going forward in time and before going backward in time since $\boldsymbol{q}_t \equiv \boldsymbol{q}''$.

Moreover, the overall phase is provided in this stationary phase approximated propagator and is equal to $e^{iS(\boldsymbol{q}',\boldsymbol{q})/\hbar}$, where

$$S(\boldsymbol{q}',\boldsymbol{q}) = S(\boldsymbol{q}_t,\boldsymbol{q};0\to t) + S(\boldsymbol{q}',\boldsymbol{q}_t;0\to t). \qquad \text{(A6)}$$

Time-dependent Hamiltonians have the same Heller-Herman-Kluk-Kay propagator as their time-independent brethren and so Eq. (8) can be rewritten without one of its double phase space integrals as Eq. (9).

[1] M. V. Berry, "Quantum scars of classical closed orbits in phase space," Proc. R. Soc. London **423**(1864), 219–231 (1989).
[2] S. Mukamel, "On the semiclassical calculation of molecular absorption and fluorescence spectra," J. Chem. Phys. **77**(1), 173–181 (1982).
[3] Q. Shi and E. Geva, "A comparison between different semiclassical approximations for optical response functions in nonpolar liquid solutions," J. Chem. Phys. **122**(6), 064506 (2005).
[4] P. L. McRobbie, G. Hanna, Q. Shi, and E. Geva, "Signatures of nonequilibrium solvation dynamics on multidimensional spectra," Acc. Chem. Res. **42**(9), 1299–1309 (2009).
[5] Z. Li, J.-Y. Fang, and C. C. Martens, "Simulation of ultrafast dynamics and pump–probe spectroscopy using classical trajectories," J. Chem. Phys. **104**(18), 6919–6929 (1996).
[6] S. A. Egorov, E. Rabani, and B. J. Berne, "Vibronic spectra in condensed matter: A comparison of exact quantum mechanical and various semiclassical treatments for harmonic baths," J. Chem. Phys. **108**(4), 1407–1422 (1998).
[7] S. A. Egorov, E. Rabani, and B. J. Berne, "Nonradiative relaxation processes in condensed phases: Quantum versus classical baths," J. Chem. Phys. **110**(11), 5238–5248 (1999).
[8] N. E. Shemetulskis and R. F. Loring, "Semiclassical theory of the photon echo: Application to polar fluids," J. Chem. Phys. **97**(2), 1217–1226 (1992).
[9] J. M. Rost, "Analytical total photo cross section for atoms," J. Phys. B **28**(19), L601 (1995).
[10] J. Vaníček and E. J. Heller, "Semiclassical evaluation of quantum fidelity," Phys. Rev. E **68**, 056208 (2003).
[11] J. Vaníček, "Dephasing representation: Employing the shadowing theorem to calculate quantum correlation functions," Phys. Rev. E **70**, 055201 (2004).
[12] J. Vaníček, "Dephasing representation of quantum fidelity for general pure and mixed states," Phys. Rev. E **73**, 046204 (2006).
[13] C. Mollica and J. Vaníček, "Beating the efficiency of both quantum and classical simulations with a semiclassical method," Phys. Rev. Lett. **107**(21), 214101 (2011).
[14] E. Zambrano, M. Sulc, and J. Vaníček, "Improving the accuracy and efficiency of time-resolved electronic spectra calculations: Cellular dephasing representation with a prefactor," J. Chem. Phys. **139**(5), 054109 (2013).
[15] J. Shao and N. Makri, "Forward–backward semiclassical dynamics without prefactors," J. Phys. Chem. A **103**(39), 7753–7756 (1999).
[16] J. Shao and N. Makri, "Forward–backward semiclassical dynamics with linear scaling," J. Phys. Chem. A **103**(47), 9479–9486 (1999).
[17] W. H. Miller, "Spiers memorial lecture quantum and semiclassical theory of chemical reaction rates," Faraday Discuss. **110**, 1–21 (1998).
[18] X. Sun and W. H. Miller, "Forward–backward initial value representation for semiclassical time correlation functions," J. Chem. Phys. **110**(14), 6635–6644 (1999).
[19] J. Liu and W. H. Miller, "Using the thermal gaussian approximation for the boltzmann operator in semiclassical initial value time correlation functions," J. Chem. Phys. **125**(22), 224104 (2006).
[20] J. Liu and W. H. Miller, "Real time correlation function in a single phase space integral beyond the linearized semiclassical initial value representation," J. Chem. Phys. **126**(23), 234110 (2007).
[21] E. Zambrano and A. M. Ozorio de Almeida, "Initial-value representation for the loschmidt echo," Phys. Rev. E **84**, 045201 (2011).
[22] M. Sulc, H. Hernandez, T. J. Martinez, and J. VaniCek, "Relation of exact gaussian basis methods to the dephasing representation: Theory and application to time-resolved electronic spectra," J. Chem. Phys. **139**(3), 034112 (2013).
[23] K. G. Kay, "Semiclassical propagation for multidimensional systems by an initial value method," J. Chem. Phys. **101**(3), 2250–2260 (1994).
[24] N. J. Wright and N. Makri, "Forward–backward semiclassical dynamics for condensed phase time correlation functions," J. Chem. Phys. **119**(3), 1634–1642 (2003).
[25] A. O. Caldeira and A. J. Leggett, "Path integral approach to quantum brownian motion," Physica A **121**(3), 587–616 (1983).
[26] C.-M. Goletz and F. Grossmann, "Decoherence and dissipation in a molecular system coupled to an environment: An application of semiclassical hybrid dynamics," J. Chem. Phys. **130**(24), 244107 (2009).
[27] H. Wang, M. Thoss, K. L. Sorge, R. Gelabert, X. Gimenez, and W. H. Miller, "Semiclassical description of quantum coherence effects and their quenching: A forward–backward initial value representation study," J. Chem. Phys. **114**(6), 2562–2571 (2001).
[28] Y. Elran and P. Brumer, "Decoherence in an anharmonic oscillator coupled to a thermal environment: A semiclassical forward-backward approach," J. Chem. Phys. **121**(6), 2673–2684 (2004).
[29] E. Jezek and N. Makri, "Finite temperature correlation functions via forwardbackward semiclassical dynamics," J. Phys. Chem. A **105**(12), 2851–2857 (2001).
[30] M. Thoss, H. Wang, and W. H. Miller, "Generalized forward–backward initial value representation for the calculation of correlation functions in complex systems," J. Chem. Phys. **114**(21), 9220–9235 (2001).