# Statistical Mechanics of Mean Field Ehrenfest Quantum/Classical Molecular Dynamics: The Damped Harmonic Oscillator†

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In this contribution, we discuss the statistical mechanical implications of the mean field Ehrenfest method of quantum/classical dynamics for a quantum harmonic oscillator in a classical heat bath using the Brownian motion Hamiltonian as a model. A mean field quantum/classical master equation is derived and compared to the corresponding Redfield master equation, and the deficiencies of the quantum/classical approach pointed out by analyzing the nature of energy/population relaxation and decoherence.

## 1. Introduction

Theoretical chemical dynamics of large systems or in condensed phases has seen in recent years a tremendously increasing interest in hybrid methods, which allow for inclusion of important quantum effects in a relevant subsystem, whereas the less important degrees of freedom (DoF) of the (solvent) environment or heat bath are treated by classical mechanics.[1−10] By partitioning the total system into a usually small quantum "core" and a large environmental subsystem, an acceptable scaling of the numerical effort with the number of DoF is maintained. Examples include electron transfer and electronically nonadiabatic processes[11−14] or proton/hydrogen transfer in chemistry and biology.[5,15,16] Vibrational energy transfer [VET, or vibrational energy relaxation (VER)] is an elementary process of fundamental importance in chemical dynamics[17] where quantum effects may also become important due to the nonnegligible zero-point energy of high-frequency vibrations and the finite energy level spacings.

It is the purpose of the present work to analyze and clarify the dynamical properties of the simplest mixed quantum/classical dynamics method (the *mean field Ehrenfest* scheme, see below), as applied to vibrational energy relaxation, from a statistical mechanical point of view.[18] Using a suitable model Hamiltonian, a mean field quantum/classical generalized master equation is derived and compared to the respective quantum generalized master equation. Focusing on the nature of energy/population relaxation and decoherence, the analytical properties of the quantum/classical master equation are used to analyze the results of model simulations. Thereby we hope to provide a starting point for improvement of the mean field quantum/classical approach, both in the regime of weak coupling between quantum and classical subsystems and possibly beyond.

In hybrid quantum/classical molecular dynamics, hereafter denoted by QCMD, quantum and classical equations of motion are solved in a self-consistent manner, but the way how this is done depends on the degree of correlation between quantum and classical subsystems that is considered to be important. As a consequence, there are essentially two categories of QCMD methods, which may be termed "weak correlation" and "strong correlation", respectively.

The lowest level of theory (weak correlation class) is represented by the so-called mean field Ehrenfest (MF) or classical path method,[1,3,10] which may be derived from the single-configuration time-dependent self-consistent field (TDSCF) approximation.[7,19] As a result, it suffers from the same approximations as involved in the derivation of TDSCF, namely, a (partial) neglect of quantum correlation between subsystems described by separate lower-dimensional time-dependent wave functions.[4] In general terms, the drawback of the mean field approach arises from the property that the motion of classical degrees of freedom is not correlated to the full reduced density operator of the quantum DoF, but only to an expectation value calculated therefrom, namely, an average Hellmann−Feynman type force.[6,20,21]

The molecular dynamics with electronic transitions method (in its fewest switches implementation),[11] widely known as trajectory surface hopping (TSH),[22,23] or its later extension, termed molecular dynamics with quantum transitions (MDQT),[15] represents the second class of QCMD schemes, and has been designed to address the strong correlation case. For a broader (re)view on both the MF and the TSH QCMD classes and their relation to (ab initio) direct quantum molecular dynamics applied to nonadiabatic problems,[24−26] see refs 6 and 9.

In this work, we apply mean field QCMD methodology to a model of condensed phase vibrational energy relaxation, i.e., a situation where the system-environment interaction is usually of the weak coupling type, and therefore its effect on the relevant subsystem dynamics may be evaluated via low-order time-dependent perturbation theory. The resultant generalized quantum master equation for the reduced density operator[27−29] takes into account the dissipative effect of the environmental DoF due to fluctuating and frictional forces. In fact, because of its convenience, this is the framework within which condensed phase VER is usually treated.[17,30] Although it is often argued[31,32] that TDSCF/MF approaches are applicable to situations with small coupling between the respective subsystems or where the interaction is of an average type, we will show that mean field Ehrenfest QCMD even performs poorly in this weak coupling regime, because friction is a correlation effect and will therefore not be correctly accounted of by an approach, which neglects an important part of the correlation, however small the system-bath interaction may be. We anticipate that our findings/arguments are at variance with the results obtained in an application of mean field QCMD to diatomic vibrational

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relaxation in aqueous solution.[32,33] Other recent examples of mean field Ehrenfest molecular dynamics as applied to vibrational energy transfer and relaxation include refs 34 and 35. See also ref 10 for an extensive review of the classical path method (including the so-called symmetrized Ehrenfest approach) and its application to rovibrationally inelastic and reactive scattering. Examples of surface hopping methodology as applied to vibrational energy transfer and relaxation include refs 36 and 37.

In a recent investigation, we have reported on mean field quantum/classical simulations of a model breathing sphere in a Lennard-Jones fluid at liquid density,[38] where some of the present issues have already been raised. Here we employ the so-called Brownian motion Hamiltonian[39−42] for a particle moving in a one-dimensional potential and coupled bilinearly to a heat bath composed of harmonic oscillators. Although restricted to a bilinear form of the interaction potential, this model provides access to a quantum mechanical solution either via the path integral technique[8,39,43−45] or through the generalized quantum master equation (QME).[27−29]

Our paper is organized as follows. In section 2, we briefly describe the mean field Ehrenfest quantum/classical approach, discuss the model Hamiltonian and the resultant dynamical properties in terms of the generalized Langevin (GLE) and quantum master equations, respectively, and then go on to derive a mean field quantum/classical master equation (QCME), and therefrom obtain some theoretical implications of the mean field Ehrenfest equations of motion. For the sake of a close comparison of the mean field QCME to the GLE/QME and the underlying approximations (if any), we give a fairly detailed yet compact discussion of the GLE and QME, respectively, for the underlying model Hamiltonian. Simulation results using an ohmic bath parametrization of the model are presented and discussed in section 3. Section 4 concludes.

## 2. Theory

Before entering this section, some words on notational matters may be useful in order to avoid ambiguity. As usual in statistical mechanics, the total (closed) system is divided into two subsystems, a small subsystem of interest (relevant subsystem, or simply the system) and a large environmental subsystem (environment, heat bath, or simply the bath). In the following, the above names for each of the two subsystems are used interchangeably. Whenever aspects of the interaction or correlation between subsystems are addressed, the term subsystems refers to the subsystem of interest and its (classical or quantum) environment.

**2.1. Mean Field Ehrenfest Molecular Dynamics.** The mean field Ehrenfest method has been reviewed many times,[1,3,4,6,9,10,46] so we try to stay very brief here. Starting from a total Hamiltonian of the general type

$$\begin{aligned}\hat{H} &= \hat{H}_{\mathrm{S}}(q,p) + \hat{V}(q,\mathbf{Q}) + \hat{H}_{\mathrm{B}}(\mathbf{Q},\mathbf{P})\\ \hat{H}_{\mathrm{S}}(q,p) &= \frac{\hat{p}^2}{2\mu} + \hat{V}_{\mathrm{S}}(q)\\ \hat{H}_{\mathrm{B}}(\mathbf{Q},\mathbf{P}) &= \sum_{\mathrm{i}} \frac{\hat{P}_{\mathrm{i}}^2}{2m_{\mathrm{i}}} + \hat{V}_{\mathrm{B}}(\mathbf{Q})\end{aligned} \tag{1}$$

where $\mathbf{Q} \equiv \{Q_{\mathrm{i}}\}$ and $\mathbf{P} \equiv \{P_{\mathrm{i}}\}$, or collectively $\mathbf{X} \equiv (\mathbf{Q}, \mathbf{P})$, the mean field Ehrenfest quantum/classical equations of motion take the form

$$\begin{aligned}\frac{\mathrm{d}}{\mathrm{d}t}|\Psi_{\mathrm{S}}(t)\rangle &= -\frac{i}{\hbar}\{\hat{H}_{\mathrm{S}} + \hat{V}[q;\mathbf{Q}(t)]\}|\Psi_{\mathrm{S}}(t)\rangle\\ \dot{\mathbf{Q}}(t) &= \left.\frac{\partial H_{\mathrm{B}}(\mathbf{X})}{\partial \mathbf{P}}\right|_{\mathbf{X}=\mathbf{X}(t)}\\ \dot{\mathbf{P}}(t) &= -\left.\frac{\partial H_{B}(\mathbf{X})}{\partial \mathbf{Q}}\right|_{\mathbf{X}=\mathbf{X}(t)} - \\ &\qquad \left.\frac{\partial}{\partial \mathbf{Q}}\langle \Psi_{\mathrm{S}}(t)|\hat{V}(q,\mathbf{Q})|\Psi_{\mathrm{S}}(t)\rangle\right|_{\mathbf{Q}=\mathbf{Q}(t)}\end{aligned} \tag{2}$$

where $\hat{H}_{\mathrm{S}}$ and $\hat{H}_{\mathrm{B}}$ denote the system and bath Hamiltonian, respectively. The equations of motion (eom) for the classical degrees of freedom thus contain a force derived from the quantum averaged interaction potential $\hat{H}_{\mathrm{SB}} = \hat{V}(q, \mathbf{Q})$ evaluated at the classical path $\mathbf{Q} = \mathbf{Q}(t)$. Although the form of this “quantum force” in eq 2, with the coordinate derivative performed after the quantum trace, takes account of a possible $\mathbf{Q}$-dependence of the state vector $|\Psi_{\mathrm{S}}(t)\rangle$, it is usually assumed that the derivative can be drawn inside the quantum bra-ket, provided the basis functions used to expand the wave function do not depend on the positions $\mathbf{Q}(t)$ of the classical DoF.[6]

In practical numerical applications a unitary scheme has to be employed in order to conserve the norm of the state vector as well as the quantum averaged total energy and momentum. A convenient integration scheme is provided by the PICKAPACK algorithm,[47,48] which has the structure of a quantum/classical symmetric split propagator and is used here in a modified form[49]

$$\begin{aligned}\mathbf{Q}_{0.5} &= \mathbf{Q}_0 + \mathbf{M}^{-1}\mathbf{P}_0\frac{\Delta t}{2}\\ |\Psi_S\rangle_{0.5} &= \exp\left\{-\frac{i}{\hbar}\hat{H}_{\mathrm{S}}\frac{\Delta t}{2}\right\}|\Psi_{\mathrm{S}}\rangle_0\\ \mathbf{P}_1 &= \mathbf{P}_0 - \left\{\left.\frac{\partial V_{\mathrm{B}}(\mathbf{Q})}{\partial \mathbf{Q}}\right|_{\mathbf{Q}=\mathbf{Q}_{0.5}} + \left\langle\left.\frac{\partial \hat{V}(q,\mathbf{Q})}{\partial \mathbf{Q}}\right|_{\mathbf{Q}=\mathbf{Q}_{0.5}}\right\rangle_{0.5}\right\}\Delta t\\ |\Psi_S\rangle_1 &= \exp\left\{-\frac{i}{\hbar}\hat{H}_{\mathrm{S}}\frac{\Delta t}{2}\right\}\exp\left\{-\frac{i}{\hbar}\hat{V}(q;\mathbf{Q}_{0.5})\Delta t\right\}|\Psi_{\mathrm{S}}\rangle_{0.5}\\ \mathbf{Q}_1 &= \mathbf{Q}_{0.5} + \mathbf{M}^{-1}\mathbf{P}_1\frac{\Delta t}{2}\end{aligned} \tag{3}$$

where $\mathbf{M}$ is the diagonal mass matrix and subscripts 0, 0.5, and 1 denote classical phase space variables and quantum wave functions at times $t$, $t + \Delta t/2$ and $t + \Delta t$, respectively.

**2.2. Model Hamiltonian and Relevant Subsystem Dynamics.** For the purpose of analytical investigations and the ability to provide an (approximate) quantum dynamical reference, we restrict ourselves to the so-called Brownian motion (Caldeira-Leggett) Hamiltonian[40−42] as a model

$$\begin{aligned}\hat{H} &= \frac{\hat{p}^2}{2\mu} + \hat{V}_{\mathrm{S}}(q) + \sum_l\left\{\frac{\hat{P}_l^2}{2} + \frac{\omega_l^2}{2}\left(\hat{Q}_l - \frac{g_l}{\omega_l^2}\hat{q}\right)^2\right\}\\ &= \hat{H}_{\mathrm{S}}(q,p) + \hat{V}_{\mathrm{solv}}(q) + \hat{H}_{\mathrm{SB}}(q,\mathbf{Q}) + \hat{H}_{\mathrm{B}}(\mathbf{Q},\mathbf{P})\end{aligned} \tag{4}$$

where $\hat{V}_{\mathrm{solv}}(q) = 1/2\sum_l(g_l/\omega_l)^2\hat{q}^2$, $\hat{H}_{\mathrm{SB}} = -\hat{q}\sum_l g_l\hat{Q}_l$ and $\hat{H}_{\mathrm{B}}$ is the unperturbed bath Hamiltonian. The mean field quantum/classical eom then read

$$
\begin{aligned}
\frac{\mathrm{d}}{\mathrm{d}t}|\Psi_{\mathrm{S}}(t)\rangle &= -\frac{i}{\hbar}\{\hat{H}_{\mathrm{solv}} - \hat{q}\sum_l g_l Q_l(t)\}|\Psi_{\mathrm{S}}(t)\rangle \\
\dot{Q}_l(t) &= P_l(t) \\
\dot{P}_l(t) &= -\omega_l^2 Q_l(t) + g_l\langle\hat{q}\rangle_t
\end{aligned}
\tag{5}
$$

where $\hat{H}_{\mathrm{solv}} = \hat{H}_{\mathrm{S}} + \hat{V}_{\mathrm{solv}}$ (solvate Hamiltonian) and $\langle ... \rangle_t = \langle\Psi_{\mathrm{S}}(t)|...|\Psi_{\mathrm{S}}(t)\rangle$.

*2.2.1. Generalized Langevin Equation.* As is well-known,[28,50−52] Hamiltonian (4) provides the basis for a microscopic derivation of the (nonlinear) generalized Langevin equation (GLE)[40,53,54]

$$
\begin{aligned}
\frac{\mathrm{d}q(t)}{\mathrm{d}t} &= \frac{p(t)}{\mu} \\
\frac{\mathrm{d}p(t)}{\mathrm{d}t} &= -\frac{\mathrm{d}V_{\mathrm{S}}(q)}{\mathrm{d}q} - \int_0^t \mathrm{d}s\, \gamma(t-s)\, p(s) + \delta F(t)
\end{aligned}
\tag{6}
$$

both in classical and in quantum dynamics. For contextual reasons, we choose the quantum picture, where the system and bath phase space variables (operators) obey the Heisenberg eom, and the intrinsic force $-\nabla_{\mathrm{q}}\hat{V}_{\mathrm{S}}(q)$ is a matrix defined by the commutator $(i/\hbar)[\hat{V}_{\mathrm{S}}(q), \hat{p}], \hat{p} = -i\hbar\nabla_q$.

The bath equations of motion are linear and can therefore be integrated out to give

$$
\hat{Q}_l(t) = \hat{Q}_l(0)\cos\omega_l t + \frac{\hat{P}_l(0)}{\omega_l}\sin\omega_l t + g_l\int_0^t \mathrm{d}s\,\frac{\sin\omega_l(t-s)}{\omega_l}\hat{q}(s) \tag{7}
$$

After partial integration of the convolution integral, this leads to

$$
\hat{Q}_l(t) - \frac{g_l}{\omega_l^2}\hat{q}(t) = \left(\hat{Q}_l(0) - \frac{g_l}{\omega_l^2}\hat{q}(0)\right)\cos\omega_l t + \frac{\hat{P}_l(0)}{\omega_l}\sin\omega_l t - g_l\int_0^t \mathrm{d}s\frac{\cos\omega_l(t-s)}{\omega_l^2}\frac{\hat{p}(s)}{\mu}, \tag{8}
$$

which by insertion into the system eom gives the GLE, eq 6, with

$$
\begin{aligned}
\delta\hat{F}(t) &= \sum_l g_l\left\{\left(\hat{Q}_l(0) - \frac{g_l}{\omega_l^2}\hat{q}(0)\right)\cos\omega_l t + \frac{\hat{P}_l(0)}{\omega_l}\sin\omega_l t\right\} \\
\gamma(t) &= \frac{1}{\mu}\sum_l \frac{g_l^2}{\omega_l^2}\cos\omega_l(t)
\end{aligned}
\tag{9}
$$

The form of the fluctuating force $\delta\hat{F}(t)$ implies that the bath degrees of freedom are to be considered initially equilibrated to the system coordinate $\hat{q}$, if $\langle\delta\hat{F}(t)\rangle_B = 0$ and translational invariance of the friction force is required.[44,50] Although, for the model chosen, the friction kernel $\gamma(t)$ is temperature-independent and the same both in classical and in quantum dynamics, the statistics of the random force $\delta\hat{F}(t)$ is different.

In the realm of classical dynamics, the autocorrelation function of the fluctuation force $\delta F(t)$ is related to the friction kernel $\gamma(t)$ via the fluctuation−dissipation relation (FDR)

$$
C_{\mathrm{cl}}(t-s) \equiv \langle\delta F(t)\delta F(s)\rangle_{\mathrm{B}} = k_{\mathrm{B}}T\sum_l \frac{g_l^2}{\omega_l^2}\cos\omega_l(t-s) \equiv \mu k_{\mathrm{B}}T\gamma(t-s) \tag{10}
$$

for a heat bath at canonical equilibrium.[51,54] In the quantum domain, the operator force $\delta\hat{F}(t)$ has the following statistical properties[29,44]

$$
\begin{aligned}
\langle\delta\hat{F}(t)\rangle_{\mathrm{B}} &= 0 \\
C(t) \equiv \langle\delta\hat{F}(t)\delta\hat{F}(0)\rangle_{\mathrm{B}} &= \sum_l \frac{\hbar g_l^2}{2\omega_l}\{(\bar{n}_l + 1)\,\mathrm{e}^{-i\omega_l t} + \bar{n}_l\,\mathrm{e}^{+i\omega_l t}\} \\
&= \sum_l \frac{\hbar g_l^2}{2\omega_l}\{(2\bar{n}_l + 1)\cos\omega_l t - i\sin\omega_l t\}
\end{aligned}
\tag{11}
$$

with the (perturbed) heat bath canonical density operator $\hat{\rho}_B \propto \mathrm{e}^{-\beta\hat{H}_B}$, $\beta = (k_{\mathrm{B}}T)^{-1}$, and $\bar{n}_l \equiv \langle\hat{a}_l^\dagger\,\hat{a}_l\rangle_{\mathrm{B}} = \{\mathrm{e}^{\beta\hbar\omega_l} - 1\}^{-1}$ the mean thermal occupation number of the $l$th bath oscillator.

In the classical limit, $\bar{n}_l \rightarrow (\beta\hbar\omega_l)^{-1} \gg 1$, the real and symmetric part of $C(t)$ is

$$
\lim_{\beta\hbar\omega_l\to 0} C_+(t) \equiv C_{\mathrm{cl}}(t) = \mu k_{\mathrm{B}}T\gamma(t) \tag{12}
$$

The antisymmetric (imaginary) part of $C(t)$ does not depend on temperature, and is (again a property of the model Hamiltonian) related to the time-derivative of the friction kernel

$$
C_-(t) = -i\sum_l \frac{\hbar g_l^2}{2\omega_l}\sin\omega_l t \equiv \frac{i\hbar}{2}\mu\frac{\mathrm{d}}{\mathrm{d}t}\gamma(t) = \frac{i\hbar}{2k_{\mathrm{B}}T}\frac{\mathrm{d}}{\mathrm{d}t}C_{\mathrm{cl}}(t) \tag{13}
$$

which will be used later in the derivation of the mean field quantum/classical master equation (section 2.3). For later reference, we also summarize here some general relations in the frequency domain.[29] The Fourier transforms of $C(t) = C_+(t) + C_-(t)$ and $C^*(t) = C_+(t) - C_-(t) \equiv C(-t)$ obey the detailed balance relationship

$$
\begin{aligned}
\hat{C}(\omega) &= \int_{-\infty}^{+\infty}\mathrm{d}t\, C(t)\,\mathrm{e}^{-i\omega t} \\
\hat{C}(-\omega) &= \int_{-\infty}^{+\infty}\mathrm{d}t\, C(t)\,\mathrm{e}^{+i\omega t} = \int_{-\infty}^{+\infty}\mathrm{d}t\, C^*(t)\,\mathrm{e}^{-i\omega t} \equiv \mathrm{e}^{\beta\hbar\omega}\,\hat{C}(\omega)
\end{aligned}
\tag{14}
$$

where $\mathrm{e}^{\beta\hbar\omega} = (\bar{n}_\omega + 1)/\bar{n}_\omega$. For the Fourier transforms of the symmetric and antisymmetric parts of $C(t)$, we thus obtain

$$
\hat{C}_+(\omega) = \frac{1}{2}\{1 + \mathrm{e}^{\beta\hbar\omega}\}\hat{C}(\omega), \qquad \hat{C}_-(\omega) = \frac{1}{2}\{1 - \mathrm{e}^{\beta\hbar\omega}\}\hat{C}(\omega) \tag{15}
$$

*2.2.2. Quantum Master Equation.* The quantum Langevin equation, eq 6, is of limited use, except for the damped harmonic oscillator, because the operator force $-\nabla_q\hat{V}_{\mathrm{S}}(q)$ is nonlinear in general.

The quantum master equation (QME) for the reduced density operator $\hat{\rho}_{\mathrm{S}}(t) = \mathrm{Tr}_{\mathrm{B}}\,\hat{\rho}(t)$ provides access to complete information about the relevant subsystem. A systematic route to the

QME is provided by the Nakajima-Zwanzig projection operator technique.[28,29,51] For comparison with the treatment in section 2.3, we take a short cut to the second order Redfield-type QME[29] using the interaction representation ("Dirac" picture, D) with respect to the bath Hamiltonian $\hat{H}_\mathrm{B}$[55]

$$\begin{aligned}\hat{\rho}^{(D)}(t) &= \hat{U}_\mathrm{B}^\dagger(t, t_0)\, \hat{\rho}(t)\, \hat{U}_\mathrm{B}(t, t_0)\\ &= \hat{U}_\mathrm{B}^\dagger(t, t_0)\hat{U}(t, t_0)\, \hat{\rho}(t_0)\, \hat{U}^\dagger(t, t_0)\hat{U}_B(t, t_0)\\ &= \hat{U}_t\, \hat{\rho}(t_0)\, \hat{U}_t^{-1} \equiv \mathscr{U}^{(D)}(t, t_0)\, \hat{\rho}(t_0) \qquad (16)\end{aligned}$$

for the total density operator, where $\hat{U}(t, t_0)$ and $\hat{U}_t$ (inverse $\hat{U}_t^{-1}$) are Hilbert space time evolution operators in the Schrödinger and Dirac picture, respectively, and $\mathscr{U}^{(D)}(t, t_0)$ is a Liouville space time evolution operator. For the model Hamiltonian eq 4, the von Neumann equation for the total density operator $\hat{\rho}^{(D)}(t)$ then reads

$$\frac{\mathrm{d}}{\mathrm{d}t}\hat{\rho}^{(D)}(t) = -\frac{i}{\hbar}[\hat{H}_\mathrm{solv} + \hat{H}_\mathrm{SB}(t), \hat{\rho}^{(D)}(t)] \qquad (17)$$

with $\hat{H}_\mathrm{SB}(t) = \hat{U}_\mathrm{B}^\dagger(t,t_0)\hat{H}_\mathrm{SB}\hat{U}_\mathrm{B}(t,t_0) = -\,\hat{q}\sum_l g_l \hat{Q}_l(t) \equiv -\hat{q}\hat{F}_\mathrm{B}(t)$, which defines the bath-induced operator force

$$\hat{F}_\mathrm{B}(t) = \sum_l g_l\left\{\hat{Q}_l(0)\cos\omega_l t + \frac{\hat{P}_l(0)}{\omega_l}\sin\omega_l t\right\} \qquad (18)$$

Note that $\hat{F}_\mathrm{B}(t)$ differs from $\delta\hat{F}(t)$, eq 9, only by the definition of initial conditions, and is assumed to have the same statistical properties, eq 11, for the unperturbed heat bath at canonical equilibrium. This difference may be taken into account by simultaneously letting $\hat{F}_\mathrm{B}(t) \rightarrow \delta\hat{F}(t)$ and $\hat{H}_\mathrm{solv} \rightarrow \hat{H}_\mathrm{S}$.

Through definition of a time-independent Liouville space projector $\mathscr{P}$ and its complement $\mathscr{Q} = 1 - \mathscr{P}$, the information contained in the total density operator $\hat{\rho}^{(D)}(t)$ may be split into *relevant* and *irrelevant* parts, respectively

$$\begin{aligned}\hat{\rho}_\mathrm{rel}^{(D)}(t) &= \mathscr{P}\hat{\rho}^{(D)}(t) = Tr_\mathrm{B}\{\hat{\rho}^{(D)}(t)\} \otimes \hat{\rho}_\mathrm{B,eq}\\ \Delta\hat{\rho}^{(D)}(t) &= \mathscr{Q}\hat{\rho}^{(D)}(t) = \hat{\rho}^{(D)}(t) - \hat{\rho}_\mathrm{rel}^{(D)}(t) \qquad (19)\end{aligned}$$

where the relevant part is a direct product of the reduced density operator $\hat{\rho}_\mathrm{S}(t) = Tr_\mathrm{B}\hat{\rho}^{(D)}(t)$ and the bath statistical operator $\hat{\rho}_\mathrm{B,eq} = \mathrm{e}^{-\beta\hat{H}_\mathrm{B}}/Tr\,\mathrm{e}^{-\beta\hat{H}_\mathrm{B}}$ at canonical equilibrium, and contains the full information on the relevant subsystem, while its complement contains the correlations (entanglement) as a result of the interaction $\hat{H}_\mathrm{SB}(t)$. The quantum Liouville equation, eq 17, can thus be reformulated in terms of two coupled equations for $\mathscr{P}\hat{\rho}^{(D)}(t)$ and $\mathscr{Q}\hat{\rho}^{(D)}(t)$. Formal elimination of the irrelevant part delivers the most general form of QME, which forms the starting point for approximations, often involving[29] (i) the neglect of initial correlations, $\mathscr{Q}\hat{\rho}^{(D)}(t_0) \cong 0$ (or their rapid decay), and (ii) the short bath correlation time approximation, related to assumption (i).

Solving Liouville eq 17 under these approximations gives (i) the non-Markovian (time-retarded) generalized master equation and (ii) the convolutionless (time-local) QME, respectively, for the relevant subsystem reduced density operator $\hat{\rho}_\mathrm{S}(t) = Tr_\mathrm{B}\{\hat{\rho}^{(D)}(t)\} = Tr_\mathrm{B}\{\mathscr{P}\hat{\rho}^{(D)}(t)\}$, directly in the Schrödinger picture

$$\begin{aligned}\frac{\mathrm{d}}{\mathrm{d}t}\hat{\rho}_\mathrm{S}(t) \cong &-\frac{i}{\hbar}[\hat{H}_\mathrm{S},\hat{\rho}_\mathrm{S}(t)] -\\ &\frac{1}{\hbar^2}\int_{t_0}^{t}\mathrm{d}s\, C(t-s)\, [\hat{q}, \mathscr{U}_\mathrm{S}(t, s)\, \hat{q}\, \hat{\rho}_\mathrm{S}^{(0)}(s)] +\\ &\frac{1}{\hbar^2}\int_{t_0}^{t}\mathrm{d}s\, C^*(t-s)\, [\hat{q}, \mathscr{U}_\mathrm{S}(t, s)\, \hat{\rho}_\mathrm{S}^{(0)}(s)\, \hat{q}] \quad \text{(i)}\\ \simeq &-\frac{i}{\hbar}[\hat{H}_\mathrm{S}, \hat{\rho}_\mathrm{S}(t)] -\\ &\frac{1}{\hbar^2}\{[\hat{q}, \hat{\Lambda}(t)\, \hat{\rho}_\mathrm{S}^{(0)}(t)] - [\hat{q}, \hat{\rho}_\mathrm{S}^{(0)}(t)\, \hat{\Lambda}^\dagger(t)]\} \quad \text{(ii)} \quad (20)\end{aligned}$$

where $\mathscr{U}_\mathrm{S}(t, s)$ is the system Liouville space propagator, $\hat{\Lambda}(t) = \int_0^{t-t_0}\mathrm{d}\tau\; C(\tau)\; \hat{q}_\mathrm{S}(-\tau)$ and $\hat{\Lambda}^\dagger(t) = \int_0^{t-t_0}\mathrm{d}\tau\; C^*(\tau)\; \hat{q}_\mathrm{S}(-\tau)$, $\hat{q}_\mathrm{S}(-\tau) = \mathscr{U}_\mathrm{S}(t, s)\, \hat{q} = \hat{U}_\mathrm{S}(t, s)\, \hat{q}\hat{U}_\mathrm{S}^\dagger(t, s)$ and $\tau = t - s$. $\hat{\rho}_\mathrm{S}^{(0)}(t)$ denotes the reduced density operator to zeroth order in the system-bath interaction. According to approximation (ii), the motion of the relevant subsystem during the time range of the convolution integral is not substantially affected by dissipation, i.e.

$$\hat{\rho}_\mathrm{S}^{(0)}(s) \simeq \mathscr{U}_\mathrm{S}^\dagger(t, s)\hat{\rho}_\mathrm{S}^{(0)}(t) = \hat{U}_\mathrm{S}^\dagger(t, s)\hat{\rho}_\mathrm{S}^{(0)}(t)\hat{U}_\mathrm{S}(t, s)$$

The *convolutionless* QME of eq 20 takes account of the system-bath correlations contained in $\Delta\hat{\rho}^{(D)}(t) = \mathscr{Q}\hat{\rho}^{(D)}(t)$ to second order in the system-bath interaction and includes *non-Markovian* effects in an approximate manner, i.e., in terms of seemingly Markovian (time-local) but frequency-dependent friction. For comparison with the mean field quantum/classical master equation (QCME), to be derived below, it may be rewritten as

$$\begin{aligned}\frac{\mathrm{d}}{\mathrm{d}t}\hat{\rho}_\mathrm{S}(t) \cong &-\frac{i}{\hbar}[\hat{H}_\mathrm{S}, \hat{\rho}_\mathrm{S}(t)] -\\ &\frac{1}{\hbar^2}\int_0^t \mathrm{d}s\, C_+(t-s)\, [\hat{q}, \mathscr{U}_\mathrm{S}(t, s)[\hat{q}, \hat{\rho}_\mathrm{S}^{(0)}(s)]] -\\ &\qquad\frac{1}{\hbar^2}\int_0^t \mathrm{d}s\, C_-(t-s)\, [\hat{q}, \mathscr{U}_\mathrm{S}(t, s)[\hat{q}, \hat{\rho}_\mathrm{S}^{(0)}(s)]_+]\\ \simeq &-\frac{i}{\hbar}[\hat{H}_\mathrm{S}, \hat{\rho}_\mathrm{S}(t)] -\\ &\frac{1}{\hbar^2}\{[\hat{q}, [\hat{\Lambda}_+(t), \hat{\rho}_\mathrm{S}^{(0)}(t)]] + [\hat{q}, [\hat{\Lambda}_-(t), \hat{\rho}_\mathrm{S}^{(0)}(t)]_+]\} \quad (21)\end{aligned}$$

with

$$\hat{\Lambda}_+(t) = \int_0^{t-t_0}\mathrm{d}\tau C_+(\tau)\, \hat{q}_\mathrm{S}(-\tau) \quad \text{and} \quad \hat{\Lambda}_-(t) = \int_0^{t-t_0}\mathrm{d}\tau C_-(\tau)\, \hat{q}_\mathrm{S}(-\tau)$$

Upon taking the limits $\lim_{t\to\infty}\hat{\Lambda}(t)$ and $\lim_{t\to\infty}\hat{\Lambda}^\dagger(t)$, QME (20) turns into the respective multilevel Redfield equation.[27,29,56,57]

At the most approximate level of description, the off-diagonal elements (coherences) $\rho_{mn}(t)$ of the reduced density operator in the energy representation, $\hat{H}_S|n\rangle = \epsilon_n|n\rangle$, are either decoupled from the diagonal elements (secular approximation[27,29,56,58]) or neglected altogether (random phase assumption[56]). This leads to a Pauli master equation[27,29] for the diagonal elements (populations) $\rho_{mm}(t) = p_m(t)$

$$\frac{\mathrm{d}}{\mathrm{d}t}p_m(t) = -p_m(t)\sum_{n\neq m} w_{m\to n}(t) + \sum_{n\neq m} p_n(t) w_{n\to m}(t) \qquad (22)$$

with (time-dependent) rate coefficients

$$\begin{aligned} w_{m\to n}(t) &= \frac{1}{\hbar^2}\{\langle n|\hat{\Lambda}(t)|m\rangle\langle m|\hat{q}|n\rangle + \langle n|\hat{q}|m\rangle\langle m|\hat{\Lambda}^{\dagger}(t)|n\rangle\} \\ &= \frac{1}{\hbar^2}|\langle n|\hat{q}|m\rangle|^2\int_{-t}^{+t} \mathrm{d}\tau\, C(\tau)\, \mathrm{e}^{-i\omega_{nm}\tau} \end{aligned} \tag{23}$$

where $C^*(-t) = C(t)$ has been used. For times larger than the bath correlation time, where $C(t) \to 0$, the Golden Rule result[29]

$$\lim_{t \gg 0} w_{m\to n}(t) = \frac{1}{\hbar^2}|\langle n|\hat{q}|m\rangle|^2\hat{C}(\omega_{nm}) \tag{24}$$

is obtained, where $\hat{C}(\omega_{nm})$ is the Fourier transform, eq 14, of the force correlation function $C(t)$ at the transition frequency $\omega_{nm} = \omega_n - \omega_m$.

For the damped harmonic oscillator (HO) of angular frequency $\omega_0$, only single-quantum transitions with rate coefficients

$$\begin{aligned} w_{n\to n+1} &= \frac{n+1}{2\mu\hbar\omega_0}\hat{C}(+\omega_0) = \frac{\hat{\gamma}(\omega_0)}{2}\bar{n}(\omega_0, T)(n+1) \\ w_{n\to n-1} &= \frac{n}{2\mu\hbar\omega_0}\hat{C}(-\omega_0) = \frac{\hat{\gamma}(\omega_0)}{2}\{\bar{n}(\omega_0, T) + 1\}n \end{aligned} \tag{25}$$

are allowed, and an exponential decay of the mean occupation number $\langle\hat{n}\rangle$ (mean energy) is obtained from the Pauli QME, eq 22, according to

$$\frac{\mathrm{d}}{\mathrm{d}t}\langle\hat{n}\rangle = -\frac{\hat{C}(\omega_0)}{2\mu\hbar\omega_0\bar{n}}\{\langle\hat{n}\rangle - \bar{n}\} \equiv -\frac{\hat{\gamma}(\omega_0)}{2}\{\langle\hat{n}\rangle - \bar{n}\} \tag{26}$$

where $\bar{n} = \bar{n}(\omega_0, T)$ is the mean thermal occupation number at frequency $\omega_0$, and the rate constant of mean energy decay $\bar{w}$ is, by way of eqs 9, 11, and 14, equal to $\bar{w} = \hat{\gamma}(\omega_0)/2$.

**2.3. Mean Field Quantum/Classical Master Equation.** Having discussed the quantum master equation approach to relaxation based on the Brownian motion Hamiltonian, we now derive a quantum/classical master equation for the same model subject to the mean field Ehrenfest equations of motion, eqs 2 and 5, which shall provide a basis for subsequent analytical investigations and for rationalizing the numerical results to be presented below. From eq 5, we obtain the von Neumann equation

$$\begin{aligned} \frac{\mathrm{d}}{\mathrm{d}t}\hat{P}_{\mathrm{S}}(t) &= -\frac{i}{\hbar}[\hat{H}_{\mathrm{solv}} - \hat{q}\sum_l g_l Q_l(t), \hat{P}_{\mathrm{S}}(t)] \\ \dot{Q}_l(t) &= P_l(t) \\ \dot{P}_l(t) &= -\omega_l^2 Q_l(t) + g_l\langle\hat{q}\rangle_t \end{aligned} \tag{27}$$

for the pure state projector $\hat{P}_{\mathrm{S}}(t) = |\Psi_{\mathrm{S}}(t)\rangle\langle\Psi_{\mathrm{S}}(t)|$, from which the classical bath eom can be eliminated via direct integration [see eqs 7−9]

$$\begin{aligned} Q_l(t) &= \\ &Q_l(0)\cos\omega_l t + \frac{P_l(0)}{\omega_l}\sin\omega_l t + g_l\int_0^t \mathrm{d}s\,\frac{\sin\omega_l(t-s)}{\omega_l}\langle\hat{q}\rangle_s \\ \sum_l g_l Q_l(t) &= F_B(t) + \frac{2i}{\hbar}\int_0^t \mathrm{d}s\, C_-(t-s)\langle\hat{q}\rangle_s \\ &= \sum_l \frac{g_l^2}{\omega_l^2}\langle\hat{q}\rangle_t + \delta F(t) - \int_0^t \mathrm{d}s\gamma(t-s)\langle\hat{p}\rangle_s \end{aligned} \tag{28}$$

to give

$$\begin{aligned} \frac{\mathrm{d}}{\mathrm{d}t}\hat{P}_{\mathrm{S}}(t) &= -\frac{i}{\hbar}[\hat{H}_{\mathrm{S}} + \hat{V}_{\mathrm{solv}}, \hat{P}_{\mathrm{S}}(t)] - \\ &\frac{2}{\hbar^2}\int_0^t \mathrm{d}s\, C_-(t-s)\langle\hat{q}\rangle_s[\hat{q}, \hat{P}_{\mathrm{S}}(t)] + \frac{i}{\hbar}[\hat{q}, \hat{P}_{\mathrm{S}}(t)]F_{\mathrm{B}}(t) \end{aligned} \tag{29}$$

where $C_-(t)$ is the antisymmetric part of the quantum bath force correlation function, eq 13, related to the friction kernel $\gamma(t)$, $F_{\mathrm{B}}(t)$ is the fluctuation force of eq 18 in the classical limit, and $\gamma(t)$ and $\delta F(t)$ conform to the classical limit of eq 9, with $\hat{q}(0)$ replaced by $\langle\hat{q}\rangle_0$. Equation 29 has the structure of a stochastic quantum/classical Liouville equation, or quantum/classical generalized Langevin equation in the Schrödinger picture, where the dynamics of the quantum subsystem is governed by time-retarded friction and fluctuation forces, respectively, in addition to the system (solvate) Hamiltonian $\hat{H}_{\mathrm{solv}} = \hat{H}_{\mathrm{S}} + \hat{V}_{\mathrm{solv}}$. Due to the mean field coupling of the classical phase space variables to the quantum subsystem, eqs 5 and 27, the non-Markovian friction force is correlated to the history of the quantum-averaged position $\langle\hat{q}\rangle_s = \langle\Psi_{\mathrm{S}}(s)|\hat{q}|\Psi_{\mathrm{S}}(s)\rangle$ (momentum $\langle\hat{p}\rangle_s$) only. Note that eq 29 is still an exact representation of the mean field Ehrenfest dynamics for the total system, subject to model Hamiltonian (4), analogous to GLE (6).

The time-evolved system pure state vector (projector) of eqs 5, 27, and 29 depends on the history of the classical path $\mathbf{Q}(t)$ through the bath initial conditions $\mathbf{X}_0 = (\mathbf{Q}_0, \mathbf{P}_0)$, i.e., $\hat{P}_{\mathrm{S}}(t) \equiv \hat{P}_{\mathrm{S}}[\mathbf{Q}(t); t] = \hat{P}_{\mathrm{S}}[\mathbf{X}_0; t]$. Upon averaging over the classical bath canonical initial state, the reduced density operator of the quantum subsystem is obtained, $\hat{\sigma}_{\mathrm{S}}(t) = Tr_{\mathrm{B}}\{\hat{P}_{\mathrm{S}}[\mathbf{X}_0; t] \otimes \rho_{\mathrm{eq}}(\mathbf{X}_0)\} = \int \mathrm{d}\mathbf{X}_0\, \hat{P}_{\mathrm{S}}[\mathbf{X}_0; t]\rho_{\mathrm{eq}}(\mathbf{X}_0)$, where $\hat{\sigma}_{\mathrm{S}}(t_0) \equiv \hat{P}_{\mathrm{S}}(t_0)$.

To derive the second-order mean field quantum/classical master equation analogous to eqs 20, 21, we start from eq 29, simultaneously replacing $\hat{H}_{\mathrm{solv}} \to \hat{H}_{\mathrm{S}}$ and $F_{\mathrm{B}}(t) \to \delta F(t)$ (see section 2.2.2), and noting that the friction term, involving $C_-(t)$, is already second order in the system-bath interaction, while the fluctuation term is of first order. The second order accumulated effect of the classical fluctuation force $\delta F(t)$ is evaluated by integrating eq 29 to

$$\hat{P}_{\mathrm{S}}(t) = \mathcal{U}_{\mathrm{det}}(t, t_0)\hat{P}_{\mathrm{S}}(t_0) + \frac{i}{\hbar}\int_{t_0}^t \mathrm{d}s\, \mathcal{U}_{\mathrm{det}}(t, s)\, [\hat{q}, \hat{P}_{\mathrm{S}}(s)]\, \delta F(s) \tag{30}$$

and reinserting into the rhs to obtain, still formally exactly

$$\begin{aligned} \frac{\mathrm{d}}{\mathrm{d}t}\hat{P}_{\mathrm{S}}(t) &= -\frac{i}{\hbar}[\hat{H}_{\mathrm{S}}, \hat{P}_{\mathrm{S}}(t)] - \\ &\frac{2}{\hbar^2}\int_0^t \mathrm{d}s\, C_-(t-s)\langle\hat{q}\rangle_s[\hat{q}, \hat{P}_{\mathrm{S}}(t)] + \\ &\frac{i}{\hbar}[\hat{q}, \mathcal{U}_{\mathrm{det}}(t, t_0)\hat{P}_{\mathrm{S}}(t_0)]\, \delta F(t) - \\ &\frac{1}{\hbar^2}\int_{t_0}^t \mathrm{d}s\, \delta F(t)\delta F(s)\, [\hat{q}, \mathcal{U}_{\mathrm{det}}(t, s)\, [\hat{q}, \hat{P}_{\mathrm{S}}(s)]] \end{aligned} \tag{31}$$

where $\mathcal{U}_{\mathrm{det}}(t, t_0)$ is the Liouville space propagator accounting for deterministic Hamiltonian dynamics and friction effects in the quantum subsystem, and $\hat{P}_{\mathrm{S}}(t_0) \equiv \hat{\sigma}_{\mathrm{S}}(t_0)$.

An overall second-order scheme implies $\mathcal{U}_{\mathrm{det}}(t, s) \to \mathcal{U}_{\mathrm{S}}(t, s)$ everywhere ($t_0 \leq s < t$), and $\hat{P}_{\mathrm{S}}(s) \to \hat{P}_{\mathrm{S}}^{(0)}(s) = \mathcal{U}_{\mathrm{S}}(s, t_0)\hat{P}_{\mathrm{S}}(t_0) \equiv \hat{\sigma}_{\mathrm{S}}^{(0)}(s)$ in the term containing the fluctuation force to second order. However, in the friction term, containing $C_-(t)$, the replacement $\hat{P}_{\mathrm{S}}(t) \to \hat{\sigma}_{\mathrm{S}}^{(0)}(t)$ is not sensible, since the expectation $\langle\hat{q}\rangle_s = Tr\{\hat{P}_{\mathrm{S}}(s)\hat{q}\}$ and thus the friction force operating on $\hat{P}_{\mathrm{S}}(t)$ reflect the single-trajectory mean field correlation between the quantum system and its classical environment. Finally, invoking the *short bath correlation time* approximation, $\hat{\sigma}_S^{(0)}(s) \simeq \mathscr{U}_S^\dagger(t, s)\hat{\sigma}_S^{(0)}(t)$ and $\langle\hat{q}\rangle_s = Tr\{\hat{P}_S(s)\hat{q}\} \simeq Tr\{\hat{q}\ \mathscr{U}_S^\dagger(t, s)\hat{P}_S(t)\} = \langle\hat{q}_S(s - t)\rangle_t$, where $\hat{q}_S(s - t) = \mathscr{U}_S(t, s)\ \hat{q}$.

Upon taking the classical statistical average over bath initial conditions, with $\langle\delta F(t)\rangle_B = 0$ and $\langle\delta F(t)\delta F(s)\rangle_B = C_{cl}(t - s)$, the resultant mean field quantum/classical generalized master equation (QCME), in its time-retarded (i) and convolutionless forms (ii), is

$$\begin{aligned}\frac{d}{dt}\hat{\sigma}_S(t) &= \int d\mathbf{X}_0\ \rho_{eq}(\mathbf{X}_0)\frac{d}{dt}\hat{P}_S[\mathbf{X}_0; t] \\ &\cong -\frac{i}{\hbar}[\hat{H}_S, \hat{\sigma}_S(t)] - \\ &\quad \frac{1}{\hbar^2}\int_0^t ds\ C_{cl}(t - s)\ [\hat{q}, \mathscr{U}_S(t, s)\ [\hat{q}, \hat{\sigma}_S^{(0)}(s)]] - \\ &\qquad \frac{2}{\hbar^2}\int_0^t ds\ C_-(t - s)\ \langle\langle\hat{q}\rangle_s[\hat{q}, \hat{P}_S(t)]\rangle_B \quad \text{(i)} \\ &\simeq -\frac{i}{\hbar}[\hat{H}_S, \hat{\sigma}_S(t)] - \frac{1}{\hbar^2}[\hat{q}, [\hat{\Lambda}_{cl}(t), \hat{\sigma}_S^{(0)}(t)]] - \\ &\qquad \frac{2}{\hbar^2}\langle\langle\hat{\Lambda}_-(t)\rangle_t[\hat{q}, \hat{P}_S(t)]\rangle_B \quad \text{(ii)} \qquad (32)\end{aligned}$$

where $\hat{\Lambda}_{cl}(t) = \int_0^t d\tau\ C_{cl}(\tau)\ \hat{q}_S(-\tau)$ and $\hat{\Lambda}_-(t) = \int_0^t d\tau\ C_-(\tau)\ \hat{q}_S(-\tau)$, $\langle\hat{q}\rangle_s$ and $\langle\hat{\Lambda}_-(t)\rangle_t$ are single-trajectory expectations, and $\langle...\rangle_B$ represents the average over bath initial conditions. Equation 32, although termed master equation here and in the following, is not a closed equation for $\hat{\sigma}_S(t)$, due to the appearance of $\hat{P}_S(t)$ and expectations calculated therefrom.

The mean field quantum/classical master equation of eq 32 is our central result to be compared with the QME of eq 21. Obviously, the mean field Ehrenfest equations of motion imply the replacements

$$\hat{\Lambda}_+(t) \rightarrow \hat{\Lambda}_{cl}(t)$$

$$[\hat{q}, [\hat{\Lambda}_-(t), \hat{\rho}_S^{(0)}(t)]_+] \rightarrow [\hat{q}, \langle[\langle\hat{\Lambda}_-(t)\rangle_t, \hat{P}_S(t)]_+\rangle_B] \qquad (33)$$

Although the first replacement, $C_+(t) \rightarrow C_{cl}(t) = \mu k_B T\gamma(t)$, changes the type of asymptotic equilibrium from quantum to classical (see below for details), the second, by itself, must lead to a loss of quantum detailed balance, since the combined effect of both operators $\hat{\Lambda}_+(t)$, $\hat{\Lambda}_-(t)$ (or $\hat{\Lambda}(t)$, $\hat{\Lambda}^\dagger(t)$) is necessary to obtain the correct transition rates, eqs 23 and 24, in the incoherent hopping regime (Pauli QME, Golden Rule). In the fully coherent (quasi-classial) wave packet regime only, as will be demonstrated below, does the mean field QCME produce sensible results.

In the following, we examine the implications of QCME (32) for energy relaxation restricting ourselves to the damped harmonic oscillator, and show that an ensemble (with respect to classical bath initial conditions!) of coherent states of the harmonic oscillator evolving subject to the underlying stochastic Liouville eq 29 represents the only situation, where the mean field QCME gives physically meaningful results.

Operator expectations $\langle\hat{O}\rangle = Tr\{\hat{\sigma}_S(t)\hat{O}\}$ obtained from the mean field QCME imply single trajectory (conditional) pure state, $\langle\hat{O}\rangle_t$, and subsequent classical bath ensemble averaging, $\langle...\rangle_B$. Wherever necessary, the occurrence of a sequence of averages is made explicit, through $\langle\hat{O}\rangle = \langle Tr\{\hat{P}_S(t)\hat{O}\}\rangle_B = \langle\langle\hat{O}\rangle_t\rangle_B$, to avoid ambiguity.

*2.3.1. Energy Relaxation.* From QME (21) it readily follows that

$$\begin{aligned}\frac{d}{dt}\langle\hat{H}_S\rangle &= \frac{i}{\hbar}\{\langle[\hat{v}, \hat{\Lambda}_+(t)]\rangle + \langle[\hat{v}, \hat{\Lambda}_-(t)]_+\rangle\} \\ &= \frac{i}{\hbar}\int_0^t d\tau\{C_+(\tau)\langle[\hat{v}, \hat{q}_S(-\tau)]\rangle + \\ &\qquad C_-(\tau)\langle[\hat{v}, \hat{q}_S(-\tau)]_+\rangle\} \qquad (34)\end{aligned}$$

where $\hat{v} = \hat{p}/\mu = (i/\hbar)[\hat{H}_S, \hat{q}]$ and $\hat{q}_S(-\tau) = \hat{q}\cos\omega_0\tau - (\hat{v}/\omega_0)\sin\omega_0\tau$. With

$$\begin{aligned}\frac{i}{\hbar}\langle[\hat{v}, \hat{\Lambda}_+(t)]\rangle &= \frac{1}{2\mu}\int_{-t}^t d\tau\ C_+(\tau)\cos\omega_0\tau \\ \frac{i}{\hbar}\langle[\hat{v}, \hat{\Lambda}_-(t)]_+\rangle &= \frac{i}{\hbar\mu}\langle[\hat{q}, \hat{p}]_+\rangle\int_0^t d\tau\ C_-(\tau)\cos\omega_0\tau - \\ &\qquad \frac{2i\langle\hat{p}^2\rangle}{\mu^2\hbar\omega_0}\int_0^t d\tau\ C_-(\tau)\sin\omega_0\tau \\ &\cong \frac{\langle\hat{p}^2\rangle}{\mu^2\hbar\omega_0}\int_{-t}^t d\tau\ C_-(\tau)e^{-i\omega_0\tau} \qquad (35)\end{aligned}$$

the rate of energy relaxation at long times, $0 \ll t \rightarrow \infty$, is given by[58,59]

$$\begin{aligned}\frac{d}{dt}\langle\hat{H}_S\rangle &\cong \frac{1}{2\mu}\hat{C}_+(\omega_0) + \frac{\langle\hat{p}^2\rangle}{\mu^2\hbar\omega_0}\hat{C}_-(\omega_0) \\ &= -\frac{\hat{\gamma}(\omega_0)}{2}\left\{\frac{\langle\hat{p}^2\rangle}{\mu} - \bar{E}(\omega_0, T)\right\} \simeq \\ &\qquad -\frac{\hat{\gamma}(\omega_0)}{2}\{\langle\hat{H}_S\rangle - \bar{E}(\omega_0, T)\} \qquad (36)\end{aligned}$$

where $\bar{E}(\omega_0, T) = \hbar\omega_0\{\bar{n}(\omega_0, T) + 1/2\}$ and the relations $\hat{C}_-(\omega_0) = -\mu\hbar\omega_0\ \hat{\gamma}(\omega_0)/2$, eq 13, and $\hat{C}_+(\omega_0) = -\{2\bar{n}(\omega_0, T) + 1\}\ \hat{C}_-(\omega_0)$, eq 15, have been used. Note that in the derivation of eq 36 a bath-induced frequency shift, appearing in eq 35 ($[\hat{q}, \hat{p}]_+$ term), has been neglected first (line 1), and then a secular/rotating wave approximation[58,59] invoked (line 2).

From QCME (32), instead, we obtain

$$\begin{aligned}\frac{d}{dt}\langle\hat{H}_S\rangle &= \frac{i}{\hbar}\{\langle[\hat{v}, \hat{\Lambda}_{cl}(t)]\rangle + \langle\langle[\hat{v}, \langle\hat{\Lambda}_-(t)\rangle_t]_+\rangle_t\rangle_B\} \\ &\cong \frac{1}{2\mu}\int_{-t}^t d\tau\ C_{cl}(\tau)\ e^{-i\omega_0\tau} + \frac{\langle\langle\hat{p}\rangle_t^2\rangle_B}{\mu^2\hbar\omega_0}\int_{-t}^t d\tau\ C_-(\tau)e^{-i\omega_0\tau} \\ &\qquad (37)\end{aligned}$$

and at long times, $t \rightarrow \infty$

$$\begin{aligned}\frac{d}{dt}\langle\hat{H}_S\rangle &\cong \frac{1}{2\mu}\hat{C}_{cl}(\omega_0) + \frac{\langle\langle\hat{p}\rangle_t^2\rangle_B}{\mu^2\hbar\omega_0}\hat{C}_-(\omega_0) \\ &= -\frac{\hat{\gamma}(\omega_0)}{2}\left\{\frac{\langle\langle\hat{p}\rangle_t^2\rangle_B}{\mu} - k_B T\right\} \simeq \\ &\qquad -\frac{\hat{\gamma}(\omega_0)}{2}\{\langle E_{cl}(t)\rangle_B - \bar{E}_{cl}(T)\} \qquad (38)\end{aligned}$$

using $\hat{C}_{cl}(\omega_0) = \mu k_B T\hat{\gamma}(\omega_0)$, eqs 10 and 12, and $\hat{C}_-(\omega_0) = -\mu\hbar\omega_0\ \hat{\gamma}(\omega_0)/2$, eq 13.

Comparison of eqs 36 and 38 shows that, although the mean rate of energy relaxation is unchanged (being a property of the model Hamiltonian), the mean field QCME drives the quantum subsystem to a classical equilibrium state, where however the nonequilibrium energy is measured "classically", i.e., in terms of single-trajectory expectations of position and momentum. The only type of quantum state, for which this is physically meaningful, is a minimum uncertainty state (coherent state of the harmonic oscillator) to which we turn below. In contrast, for quantum states delocalized in phase space, the mean energy is encoded in the detailed (nodal) structure of the wave packet or density matrix, and not simply related to the quantum first moments of the phase space variables.

*2.3.2. Coherent State Evolution.* The stochastic quantum Liouville eq 29 with $\hat{H}_S = \hbar\omega_0(\hat{a}^+\hat{a} + 1/2)$ describes a forced harmonic oscillator subject to linear damping and fluctuation, where

$$\frac{d}{dt}\langle\hat{q}\rangle_t = \frac{\langle\hat{p}\rangle_t}{\mu}$$
$$\frac{d}{dt}\langle\hat{p}\rangle_t = -\mu\omega_0^2\langle\hat{q}\rangle_t - \int_0^t ds\, \gamma(t-s)\langle\hat{p}\rangle_s + \delta F(t) \quad (39)$$

or

$$\frac{d}{dt}\langle\hat{a}\rangle_t = -i\omega_0\langle\hat{a}\rangle_t - \frac{1}{2}\int_0^t ds\, \gamma(t-s)\{\langle\hat{a}\rangle_s - \langle\hat{a}^+\rangle_s\} + \frac{i\,\delta F(t)}{\sqrt{2\mu\hbar\omega_0}} \quad (40)$$

in terms of boson-type second quantization operators. Consequently, a coherent state (minimum uncertainty Gaussian wave packet)

$$|\alpha(t)\rangle = \exp\left\{-\frac{1}{2}|\alpha(t)|^2 + \alpha(t)\,\hat{a}^+\right\}|0\rangle \quad \hat{a}|\alpha(t)\rangle = \alpha(t)|\alpha(t)\rangle$$
$$\langle\alpha(t)| = \langle 0|\exp\left\{-\frac{1}{2}|\alpha(t)|^2 + \alpha^*(t)\,\hat{a}\right\} \quad \langle\alpha(t)|\hat{a}^+ = \langle\alpha(t)|\alpha^*(t) \quad (41)$$

with the properties[60]

$$\frac{\partial|\alpha(t)\rangle}{\partial\alpha(t)} = \left\{-\frac{\alpha^*(t)}{2} + \hat{a}^+\right\}|\alpha(t)\rangle \quad \frac{\partial|\alpha(t)\rangle}{\partial\alpha^*(t)} = \left\{-\frac{\alpha(t)}{2}\right\}|\alpha(t)\rangle$$
$$\frac{\partial\langle\alpha(t)|}{\partial\alpha^*(t)} = \langle\alpha(t)|\left\{-\frac{\alpha(t)}{2} + \hat{a}\right\} \quad \frac{\partial\langle\alpha(t)|}{\partial\alpha(t)} = \langle\alpha(t)|\left\{-\frac{\alpha^*(t)}{2}\right\} \quad (42)$$

will evolve without changing (the product of) its position and momentum uncertainties.[61] Via the chain rule

$$\frac{d}{dt}|\alpha(t)\rangle = \frac{\partial|\alpha(t)\rangle}{\partial\alpha(t)}\frac{d}{dt}\alpha(t) + \frac{\partial|\alpha(t)\rangle}{\partial\alpha^*(t)}\frac{d}{dt}\alpha^*(t) \quad (43)$$

using eqs 40−42 together with eqs 28 and 29, it is straightforward (although a little tedious) to show that

$$\frac{d}{dt}\langle\alpha(t)|\hat{P}_S(t)|\alpha(t)\rangle = \langle\dot{\alpha}(t)|\hat{P}_S(t)|\alpha(t)\rangle + \langle\alpha(t)|\hat{P}_S(t)|\dot{\alpha}(t)\rangle + \langle\alpha(t)|\left\{\frac{d}{dt}\hat{P}_S(t)\right\}|\alpha(t)\rangle \equiv 0 \quad (44)$$

if $\hat{P}_S(t) \equiv |\alpha(t)\rangle\langle\alpha(t)|$. Thus, the probability $Tr\{\hat{P}_S(t)|\alpha(t)\rangle\langle\alpha(t)|\} = \langle\alpha(t)|\hat{P}_S(t)|\alpha(t)\rangle$ for staying in the coherent state $\hat{P}_\alpha(t) \equiv |\alpha(t)\rangle\langle\alpha(t)|$ with

$$\frac{d}{dt}\alpha(t) = -i\omega_0\alpha(t) - \frac{1}{2}\int_0^t ds\, \gamma(t-s)\{\alpha(s) - \alpha^*(s)\} + \frac{i\,\delta F(t)}{\sqrt{2\mu\hbar\omega_0}} \quad (45)$$

is conserved along a single mean field quantum/classical trajectory.

Equation 38 then reads

$$\hbar\omega_0\frac{d}{dt}\langle\hat{a}^+\hat{a}\rangle \simeq -\frac{\hat{\gamma}(\omega_0)}{2}\hbar\omega_0\left\{\langle|\alpha(t)|^2\rangle_B - \frac{k_BT}{\hbar\omega_0}\right\} \quad (46)$$

where

$$\hbar\omega_0|\alpha(t)|^2 = \frac{\langle\hat{p}\rangle_\alpha^2}{2\mu} + \frac{\mu\omega_0^2}{2}\langle\hat{q}\rangle_\alpha^2 \equiv E_{cl}(t)$$

which is the classical limit of eqs 36 and 26. Thus, subject to the mean field Ehrenfest equations of motion, an ensemble of minimum uncertainty Gaussian wave packets settles into a quasi-classical equilibrium state of mean energy $\hbar\omega_0\bar{n}_{cl}(\omega_0, T) = k_BT$ (provided anharmonicity does not play a role), but the discrete energy levels only apparently lose their meaning (see section 3.2.3).

However, in the case of a general quantum initial state (e.g., an energy eigenstate of the HO), the situation is even worse, because the mean field correlation between subsystems implies that the nonequilibrium energy is measured classically, as shown above (section 2.3.1). As a result, all quantum initial states other than minimum uncertainty states must settle into an unphysical asymptotic equilibrium state, depending on their apparent classical initial energy. This will be demonstrated in numerical simulations with a quantum harmonic oscillator initialized in one of its energetically excited eigenstates.

When anharmonicity of the potential energy surface can no longer be neglected, it is expected that even a coherent state ensemble will asymptotically fail to obey quasi-classical equilibrium statistics, because of the inevitable broadening of the wave packet in position and momentum space during a single quantum/classical trajectory.

## 3. Simulation Results

### 3.1. Model Parameterization and Simulations.

In the simulations, an ohmic spectral density of bath oscillators[29,44]

$$J(\omega) \equiv \frac{\pi}{2}\sum_l \frac{g_l^2}{\omega_l}\delta(\omega - \omega_l) = \mu\gamma\omega e^{-\omega/\omega_c} \quad (47)$$

with exponential cutoff has been assumed, where the fluctuating force correlation function is given by

$$C(t) = \frac{1}{\pi}\int_0^\infty d\omega\, \hbar J(\omega)\{(\bar{n}(\omega, T) + 1)\, e^{-i\omega t} + \bar{n}(\omega, T)\, e^{+i\omega t}\}$$
$$C_{cl}(t) = k_BT\frac{2}{\pi}\int_0^\infty d\omega\, \frac{J(\omega)}{\omega}\cos\omega t \quad (48)$$

and the correlation spectrum ($\omega \geq 0$) becomes

$$\hat{C}(\omega) = 2\hbar\, J(\omega)\, \bar{n}(\omega, T) \equiv 2\mu\gamma\, \hbar\omega\bar{n}(\omega, T)\, e^{-\omega/\omega_c}$$
$$\hat{C}_{cl}(\omega) = 2k_BT\frac{J(\omega)}{\omega} \equiv 2\mu\gamma\, k_BT\, e^{-\omega/\omega_c} \quad (49)$$

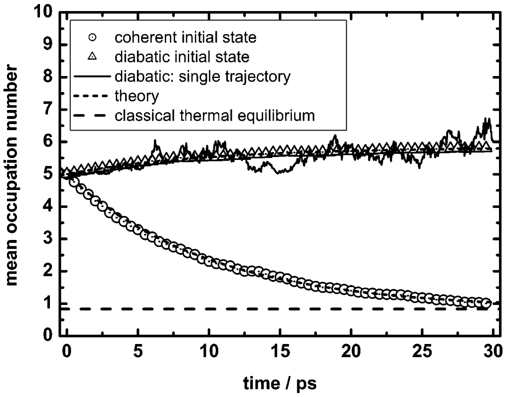

**Figure 1.** Decay of mean vibrational quantum number (occupation number) for an ensemble of coherent and diabatic initial states of the damped harmonic oscillator, respectively, toward mean field Ehrenfest quantum/classical equilibrium. For the theoretical analysis, see text.

For the system oscillator a harmonic frequency of $\omega_0/2\pi = 250$ cm$^{-1}$ has been chosen, and the bath spectral density adjusted such that $\hat{\gamma}(\omega_0)/2 \cong 0.1$ ps$^{-1}$ ($\gamma = 1.0$ ps$^{-1}$, $\omega_c/2\pi = 108.574$ cm$^{-1}$), and discretized using 2000 classical oscillators in the range $0-10\omega_c$. The choice of a rather low-frequency system oscillator helps avoiding small integration steps, while classical and quantum equilibrium statistics are still distinguishable.

An ensemble of 400 quantum/classical nonequilibrium trajectories starting from a mean energy of $\langle\hat{n}\rangle_0 = 5$ vibrational quanta and a classical canonical distribution of bath initial conditions at $T = 300$ K has been run for up to 30 ps, where the initial wave function was chosen to be (i) a coherent state, with initial phase $\alpha(0) = +\sqrt{\langle\hat{n}\rangle_0}$, or (ii) an eigenstate $|n_0\rangle = |5\rangle$ of $\hat{H}_S$ (diabatic state). The heat capacity $C_V = 2000k_B$ of the classical bath ensures that the rise (change) of bath temperature is kept below 1 K.

The classical canonical statistics of bath initial conditions was obtained by Monte Carlo sampling for each bath oscillator from an exponential distribution of energy, $\rho_{eq}(E) \propto e^{-\beta E}$, and then assigning a random vibrational phase at given energy. The mean field Ehrenfest equations of motion, eqs 2 and 5, were solved numerically via the symplectic scheme (3), using a combination of $\hat{H}_S$ ($\hat{H}_{solv}$) eigenstate and position space (sinc-DVR) representations for the quantum split propagator,[46] whereas the classical mechanical part is identical to the leapfrog algorithm.[62]

**3.2. Results and Discussion.** *3.2.1. Energy Relaxation.* In Figure 1 is shown the relaxation of mean occupation number $\langle\hat{n}\rangle$ (mean energy) for different quantum initial conditions, subject to the quantum/classical equations of motion. Obviously, the ensemble of coherent initial states exhibits energy dissipation and settles into a state of lower energy, while the ensemble of diabatic initial states does not, but relaxes toward a state of higher energy. Comparison to the theoretical prediction based on eqs 38 and 46 confirms that the energy relaxation time is $\tau_{VER} \cong 10$ ps in both cases. Although the asymptotic equilibrium for the coherent state ensemble corresponds to $\hbar\omega_0\langle\hat{n}\rangle \rightarrow \hbar\omega_0\bar{n}_{cl}(\omega_0, T) = k_BT$, i.e., 'classical energy statistics' (see below, however), it is $\hbar\omega_0\langle\hat{n}\rangle \rightarrow \hbar\omega_0\langle\hat{n}\rangle_0 + k_BT$ for the ensemble of diabatic initial states. Both results are easily understood on the basis of eq 38 in terms of an effectively classical dynamical correlation between subsystems, where the classical energy assigned to the quantum wave packet is $E_{cl}(t) = \hbar\omega_0|\langle\hat{a}\rangle_t|^2$. For a coherent state $E_{cl}(t) = \hbar\omega_0|\alpha(t)|^2 \equiv \hbar\omega_0\langle\hat{n}\rangle_t$, for a diabatic initial state, however, $E_{cl}(t) \neq \hbar\omega_0\langle\hat{n}\rangle_t$ and in particular $E_{cl}(0) = 0$. For the same reason, an oscillator starting in an energy eigenstate does not fall below its initial quantum energy $\hbar\omega_0$ ($\langle\hat{n}\rangle_0 + 1/2$) even during a single mean field quantum/classical trajectory, as also shown in Figure 1. Since the quantum wave packet is monitored by the environment through $\langle\hat{q}\rangle_t$ ($\langle\hat{p}\rangle_t$), the initial energy eigenstate behaves like a classically motionless ("cold") state of the oscillator, whereas its true quantum energy is not detected by the classical heat bath. Consequently, thermal relaxation of the oscillator corresponds to a heating process. As shown recently,[38] for an initial superposition state intermediate between a pure $\hat{H}_S$ eigenstate and a coherent state of the harmonic oscillator, only the classical part $E_{cl}(0) = \hbar\omega_0|\langle\hat{a}\rangle_0|^2$ of the initial excess energy can be dissipated into the classical heat bath, while the remaining quantum part is "inert" with respect to dissipation.

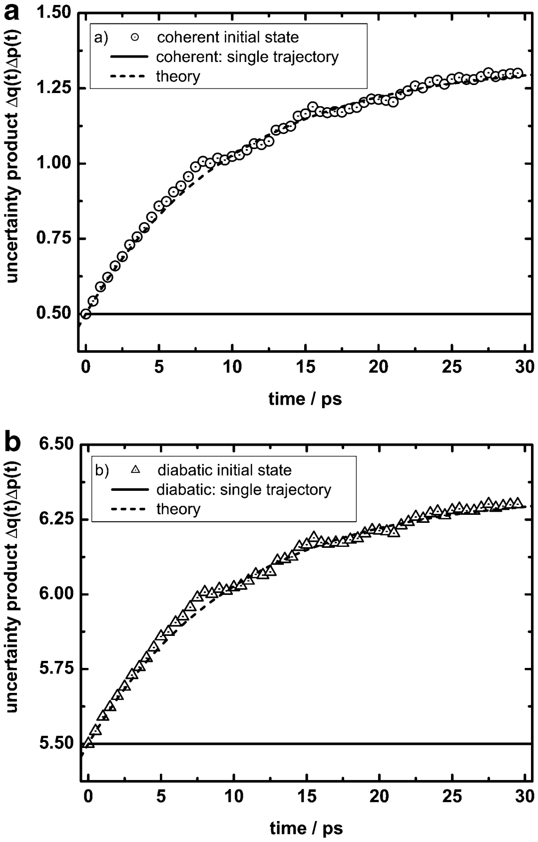

**Figure 2.** Time evolution of the product of (ensemble averaged) position and momentum uncertainties (in units of $\hbar$) for a) an ensemble of coherent initial states, b) an ensemble of diabatic initial states. See text, for the theoretical analysis.

Using the term 'classical energy statistics' above, we referred to the first moment of the respective equilibrium energy distribution only (see section 3.2.3).

*3.2.2. Decoherence.* Energy relaxation of the open quantum subsystem oscillator is accompanied by phase relaxation (dephasing), or decoherence in the energy representation, which in the present case corresponds to the absence of pure dephasing;[58] that is, the phase (position and momentum) relaxation time is $\tau_2 = 2\tau_1$, where $\tau_1^{-1} \simeq \hat{\gamma}(\omega_0)/2$ is the rate of energy dissipation. As an additional global measure of dephasing, the decay of the position and momentum variances toward thermal equilibrium may be used, which in turn must be related to energy relaxation. In Figure 2a,b is shown the time evolution of the product of ensemble averaged vs single trajectory position and momentum uncertainties, $\Delta q\Delta p$ in units of $\hbar$, where $\Delta q = (\langle\hat{q}^2\rangle - \langle\hat{q}\rangle^2)^{1/2} \equiv \sigma_q$ and $\Delta p = (\langle\hat{p}^2\rangle - \langle\hat{p}\rangle^2)^{1/2} \equiv \sigma_p$, starting from the different quantum initial conditions, (a) a coherent state (constructed from eigenstates of $\hat{H}_S$), and (b) a diabatic state, respectively. Apart from the different offsets (origins at time zero), the temporal behavior is the same in both cases, where relaxation toward some equilibrium value is observed for the ensemble averaged quantities, to be analyzed below. The time-independence (on a coarse-grained time scale) of the single trajectory uncertainty product is immediately clear from the analysis in section 2.3.2. On a sub-ps time scale, weak amplitude reversible oscillations are observed (not shown), due to the presence of the quadratic $\hat{V}_{\mathrm{solv}}$ term in the model Hamiltonian. Note that the same sequence of random numbers has been used in both cases to initialize the classical bath oscillators such that the remaining noise leaves the same "fingerprint" in parts a and b of Figure 2.

From the convolutionless quantum master equation (QME), eqs 20 and 21, we obtain the following equations for the first and second moments of phase space variables,[58,59] valid at long times ($0 \ll t < \infty$)

$$\frac{\mathrm{d}}{\mathrm{d}t}\langle\hat{q}\rangle = \frac{\langle\hat{p}\rangle}{\mu}$$

$$\frac{\mathrm{d}}{\mathrm{d}t}\langle\hat{p}\rangle \simeq -\mu\omega_0^2\langle\hat{q}\rangle - \frac{\hat{\gamma}(\omega_0)}{2}\langle\hat{p}\rangle \qquad (50)$$

$$\frac{\mathrm{d}}{\mathrm{d}t}\langle\hat{q}^2\rangle = \frac{\langle[\hat{q},\hat{p}]_+\rangle}{\mu}$$

$$\frac{\mathrm{d}}{\mathrm{d}t}\langle\hat{p}^2\rangle \simeq -\mu\omega_0^2\langle[\hat{q},\hat{p}]_+\rangle - \hat{\gamma}(\omega_0)\{\langle\hat{p}^2\rangle - \mu\bar{E}(\omega_0, T)\}$$

$$\frac{\mathrm{d}}{\mathrm{d}t}\langle[\hat{q},\hat{p}]_+\rangle \simeq \frac{2\langle\hat{p}^2\rangle}{\mu} - 2\mu\omega_0^2\langle\hat{q}^2\rangle - \frac{\hat{\gamma}(\omega_0)}{2}\langle[\hat{q},\hat{p}]_+\rangle \qquad (51)$$

from which the evolution equations for the variances $\sigma_q^2(t) = \langle\hat{q}^2\rangle - \langle\hat{q}\rangle^2$ and $\sigma_p^2(t) = \langle\hat{p}^2\rangle - \langle\hat{p}\rangle^2$, and the covariance $C_{q,p}(t) = (1/2)\langle[\hat{q},\hat{p}]_+\rangle - \langle\hat{q}\rangle\langle\hat{p}\rangle$ follow.

From the mean field quantum/classical master equation (QCME), eq 32, we obtain eq 50 for the first moments and

$$\frac{\mathrm{d}}{\mathrm{d}t}\langle\hat{q}^2\rangle = \frac{\langle[\hat{q},\hat{p}]_+\rangle}{\mu}$$

$$\frac{\mathrm{d}}{\mathrm{d}t}\langle\hat{p}^2\rangle \simeq -\mu\omega_0^2\langle[\hat{q},\hat{p}]_+\rangle - \hat{\gamma}(\omega_0)\{\langle\langle\hat{p}\rangle_t^2\rangle_{\mathrm{B}} - \mu k_{\mathrm{B}}T\}$$

$$\frac{\mathrm{d}}{\mathrm{d}t}\langle[\hat{q},\hat{p}]_+\rangle \simeq \frac{2\langle\hat{p}^2\rangle}{\mu} - 2\mu\omega_0^2\langle\hat{q}^2\rangle - \frac{\hat{\gamma}(\omega_0)}{2}\langle\langle[\hat{q},\langle\hat{p}\rangle_t]_+\rangle_t\rangle_{\mathrm{B}} \qquad (52)$$

for the second moments, which is the quasi-classical limit of (51) with the replacements $\langle\hat{p}^2\rangle \rightarrow \langle\langle\hat{p}\rangle_t^2\rangle_{\mathrm{B}}$ and $\langle[\hat{q},\hat{p}]_+\rangle \rightarrow \langle\langle[\hat{q},\langle\hat{p}\rangle_t]_+\rangle_t\rangle_{\mathrm{B}} = 2\langle\langle\hat{q}\rangle_t\langle\hat{p}\rangle_t\rangle_{\mathrm{B}}$ on the rhs of lines 2 and 3, respectively. Thus, the equations of motion for the variances read

$$\frac{\mathrm{d}}{\mathrm{d}t}\sigma_q^2(t) = 2\frac{C_{q,p}(t)}{\mu}$$

$$\frac{\mathrm{d}}{\mathrm{d}t}\sigma_p^2(t) \simeq -2\mu\omega_0^2\,C_{q,p}(t) - \hat{\gamma}(\omega_0)\{\langle\langle\hat{p}\rangle_t^2\rangle_{\mathrm{B}} - \langle\hat{p}\rangle^2 - \mu k_{\mathrm{B}}T\}$$

$$\frac{\mathrm{d}}{\mathrm{d}t}C_{q,p}(t) \simeq \frac{\sigma_p^2(t)}{\mu} - \mu\omega_0^2\,\sigma_q^2(t) - \frac{\hat{\gamma}(\omega_0)}{2}\{\langle\langle\hat{q}\rangle_t\langle\hat{p}\rangle_t\rangle_{\mathrm{B}} - \langle\hat{q}\rangle\langle\hat{p}\rangle\} \qquad (53)$$

where on the rhs $\sigma_p^2(t)$ and $C_{q,p}(t)$ appear as their quasi-classical counterparts. At thermal equilibrium, the variances obtained from the QME (20 and 21) must assume the values $\sigma_q^2 = \bar{E}(\omega_0, T)/\mu\omega_0^2$, $\sigma_p^2 = \mu\bar{E}(\omega_0, T)$ and $C_{\mathrm{q,p}} = 0$.[58] Therefore, it is concluded that, subject to the mean field Ehrenfest equations of motion, $\sigma_q^2(t)$ and $\sigma_p^2(t)$ must relax toward the quasi-classical equilibrium $\sigma_q^2(t) \rightarrow k_{\mathrm{B}}T/\mu\omega_0^2 + \sigma_q^2(0)$ and $\sigma_p^2(t) \rightarrow \mu k_{\mathrm{B}}T + \sigma_p^2(0)$ depending on their initial values, with the damping rate $\hat{\gamma}(\omega_0)/2$, and hence $\sigma_q(t)\sigma_p(t) \rightarrow k_{\mathrm{B}}T/\omega_0 + \hbar(n_0 + 1/2)$ according to

$$\sigma_q(t)\,\sigma_p(t) = \hbar\left\{-\frac{k_{\mathrm{B}}T}{\hbar\omega_0}\right\}\exp\left\{-\frac{\hat{\gamma}(\omega_0)}{2}t\right\} + \hbar\left\{\frac{k_{\mathrm{B}}T}{\hbar\omega_0} + \left(n_0 + \frac{1}{2}\right)\right\} \qquad (54)$$

instead of

$$\sigma_q(t)\,\sigma_p(t) \simeq \hbar\{n_0 - \bar{n}(\omega_0, T)\}\exp\left\{-\frac{\hat{\gamma}(\omega_0)}{2}t\right\} + \hbar\left\{\bar{n}(\omega_0, T) + \frac{1}{2}\right\} \qquad (55)$$

subject to the QME, where (a) $n_0 = 0$ for the coherent initial state and (b) $n_0 = \langle\hat{n}\rangle_0 = 5$ for the diabatic initial state. Comparing the analysis with the quantum/classical simulation results, also shown in Figure 2a,b, gives excellent agreement, given the finite ensemble size. Note that these findings are in accord with the results on energy relaxation in the previous subsection. Again, only for the ensemble of coherent initial states is the quasi-classical nature of the phase relaxation physically meaningful, where eq 54 for $n_0 = 0$ is the quasi-classical limit of eq 55. For the ensemble of initial energy eigenstates (diabatic states) with $n_0 > \bar{n}(\omega_0, T)$, the relaxation of the position-momentum uncertainty product according to eq 55 should correspond to a localization in position/momentum space. Under the mean field equations of motion, however, the delocalized nature of the wave function is not detected by the classical environment. Even on the single-trajectory level, the uncertainty product is not allowed to fall below its initial value, as observed for the mean energy.

From the perspective of quantum-classical correspondence, eq 53 is equivalent to the time evolution of second moments as obtained from the Klein-Kramers Fokker−Planck equation,[52,58,59,63] except for the presence of a minimal position-momentum indeterminacy.

In summary, energy relaxation and decoherence subject to mean field Ehrenfest quantum/classical dynamics suffer from the unphysical survival of position/momentum-delocalized superposition states, as a result of the essentially classical dynamical correlation between the respective subsystems. The method gives physically meaningful results only for wave packets which remain in a state of maximum localization relative to the form of system-environment interaction. Due to the extremely localized nature of classical mechanics, there exists no mechanism in mean field QCMD by which the environment is able to monitor and destroy delocalized states of the quantum subsystem.

*3.2.3. Population Relaxation.* In Figure 3a,b, the nature of population relaxation observed for the coherent initial state ensemble (3a) is contrasted with that obtained for the ensemble of diabatic initial states (3b). Although in the former case relaxation toward a canonical equilibrium distribution is observed (see below), a (biased) diffusion-type relaxation in energy space toward an obviously noncanonical equilibrium is obtained in the latter, indicating a breakdown of quantum detailed

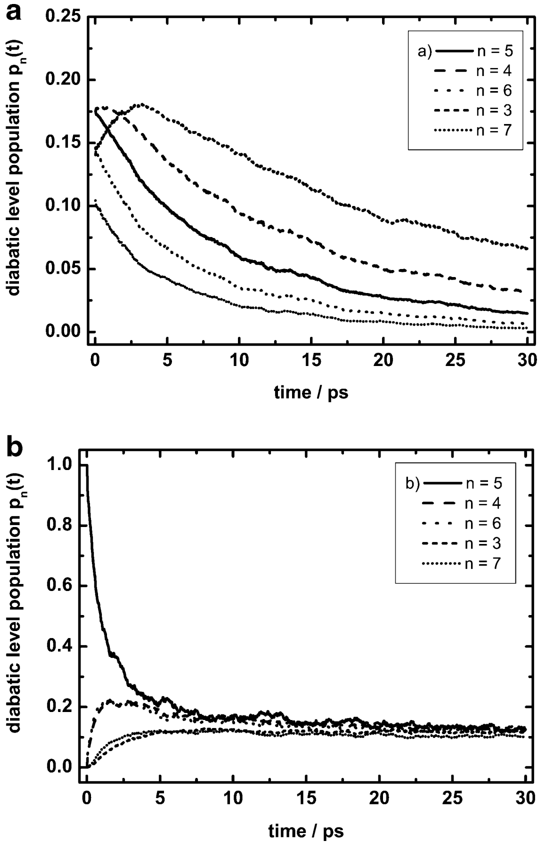

**Figure 3.** Decay of diabatic energy level populations ($n = 5, 5 \pm 1, 5 \pm 2$) for (a) an ensemble of coherent initial states and (b) an ensemble of diabatic initial states.

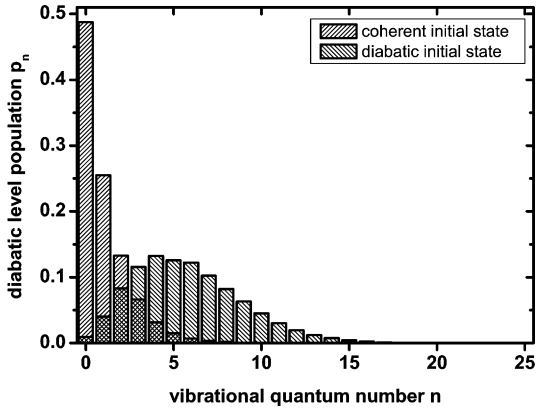

**Figure 4.** Diabatic energy level populations close to mean field quantum/classical equilibrium ($t = 30$ ps).

balance. This is also illustrated in Figure 4, comparing the level populations at long times (30 ps). As shown recently,[38] in the coherent initial state case, population relaxation is in accord with a Pauli QME treatment (or the secular approximation), eqs 22−25, where the mean thermal occupation number $\bar{n}(\omega_0, T)$ appearing in the expressions for the state-to-state transition rates, eq 25, is replaced by its classical limit $\bar{n}_{\mathrm{cl}}(\omega_0, T) = (\beta\hbar\omega_0)^{-1}$, leading to an apparently quantum thermal equilibrium distribution[60]

$$p_n = \left(\frac{\bar{n}}{\bar{n}+1}\right)^n \frac{1}{\bar{n}+1} \rightarrow \left(\frac{k_{\mathrm{B}}T}{k_{\mathrm{B}}T + \hbar\omega_0}\right)^n \frac{\hbar\omega_0}{k_{\mathrm{B}}T + \hbar\omega_0} \quad (56)$$

Note that, although the mean thermal energy in excess of the zero-point level, $\hbar\omega_0\bar{n}_{\mathrm{cl}}(\omega_0, T) = k_{\mathrm{B}}T$, is in accord with classical statistical mechanics, the mean squared energy fluctuation following from eq 56, $(\hbar\omega_0)^2\bar{n}_{\mathrm{cl}}(\bar{n}_{\mathrm{cl}} + 1) = k_{\mathrm{B}}T(k_{\mathrm{B}}T + \hbar\omega_0) > (k_{\mathrm{B}}T)^2$, is even larger than predicted by classical equilibrium statistics at finite temperature. The latter is an unavoidable consequence of the quantum mechanical description of the respective subsystem in mean field Ehrenfest quantum/classical dynamics, as has been confirmed by monitoring the ensemble averaged mean squared quantum number fluctuation $\langle(\delta\hat{n})^2\rangle_t = \langle\hat{n}^2\rangle_t - \langle\hat{n}\rangle_t^2$ for the coherent initial state case (not shown here, but see below).

*3.2.4. Approach to Thermal Equilibrium.* Finally, we demonstrate that for an ensemble of coherent initial states, subject to mean field Ehrenfest QCMD, the equilibrium quantum energy level populations of the damped harmonic oscillator have indeed the form given by eq 56, using the nonequilibrium (information) entropy[54,60]

$$S(t) = -\mathrm{Tr}\{\hat{\sigma}_{\mathrm{S}}(t) \ln \hat{\sigma}_{\mathrm{S}}(t)\} \simeq -\sum_n p_n(t) \ln p_n(t) \equiv \ln N_{\mathrm{eff}}(t) \quad (57)$$

as a global measure for the shape of the evolving distribution $\{p_n(t)\}$. For the sake of an intuitive physical picture, the identity $S(t) = \ln N_{\mathrm{eff}}(t)$ is employed, defining a reference distribution where $N_{\mathrm{eff}}(t)$ states are equally populated. As soon as the distribution $\{p_n(t)\}$ acquires the form of eq 56 with $\bar{n} \rightarrow \langle\hat{n}\rangle_t$, the nonequilibrium entropy may be expressed as

$$S_{\mathrm{canonical}}(t) = (\langle\hat{n}\rangle_t + 1) \ln (\langle\hat{n}\rangle_t + 1) - \langle\hat{n}\rangle_t \ln\langle\hat{n}\rangle_t \quad (58)$$

and the distribution as a whole characterized by a nonequilibrium temperature. Figure 5a shows that, within a time scale on the order of the energy relaxation time, the ensemble of coherent initial states indeed relaxes toward a nonequilibrium quasi-canonical distribution,[38] where $\langle(\delta\hat{n})^2\rangle_t = \langle\hat{n}\rangle_t(\langle\hat{n}\rangle_t + 1)$, whereas the ensemble of diabatic initial states, Figure 5b, obviously does not. It is, however, interesting to note that in the latter case $\lim_{t\rightarrow\infty}\{N_{\mathrm{canonical}}(t) - N_{\mathrm{eff}}(t)\} \cong 5 \equiv \langle\hat{n}\rangle_{t=0}$.

To summarize, if conditions are such that mean field Ehrenfest QCMD gives physically meaningful results, the asymptotic thermal equilibrium between the quantum subsystem and the classical heat bath is of a quasi-classical nature, where the first moment of energy is in accord with classical equilibrium statistics but the energy fluctuations are larger than predicted by classical statistical mechanics.

## 4. Conclusion

In the present work, we have presented a detailed comparison of mean field Ehrenfest quantum/classical molecular dynamics (QCMD) and its underlying assumptions to the corresponding Redfield second order quantum master equation (QME), using the Brownian motion Hamiltonian as a model applied to vibrational energy relaxation of a harmonic oscillator. We were able to bring the mean field quantum/classical equations of motion into an ensemble averaged form with respect to the classical bath initial conditions, where the resultant evolution equation for the quantum subsystem reduced density operator and the assumptions made in mean field QCMD can be discussed in terms of deviations from the QME. In particular, the real and symmetric part of the quantum bath force correlation function is replaced by its classical limit, whereas the antisymmetric part is retained, its effect, however, taken into account only via the (single-trajectory) time-dependent expectation of the respective operator appearing in the dissipative part of the

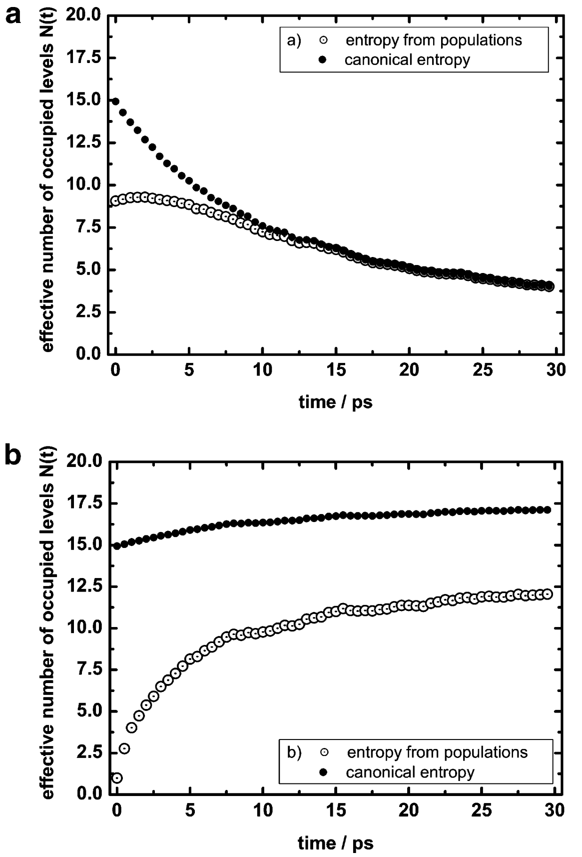

**Figure 5.** Time evolution of the nonequilibrium entropy $S(t) = \ln N(t)$ (in terms of an effective number of occupied energy levels) as calculated from the diabatic energy level populations and as obtained from the mean occupation number (assuming a quasi-canonical distribution) for (a) an ensemble of coherent initial states and (b) an ensemble of diabatic initial states.

quantum master equation. The result is a loss of quantum detailed balance.

Subsequent analytical investigation of the mean field quantum/classical master equation (QCME) allows for a rationalization of simulation results partly obtained earlier, but for a nonintegrable system-bath Hamiltonian.[38] In particular, energy relaxation and decoherence, population relaxation and the nature of asymptotic thermal equilibrium are analyzed. For the linearly damped harmonic oscillator, an ensemble of minimum uncertainty Gaussians (coherent states), due to optimum localization with respect to the system-bath coupling, is the only type of quantum initial states, which gives physically meaningful results, namely energy/population relaxation and dephasing toward quasi-classical thermal equilibrium, whereas a breakdown of quantum detailed balance as well as unphysical decoherence is observed in general, e.g., for an initial energy eigenstate. However, even for an ensemble of coherent initial states the nature of thermal equilibrium with mean energy $\hbar\omega_0\bar{n}_{\rm cl}(\omega_0, T) = k_{\rm B}T$ is not entirely classical, since the mean squared energy fluctuation is $(\hbar\omega_0)^2\bar{n}_{\rm cl}(\bar{n}_{\rm cl} + 1) > (k_{\rm B}T)^2$, owing to the discrete energy scale of the quantum subsystem oscillator. This issue deserves further consideration, also in other applications of quantum/classical methodology. It is in contrast to our earlier erroneous claim,[38] that the quantum subsystem energy scale behaves as if continuous.

Although the present statistical mechanical analysis of mean field Ehrenfest quantum/classical molecular dynamics has been restricted to the simple case of a damped harmonic oscillator, the role of anharmonicity and its effect on the performance of this QCMD method remains to be evaluated. This seems to be relevant also for the interpretation of simulation results reported for the case of a damped anharmonic oscillator in a molecular solvent.[32,33] As stated above, our general expectations are that anharmonicity will tend to further weaken the applicability of mean field QCMD.

In summary, mean field Ehrenfest quantum/classical dynamics gives essentially a classical dynamical correlation between the quantum subsystem and its classical environment,[3] and suffers from the absence of a physical mechanism for environment-induced decoherence, a quantum bath effect of fundamental importance for open quantum systems.[64,65] Mean field QCMD therefore seems to be inapplicable to most of the realistic situations encountered in condensed phase dynamics. We want to argue, that this failure is not (so much) a matter of the strength of system-environment interaction, but is related to an improper treatment of the relevant subsystem in terms of pure state Schrödinger/Liouville-type time evolution, coupled to classical environmental dynamics. As noted by other groups,[6,66−70] a proper treatment of *decoherence* in the open quantum system is of crucial importance for achieving maximum correlation between quantum and classical subsystems. However, this necessitates inclusion of (approximate) quantum environmental effects. The nature of decoherent states (or pointer states[65]), selected by the process of decoherence, will in general depend on the form of system-bath interaction, i.e., on the system observable which is “monitored” by the environment. In the present context of vibrational energy transfer, position is the relevant subsystem observable. Therefore, states of optimum localization in position (and momentum) space are expected to play the role of pointer states.

It is our hope that the present investigation may prove useful as a starting point for finding the (minimal) “missing link” for improving mean field Ehrenfest QCMD, while trying to avoid the ad hoc application of a vibrational surface hopping procedure.[37] The basic idea is, to replace the classical phase space point of mean field QCMD by a (minimum uncertainty) Gaussian wave packet (GWP). We have recently suggested the use of a time-dependent Gauss-Hermite (TDGH) basis set,[10,71] the ground state of which is a GWP, for going beyond the mean field classical path of the environmental degrees of freedom (DoF), by treating these DoF semiclassically and adding Gaussian (initial) fluctuations around the classical path in terms of boson-type second quantization operators defined in the trajectory-driven TDGH basis.[72,73] The use of a projection operator technique then allows for a perturbative evaluation of the correlation effect due to quantum fluctuations. Work along these lines is in progress. Results obtained for the damped harmonic oscillator (HO) indeed reveal, that HO coherent states are dynamically stable, whereas energy eigenstates decohere into a statistical mixture of HO coherent states.

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