Lindblad approach to quantum dynamics of open systems

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A Lindblad approach is presented to describe quantum dynamics of open systems. It is based on a construction of a Lindblad functional from the microscopic Caldeira-Leggett model for linear dissipation. It leads to a master equation for the reduced density matrix, which preserves positive evolution on short times and asymptotically approaches equilibrium at high and low temperatures. This master equation is applied to study the femtosecond dynamics of vibrational heating, relaxation, and bond breaking at a metal surface. Both a direct solution of the density matrix and an indirect solution with stochastic wave functions are presented. The latter, besides its statistical equivalence to the density matrix, provides a more physical picture about quantum jumps of individual open systems. [S0163-1829(98)05507-6]

I. INTRODUCTION

A variety of physical and chemical systems in nature are open or dissipative systems, whose dynamical variables couple to an infinite number of degrees of freedom surrounding them. Interaction between an open system and its environment often leads to dissipation, fluctuation, and an irreversible evolution of the system. The study of the dissipative dynamics of open systems[1-4] has been a central issue in many different areas such as quantum noise in tunnel junctions,[1] quantum-to-classical transition in the theory of measurement,[4] and reaction rate theory in condensed phase.[5]

Our particular interest in open system dynamics originates from our earlier experience in ultrafast dynamics at a solid surface, particularly in atomic and molecular processes such as femtosecond desorption,[6,7] sticking, and photo- and electron-induced surface reactions.[8] In principle, description of a molecule-surface process always involves a proper treatment of both the molecule under investigation and the surface coordinates, with which the molecule comes into contact. There has been increasing experimental evidence indicating that many interesting surface processes are initiated by the adiabatic and nonadiabatic interactions between the molecule and electronic/phononic excitations at surfaces. One example is the photoinduced chemistry at surfaces, where hot electrons generated by a laser pulse lead to desorption and dissociation of adsorbed molecules within a short time scale.[9] It has also been realized that the dynamics of such processes often finds itself in the quantum regime due to the quantization of vibrational motion[6] and/or the finite time of coherence and decoherence.[7] It is thus essential to describe these phenomena quantum mechanically in order to gain deeper insight into the underlying mechanism and microscopic dynamics.

Historically, description of open system dynamics has largely been based on the reduced density matrix formalism,[10,11] within which both intrinsic quantum-mechanical fluctuation of the system and external noise of its environment can be conveniently incorporated in a unified manner. During the past few decades, efforts have been made to devise various phenomenological models[12] and more recently to derive in a first-principles way the dissipa-

tion functional from microscopic Hamiltonians.[13-19] Pertinent to surface dynamics, there have been several efforts to include the effect of surface degrees of freedom into molecule-surface dynamics within the density matrix approach.[20-22]

In the density matrix formalism, one looks for an effective Liouville/influence functional, $L_D[\rho]$, governing the dissipative evolution of the reduced density matrix ρ of an open system via the following equation of motion:

$$\frac{d\rho}{dt} + \frac{i}{\hbar}[H,\rho] = L_D[\rho]; \tag{1}$$

here H is the Hamiltonian of the system alone. Derivation of L_D from microscopic Hamiltonians leads usually to a quantum master equation, in analogy with the classical Fokker-Planck equation, which uniquely determines the dynamics of the open system. One example of this type was given in a pioneering work[13] by Caldeira and Leggett (CL) for an oscillator linearly coupled to an Ohmic environment (linear dissipation), where the master equation was obtained as

$$\frac{d\rho}{dt} + \frac{i}{\hbar}[H,\rho] = -\frac{\gamma}{\hbar}\left\{\frac{2mkT}{\hbar}[x,[x,\rho]] + i[x,[p,\rho]_+]\right\}; \tag{2}$$

here $\gamma = \eta/(2m)$ is the characteristic damping rate of the oscillator with mass m, and η and T are the friction coefficient and bath temperature. Similar master equations have been obtained along this line for a particle in more general environment[14,15,17] with linear and nonlinear coupling. Such an approach is quite appealing in comparison with earlier phenomenological models, for it represents a first-principles approach to the reduced dynamics if the Hamiltonian of the whole system is known.

Master equation (2) is known to have a few drawbacks. First, it is only valid at high temperatures, or equivalently, the classical limit. This is a pity because quantum-mechanical behaviors are known to be important only in the low-temperature regime. A less obvious problem with this equation is the nonpositivity in ρ on a time scale proportional to $t \sim \gamma^{-1}$, as demonstrated in a number of recent works.[16-18] For vibrational motion in condensed phase and at

surfaces, $\gamma^{-1} \simeq 1$ ps. This means that Eq. (2) is inapplicable to ultrafast processes on femtosecond to picosecond time scales, a regime that most quantum coherent and decoherent phenomena might be of importance. We would also like to point out that such drawbacks are not specific to the CL master equation. On the contrary, they are quite general, as we demonstrate further in Sec. II, and are often encountered in a first-principles derivation of the reduced dynamics.

Recently, there are several attempts to derive master equations preserving positive density evolution from microscopic Hamiltonians. Such derivations are yet mainly limited to the weak-coupling[18,7] or high-temperature regime.[17] For example, Diósi tried to go beyond the lowest-order Markovian approximation of the CL model, by including the next order term in the expansion of the noise kernel. A master equation valid at medium and high temperatures has been obtained. This work was inspiring indeed, indicating one way to remedy the nonpositivity by further course graining in time. Technically, his derivation was problematic,[18] since other terms that were dropped out can be more important than the ones captured in the equation, especially in the low-temperature regime. In addition, it introduced a free parameter[17] to the master equation.

The problem of nonpositivity does not exist in an alternative approach of open quantum systems, namely, the theory of quantum dynamical semigroups by Lindblad[23] and Kossakowski and colleagues.[24] In particular, Lindblad showed that the generator[23] for a completely positive map should be of the following form:

$$L_D = \sum_m \{[V_m, \rho V_m^\dagger] + [V_m \rho, V_m^\dagger]\}, \qquad (3)$$

where the V_m's are the Lindblad dissipation operators. However, these operators are in general unknown, and the compact structure (3) does not generally assure equilibrium of the system with the bath. The Lindblad theory, in spite of its neat and concise layout, remains more like a formal structure than an approach of practical applications, although a few constructions of such operators have been available in the literature.[25,26]

Here, we present a Lindblad approach to quantum dynamics of open systems with linear dissipation, taking advantage of the positivity of the Lindblad structure and the equilibrium behavior of microscopic Hamiltonian models. We construct a single Lindblad operator, the explicit form of which is so determined as to reproduce the dissipation terms of the Caldeira-Leggett master equation at high temperatures and their generalizations to low temperatures. We arrive at a new master equation that preserves positive density evolution on short times and leads to equilibrium at high and low temperatures. This master equation closely connects two formally well-developed theories of open quantum systems, namely, the Lindblad formalism and the first-principles quantum master equations. In addition, it provides an efficient scheme to study open-system quantum dynamics, for it can be solved by propagating either the density matrix in a double-space representation $\rho(x, x', t)$ or a set of stochastic wave functions[27] $\{|\Psi(x,t)\rangle\}$ with the given Lindblad operator. As an example of application, we apply the master equation to study vibrational heating and damping at a metal surface. Both a direct solution of the density matrix and an indirect solution with stochastic wave functions are given.

At this point, we'd like to comment on the recent discussions in the literature regarding the positivity of the reduced dynamics.[28–30,19] It has been claimed that the reduced dynamics does not need to be completely positive and the dissipation functional, although it can be, need not be of the Lindblad form. This point has been elaborated particularly for a system with entangled initial density distribution with its environment.[28–30] What we would like to point out here is the fact that nonpositive density distribution often leads in practice to unphysical results, that contradict our physical intuition and observations in reality (one such example will be given below for the desorption rate). The necessity of positive evolution of the reduced dynamics is often essential to give a qualitatively correct account of many dynamical phenomena. This viewpoint has been taken as the starting basis of this work.

The rest of the manuscript is organized as follows: Section II briefly reviews the Caldeira-Leggett model (CLM) for the convenience of later reference. Section III constructs a Lindblad functional with a single dissipation operator. Its functional form is then determined based on the CLM and its generalization to low temperatures. It leads to a master equation of Lindblad class. This equation is subsequently applied to study vibrational heating and damping at a surface in Sec. IV, where both a direct and an indirect solution with stochastic wave functions will be given. Section V contains a short summary. A Brief Report of this work has been published in a previous paper;[31] here the various details are given together with further applications. Generalization of this approach to nonlinear coupling has also been worked out and will appear in a separate paper.

II. MODEL OF LINEAR DISSIPATION

This section briefly reviews the CLM for a particle (an oscillator or an open system) coupled with a phononic bath. It highlights particularly the relationship between the diffusion coefficients of Eq. (2) and the Markovian approximation of the fluctuation and dissipation kernels. These relations will be referred later in Sec. III to determine the Lindblad functional. Those who are familiar with such background materials can skip reading this part and go directly to the next section.

The model Hamiltonian of the CLM describes a linear coupling between a particle, with canonical variables x and p, and a bath of phonons, with variables $\{q_k, p_k\}$,

$$\mathcal{H} = \frac{p^2}{2m} + U(x) + \sum_k C_k x q_k + \sum_k \left(\frac{p_k^2}{2M} + \frac{1}{2} M \omega_k^2 q_k^2\right). \qquad (4)$$

Similar model Hamiltonian has been studied as an exactly solvable model of quantum Brownian motion before.[32] Caldeira and Leggett solved the reduced dynamics of the particle within the path-integral formalism developed by Feynman and Vernon.[11] One can also apply the standard field-theoretic technique to obtain the same solution, as pursued recently by Hu, Paz, and Zhang[15] and Diósi.[17]

From the evolution of the total density matrix for the system and the bath, the time-development of the reduced density matrix of the system ρ can be written as

$$\rho(t) = \hat{S}(t)\rho(0), \qquad (5)$$

where superoperator $\hat{S}$ takes the following exact form

$$
\begin{aligned}
\hat{S}(t) = \hat{T}\exp\bigg(&-\frac{1}{\hbar}\int_0^t d\tau \int_0^\tau ds\{i[x_+(\tau)-x_-(\tau)]\alpha_I(\tau-s) \\
&\times[x_+(s)+x_-(s)]+[x_+(\tau)-x_-(\tau)]\alpha_R(\tau-s) \\
&\times[x_+(s)-x_-(s)]\}\bigg).
\end{aligned}
\qquad (6)
$$

This equation has been derived with both the path-integral approach[13,15] and the field-theoretic method.[15,17] Operator $\hat{T}$ prescribes time ordering for the superoperators with $+$ index and anti-time-ordering for those with $-$ sign. These superoperators act by convention on ρ from the left/right side when they are $+/-$ indexed.

In Eq. (6), the influence of the bath resides entirely on the force-force autocorrelation function (kernel), $\alpha(t) = 1/\hbar\langle\hat{F}(t)\hat{F}(0)\rangle_T$, whose real and imaginary parts read

$$\alpha_R(t,T) = \int_0^{\Omega_c} I(\omega)\coth\left(\frac{\hbar\omega}{2kT}\right)\cos(\omega t)d\omega, \qquad (7)$$

$$\alpha_I(t) = -\int_0^{\Omega_c} I(\omega)\sin(\omega t)d\omega, \qquad (8)$$

where $I(\omega) = \Sigma_k(C_k^2/2M\omega_k)\delta(\omega-\omega_k)$ is the spectral function of the phonon bath, and Ω_c is the bandwidth (cutoff frequency). For an Ohmic bath, $I(\omega)$ is phenomenologically approximated by $I(\omega) = \eta\omega/\pi$, where η is the friction coefficient.

Caldeira and Leggett approximated Eqs. (7) and (8) by the lowest-order expansion of $\alpha_R(t,T)$ in the high-temperature limit $(\hbar\omega/kT) \ll 1$, as such, the kernels become local in time,

$$\alpha_R(t,T) = \frac{2\eta kT}{\hbar}\delta(t), \qquad (9)$$

$$\alpha_I(t) = \eta\delta'(t). \qquad (10)$$

Differentiating Eq. (5) with time and using Eqs. (9) and (10), they were able to obtain master equation (2). The derivation is, though tedious and long, straightforward.[13,17]

Before we move on, we would like to make a few remarks about the CLM:

(i) The two dissipation terms on the right hand side of Eq. (2) result from the Markovian approximation of the fluctuation kernel α_R and its dissipation counterpart α_I, respectively. These two terms are connected by the fluctuation-dissipation relation. The balance between them leads the system to thermal equilibrium with the bath.

(ii) The superoperator $\hat{S}$ in Eq. (6) depends on the bath only through α_R and α_I. This is a quite general feature for linear as well as nonlinear coupling. For example, the same structure applies to a system linearly coupled to an electron

bath, where the only modification needed is to replace the spectral function $I(\omega)$ with that of the electronic bath.

(iii) As discussed in the introduction, master equations like Eq. (2) obtained from microscopic models are often ill behaved, particularly in the low-temperature regime, leading to nonpositive evolution of ρ. This is a quite general drawback often encountered in a first-principles derivation of the reduced dynamics.[16,18,19]

III. A LINDBLAD APPROACH

In this section, a simple Lindblad functional is constructed based on the microscopic CLM. The resultant master equation is of the Lindblad form. It can be solved either in a double-space representation or by a set of wave functions, which obey a stochastic differential equation (SDE), or equivalently, a nonlinear Schrödinger equation.

A. Construction of a Lindblad operator

We look for a single Lindblad operator V, which is a linear combination of x and p,

$$V = \mu x + i\nu p, \qquad (11)$$
$$V^\dagger = \mu x - i\nu p,$$

where μ and ν are arbitrary c numbers to be determined below. This particular choice has been motivated by the following physical observations: (i) The known form of the dissipation operator for a damped harmonic oscillator[24] $V \propto a = \sqrt{m\Omega/2\hbar}[x+(i/m\Omega)p]$, which is a linear combination of x and p; (ii) The known dissipation terms of the master equation (2), which involves both x and p operators; (iii) The Dekker's constraints[33] for the diffusion coefficients of the master equation for a damped oscillator, namely,

$$D_{xx} > 0,$$
$$D_{pp} > 0, \qquad (12)$$
$$D_{xx}D_{pp} - D_{xp}D_{px} \geq \gamma^2\hbar^2/4,$$

which also implies a symmetry between x and p. These conditions must be fulfilled in order to preserve the intrinsic quantum fluctuation, i.e., the Heisenberg uncertainty principle.

A more general linear combination similar to Eq. (11) has been discussed by A. Sandulescu and H. Scutaru,[26] who obtained a general master equation that could reproduce various particular master equations available in the literatures.[26] Our work aims, however, at looking for a *particular* but *unique* linear combination, the coefficient of which is determined from a microscopic Hamiltonian model, like the CLM.

B. Determination of the Lindblad functional from the CLM

To determine coefficients μ and ν, let's first write out the Lindblad functional explicitly from Eqs. (3) and (11), noticing that $[x,p] = i\hbar$,

$$L_D = 2V\rho V^{\dagger} - V^{\dagger}V\rho - \rho V^{\dagger}V$$

$$= \mu^2(2x\rho x - x^2\rho - \rho x^2) + \nu^2(2p\rho p - p^2\rho - \rho p^2)$$

$$+ 2i\mu\nu(p\rho x - x\rho p - \rho[x,p])$$

$$= -\mu^2[x,[x,\rho]] - \nu^2[p,[p,\rho]] - 2i\mu\nu([x,[p,\rho]_+])$$

$$- [xp,\rho])$$

where $[A,B]_+$ represents an anticommutation relation between operator A and B. The equation of motion for ρ takes the following form:

$$\frac{d\rho}{dt} + \frac{i}{\hbar}[H',\rho] = -\mu^2[x,[x,\rho]] - 2i\mu\nu[x,[p,\rho]_+]$$

$$- \nu^2[p,[p,\rho]], \qquad (13)$$

$$H' = H - 2\mu\nu\hbar xp. \qquad (14)$$

The three terms on the right-hand side of Eq. (13) and the last one on the left are all traceless due to the cyclic property of trace, which guarantees $(d/dt)\mathrm{Tr}\rho = 0$, i.e., the norm conservation of the reduced density matrix. In fact, the general Lindblad form Eq. (3) is traceless and the Lindblad approach is thus universally norm conserving.

One may easily realize that the first two terms on the right-hand side of Eq. (13) are essentially the same as those in the CL master equation (2). This comparison suggests the following conditions for choosing μ and ν:

$$\mu^2 = \gamma 2kTm/\hbar^2,$$

$$2\mu\nu = \gamma/\hbar \quad \text{as} \quad T \rightarrow \infty, \qquad (15)$$

$$\nu^2 = 0,$$

which yields straightforwardly $\nu^2 = \gamma/(8mkT)$. This ν^2 is vanishing in the high-temperature limit, but becomes significant at low temperatures.

It is interesting to compare this naive choice with Diósi's master equation,[17] which contains, among several other terms, also a term $D_{xx}[p,[p,\rho]]$ with a slightly different coefficient $D_{xx} = \gamma/(6mkT)$. The latter was derived from the CLM by going beyond the lowest-order Markovian approximation of the noise kernel. This term, as it appeared in Eq. (13), stems naturally from the general Lindblad structure.

Indeed, Eq. (13) together with Eq. (15) represents the simplest Lindblad master equation.[17] It provides a remedy for the nonpositivity problem of the CLM. This naive choice is, however, only valid at temperatures higher than or comparable with the vibrational quantum, $kT \gtrsim \hbar\Omega$, for the original CL master equation, on which Eq. (15) is based, becomes invalid at low temperatures. Technically, this is due to the fact that μ^2 goes to zero as $T \rightarrow 0$, which violates Dekker's constraint $D_{pp} > 0$.

C. Extension to low temperatures

To extend the functional to low temperatures, we notice that the two dissipation terms of Eq. (2) have different physical origin. The second term, which results from the approximation of $\alpha_I(t)$ by Eq. (10), describes the dissipation induced by the bath and is temperature independent as shown in Eq. (8). This suggests to us one simple generalization of Eq. (15),

$$2\mu\nu = \gamma/\hbar, \qquad (16)$$

being valid at all temperatures. In contrast, the first term of Eq. (2), which resulted from the approximation of $\alpha_R(t,T)$ by Eq. (9), describes environment-induced fluctuation and depends on T as in Eq. (7). The high-temperature approximation (9), which was used in all previous derivations,[13,15,17] is obviously inapplicable in the low-temperature regime.

We therefore adopt a different approximation of the noise kernel at low temperatures, by observing that, at low T, $I(\omega)\coth(\hbar\omega/2kT)$ is a smooth function of ω, while $\cos(\omega t)$ is fast oscillating. This observation leads us to the following approximation, noting that $I(\omega) = \eta\omega/\pi$ for the phenomenological representation of the Ohmic bath,

$$\alpha_R(t,T) \simeq \frac{\eta}{\pi}\omega_c\coth\left(\frac{\hbar\omega_c}{2kT}\right)\int_0^{\Omega_c}\cos(\omega t)d\omega$$

$$= \eta\omega_c\coth\left(\frac{\hbar\omega_c}{2kT}\right)\tilde{\delta}(t), \qquad (17)$$

where $\tilde{\delta}(t) = 1/\pi\int_0^{\Omega_c}\cos(\omega t)d\omega$, and ω_c is a parameter factorizing the noise kernel and has approximately the physical meaning as the center of the $I(\omega)$ band. The Markovian limit is recovered if $\Omega_c \rightarrow \infty$ and thus $\tilde{\delta}(t)$ approaches $\delta(t)$. It leads to a replacement of $2kT \rightarrow \hbar\omega_c\coth(\hbar\omega_c/2kT)$ in the first diffusion term of Eq. (2) and thus in our choice of μ^2, i.e.,

$$\mu^2(T) = \gamma m\omega_c/\hbar\coth\left(\frac{\hbar\omega_c}{2kT}\right). \qquad (18)$$

In fact this is a simple generalization of the fluctuation-dissipation relation to the quantum regime.

Please note the order between the factorization of Eq. (17) and the Markovian approximation. The former is physical. The narrower the bandwidth of $I(\omega)$ (smaller Ω_c) is, the better the approximation of Eq. (17) will be. The second step $\Omega_c \rightarrow \infty$ is mathematical, and is consistent with the Lindblad formalism, which itself is based on the Markovian approximation.

The parameter ω_c can be uniquely determined by a harmonic oscillator approximation at $T = 0$, where the system should essentially occupy its ground state near its potential minimum. The Lindblad operator V should then degenerate with the annihilation operator of the harmonic oscillator, $a = \sqrt{m\Omega/2\hbar}[x + (i/m\Omega)p]$, implying $\mu/\nu = m\Omega$. On the other hand, from Eqs. (16) and (18), we have $\mu/\nu = 2m\omega_c$ at $T = 0$. The harmonic approximation thus gives $\omega_c = \Omega/2$, i.e., half of the oscillator frequency. So the temperature dependence of the two coefficients reads,

$$\mu^2(T) = \frac{\gamma m\Omega}{2\hbar}\coth\left(\frac{\hbar\Omega}{4kT}\right), \qquad (19)$$

$$\nu^2(T) = \frac{\gamma}{2\hbar m\Omega}\tanh\left(\frac{\hbar\Omega}{4kT}\right), \qquad (20)$$

with the accompanying relation $2\mu\nu=\gamma/\hbar$. Both expressions reduce to Eq. (15) in the high-temperature regime, and have their physical bases on the fluctuation-dissipation relation. They therefore bring the equilibrium behavior into the Lindblad formalism through their temperature dependence. It is straightforward to check that Eqs. (19) and (20) fulfill all the Dekker's constraints at any temperature.

In coordinate space, the master equation (13) takes the following form:

$$\frac{\partial\rho(x,x',t)}{\partial t}+\frac{i}{\hbar}[\widetilde{H}(x)-\widetilde{H}^{\star}(x')]\rho(x,x',t)$$

$$=-\left\{\mu^2(T)(x-x')^2+\gamma(x-x')\left(\frac{\partial}{\partial x}-\frac{\partial}{\partial x'}\right)\right.$$

$$\left.-\nu^2(T)\hbar^2\left(\frac{\partial}{\partial x}+\frac{\partial}{\partial x'}\right)^2\right\}\rho(x,x',t), \qquad (21)$$

$$\widetilde{H}(x)=H(x)+i\hbar\gamma x\frac{\partial}{\partial x}+i\frac{\hbar\gamma}{2}. \qquad (22)$$

The last two terms of Eq. (22) come from Eq. (14), i.e.,

$$\langle x|[-2\mu\nu\hbar xp,\rho]|x'\rangle=-2\mu\nu\hbar\langle x|xp\rho-\rho px-i\hbar\rho|x'\rangle$$

$$=i\hbar\gamma\left(x\frac{\partial}{\partial x}+x'\frac{\partial}{\partial x'}+1\right)\rho(x,x',t).$$

This master equation differs from all previous ones in two aspects: (i) a renormalized Hamiltonian with a frictional force and an imaginary term; and (ii) an additional diffusion term (the ν^2 term) with temperature-dependent diffusion coefficient. As Eq. (21) is directly constructed from the Lindblad functional, it therefore guarantees the positivity of the density matrix even on short times.

One may question about the consistency between Eqs. (2) and (21), or equivalently, the essence of the additional term in Eq. (21). In general, a Markovian master equation can be, but need not be of the Lindblad form. It has been shown in several cases that a non-Lindblad master equation can be put to a Lindblad form by further course graining in time.[17–19] Our simple Lindblad functional constructed from the microscopic CLM represents a similar physical spirit. The appearance of the additional term is not astonishing. It adequately guarantees the positive evolution of the reduced dynamics.

Before closing this section, let's prove the norm conservation of Eq. (21), though the imaginary terms in Eq. (22) are non-Hermitian and seem to increase the total norm of the density matrix. From the diagonal part of Eq. (21),

$$\frac{\partial}{\partial t}\rho(x,x,t)-\gamma\left(x\frac{\partial}{\partial x}+x'\frac{\partial}{\partial x'}+1\right)\rho(x,x',t)\Bigg|_{x'=x}$$

$$=\nu^2\hbar^2\left(\frac{\partial}{\partial x}+\frac{\partial}{\partial x'}\right)^2\rho(x,x',t)_{x'=x}, \qquad (23)$$

the evolution of the norm of ρ can be calculated by integration over x,

$$\frac{d}{dt}\int dx\,\rho(x,x,t)=\gamma\int dx\frac{d}{dx}[x\rho(x,x,t)]$$

$$+\nu^2\hbar^2\int dx\frac{d^2}{dx^2}\rho(x,x,t)$$

$$=\left[\gamma x\rho(x,x,t)+\nu^2\hbar^2\frac{d}{dx}\rho(x,x,t)\right]\Bigg|_{x=-\infty}^{x=+\infty}$$

$$=0. \qquad (24)$$

The last step vanishes due to the boundary condition of the density distribution. The norm is thus conserved. Physically the effect of the norm-increasing term is exactly canceled by the frictional terms in the renormalized Hamiltonian.

D. Solution of the master equation with stochastic wave functions

While the master equation (21) can be directly solved in a double-space (two-dimensional) representation, as in a previous paper,[31] it can alternatively be solved using a set of stochastic wave functions. This can be a possible advantage of the Lindblad approach, when dimensionality is a problem for a direct solution.

As shown by Gisin and Percival,[27] a master equation of Lindblad class can be equivalently solved by a set of wave functions $\{|\psi\rangle\}$ via representing the density matrix by

$$\rho=M|\psi\rangle\langle\psi|. \qquad (25)$$

Each $|\psi\rangle$ obeys the following stochastic differential equation (SDE):

$$d|\psi\rangle=-\frac{i}{\hbar}H|\psi\rangle dt+\sum_m\,(2\langle V_m^\dagger\rangle V_m-V_m^\dagger V_m)|\psi\rangle dt$$

$$+\sum_m\,(V_m-\langle V_m\rangle)|\psi\rangle d\xi_m. \qquad (26)$$

Here $\{d\xi_m\}$ are complex stochastic variables, the Wiener processes, with the following properties in the mean average M: $M[d\xi_m d\xi_n^\star]=2dt\,\delta_{mn}$, $M[d\xi_m^\star d\xi_n^\star]=0$, and $M[d\xi_m d\xi_n]=0$. Equation (26) is nonlinear due to $\langle V\rangle=\langle\psi|V|\psi\rangle$ and norm nonconserving, since the stochastic noise induces quantum jumps between different eigenstates.

For our specific choice, $V=\mu x+i\nu p$, the corresponding SDE takes the following form:

$$d|\psi\rangle=-\frac{i}{\hbar}H|\psi\rangle dt-\left[\mu^2(x-\bar{x})^2+\nu^2(p-\bar{p})^2\right.$$

$$\left.+\frac{i\gamma}{\hbar}(\bar{p}x-\bar{x}p)\right]|\psi\rangle dt$$

$$+[\mu(x-\bar{x})+i\nu(p-\bar{p})]|\psi\rangle d\xi. \qquad (27)$$

where $\bar{x}=\langle x\rangle$, $\bar{p}=\langle p\rangle$. This equation not only reduces the dimension of ρ from N^2 to $\sim N$, but also gives rise to quantum jumps, which exist in reality in open individual systems. These quantum events are ''smeared'' out in the density matrix formalism by ensemble average. In this perspective, we believe that the SDE provides, besides its statistical equiva-

lence to the master equation, a physically more correct description of individual systems. This is important for the current study of quantum noise in mesoscopic systems and individual molecules, where discrete jump events have been recorded in the time and space domain.[35] One application of the SDE will be given in the next section to study the vibrational dynamics induced by electronic fluctuations at a surface. Bond breaking is demonstrated as quantum jumps.

IV. APPLICATIONS: DISSIPATIVE DYNAMICS OF O_2/PT

The Lindblad approach given in the proceeding section is generally applicable to open systems with linear dissipation. Here, it is applied to study a problem in surface physics: damping and heating of a molecular vibration on a solid surface induced by equilibrium and nonequilibrium hot electrons. This problem has its physical origin in the field of femtosecond surface photochemistry. In a typical experiment, a femtosecond laser pulse is sent onto a surface that generates, within a few femtoseconds, highly excited hot electrons with temperature of several thousand K. Such hot electrons interact nonthermally with the adsorbed atoms and molecules on the surface, leading to vibrational excitation, relaxation, and bond breaking at the surface. On the femtosecond to picosecond time scale, the lattice is relatively cool and thermal-induced effect is negligible. This problem can be described by a model of linear dissipation.[7] The master equation obtained from the CLM can be used if the damping rate γ is interpreted as that of electrons.

A. Vibrational damping: equilibrium and positivity

We study first the dynamics of vibrational relaxation of a Morse oscillator, mimic the O_2-Pt bond, induced by equilibrium electrons, via a direct solution of the master equation (21). For O_2 on a Pt(111) surface, electronic excitation is believed to be the dominant mechanism of dissipation with $\gamma^{-1}=3$ ps.[6] The Hamiltonian of the free oscillator takes the following form,

$$H = -\frac{\hbar^2}{2m}\frac{d^2}{dx^2} + D[e^{-2ax} - 2e^{-ax}], \quad (28)$$

with parameters ($\hbar\Omega = 0.049$ eV, $a = 2.545$ a.u., and $D = 0.4$ eV) chosen to represent those of the adsorbed O_2 molecule on the Pt(111).[6] The relaxation dynamics is obtained by propagating an initial density matrix, $\rho(x,x',0) = \phi_1(x)\phi_1(x')^\dagger$, corresponding to the first vibrationally excited state of the oscillator. Equation (21) is numerically solved using the splitting operator technique, together with the fast Fourier transform (FFT).[37] The terms with only x or p operators are propagated in the coordinate or momentum space, respectively. The cross terms of x and p are propagated by the two-step Wendroff-Lax scheme for the flux-conservative differential equations[37]. We used a time step $\Delta t = 10$ a.u. and $N_x = 512$ grid points sampled in a region $x \in [-0.5:2.5]$. An imaginary potential[8] has been used in the asymptotic region to absorb the outgoing density flux. The damping constant $\gamma^{-1}=3$ ps is chosen from an earlier study.[6]
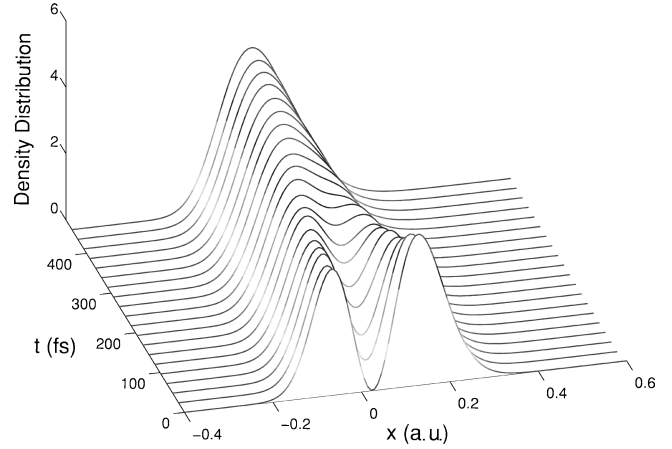

FIG. 1. The relaxation of the diagonal density $\rho(x,x,t)$ of a Morse oscillator as a function of time at $T=200$ K from an initial distribution corresponding to the first excited state. The parameters are chosen to represent an O_2-Pt(111) bond with a damping rate $\gamma = 3.3 \times 10^{11}$ s^{-1} due to coupling to electrons at the surface.

Figure 1 shows the wave packet, the diagonal density matrix, as a function of time. Without dissipation, i.e., $\gamma = 0$, the initial wave packet would remain in the excited pure state for infinitely long time. Due to coupling to electrons, any nonthermal distribution relaxes and approaches equilibrium with its environment. Figure 1 shows this dynamical process during the first 500 fs. The wave packet evolves from the $n = 1$ excited state to a thermalized Gaussian wave packet.

Figure 2 shows the development of a vibrational temperature, defined by $T_v = \hbar\Omega/[k\ln(P_0/P_1)]$, at longer times for different electron temperatures, $T = 800$, 600, 400, 200, and 80 K. Here $P_i(t) = \int dx \int dx' \phi_i(x)^\dagger \rho(x,x',t)\phi_i(x')$ is the time-dependent population of the ith eigenstate. The density distribution approaches the electron temperature within the lifetime $\gamma^{-1}=3$ ps, even in the low-temperature, $kT \ll \hbar\Omega$, regime. We would like to point out that the equilibrium
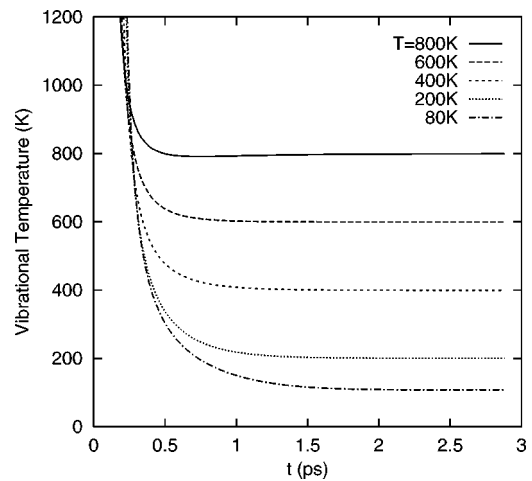

FIG. 2. The development of the vibrational temperature for the same initial density distribution shown in Fig. 1 at different bath temperatures (T). Initially the wave packet has a nonthermal distribution and the temperature is not well defined. Note that the vibrational quantum of the oscillator corresponds to a temperature of $\hbar\Omega/k = 570$ K. The wave packet approaches equilibrium with the electron bath at both high and low temperatures.
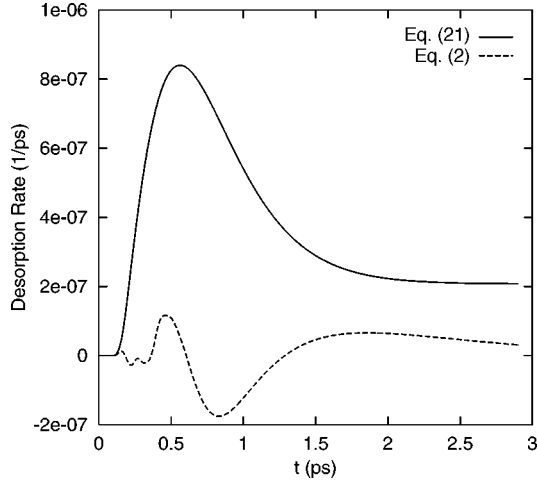
FIG. 3. The calculated desorption rate as a function of time before absorption boundary at $T=200$ K. The rate given by the CLM equation does not have the right sign in the subpicosecond regime due to the unphysical negative density distribution. This problem does not exist in the rate given by the master equation (21).
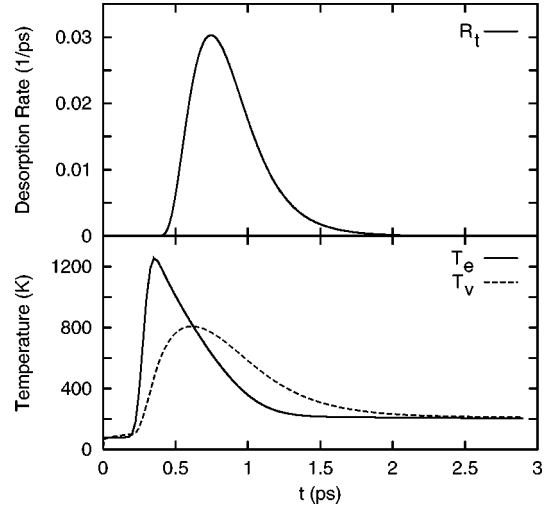

FIG. 4. Hot electron induced vibrational heating and desorption. The electron temperature is taken from Refs. 6 and 7. See the text for further explanations.

shown in Fig. 2 cannot be obtained by the CL master equation in the low-temperature regime. Furthermore, the thermal equilibrium that the oscillator establishes does not depend on the initial distribution of the density matrix. In other words, one can obtain the same asymptotic distributions from an arbitrary initial wave packet.

To illustrate the importance of positivity of the density matrix, we plot in Fig. 3 the desorption rate (current), $j(t)$ $=-i\hbar/2m[(\partial/\partial x)-(\partial/\partial x')]\rho(x,x',t)|_{x=x'=x_d}$ at a desorption boundary $x_d=2.3$ a.u., as a function of time during the vibrational relaxation. This provides a critical test of a model because the evolution from a pure state to equilibrium is a transient and extremely nonequilibrium process. The rate given by Eq. (2) does not have the correct sign in the subpicosecond regime due to the unphysical negative density distribution at the desorption boundary. In comparison, the new master equation (21) correctly describes the desorption rate as a function of time during relaxation.

B. Vibrational heating by hot electrons

Having shown the positivity and equilibrium properties of the present approach, we next apply the master equation to study vibrational heating induced by hot electrons, which is, loosely speaking, the inverse problem of the vibrational damping.

We simulate a hot electron gas at a Pt(111) surface generated by a short femtosecond laser pulse with duration of 80 fs and a fluence of 1.0 mJ/cm^2. The temperature profile of the hot electrons, $T_e(t)$, was calculated in Ref. 6, and is replotted in the lower panel of Fig. 4 (the solid line). The vibrational response of the oscillator is obtained by solving the master equation with the given $T_e(t)$ as the bath temperature. For simplicity, the initial density matrix is constructed from the ground-state wave function, $\rho(x,x',0)$ $=\phi_1(x)\phi_1(x')^\dagger$, by which the small fraction of excitations, at an initial temperature $T_e(0)=80$ K, has been neglected. The dashed line of the lower panel of Fig. 4 shows the vibrational temperature as a function of time, while the upper

panel shows the rate of desorption. The oscillator exhibits a delayed response to electronic heating and a smaller increase in the vibrational temperature. The latter asymptotically approaches that of the electrons in the long time limit. All the qualitative features shown in Fig. 4, including the delay between electronic and vibrational heating, the time scale of desorption, are quite similar to those obtained earlier with a truncated harmonic oscillator model.[7] We found, however, a few quantitative differences such as a higher peak vibrational temperature of 800 K, and a higher yield of desorption in this calculation. The present scheme represents an improvement on the earlier model in the sense that (i) it goes beyond the approximation of the truncated harmonic oscillator; and (ii) it fully accounts for the quantum coherence of the density matrix, which was neglected in the previous solution using the Pauli master equation.[7]

C. Solution with stochastic wave functions

As an example of application of the SDE, we solve the vibrational heating problem shown in Fig. 4 with stochastic wave functions. Equation (27) is solved with the splitting
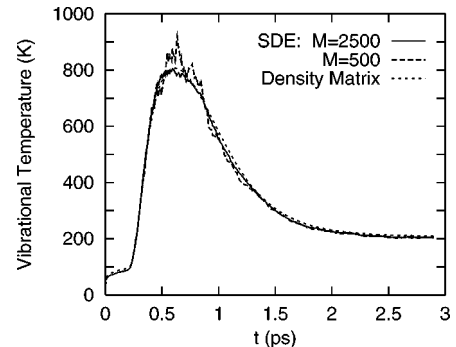

FIG. 5. Vibrational response to electronic heating shown in Fig. 4. The vibrational temperature is calculated by solving the stochastic differential equation. With $M=2500$ realizations, the result given by SDE is very close to that given by the density matrix.
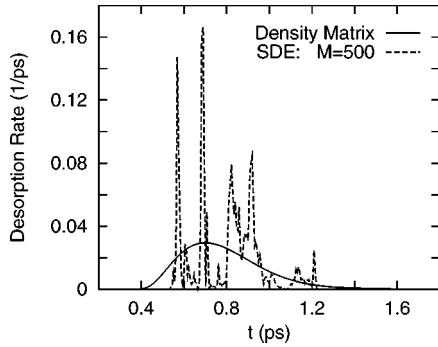
FIG. 6. The desorption rate calculated by SDE with $M=500$. The desorption occurs as discrete quantum jumps instead of a smooth function of time as given by the density matrix.

FIG. 7. The same as Fig. 6 for $M=10\,000$. The desorption rate, though closer, does not fully converge to that given by the density matrix.

operator method together with the fast Fourier transform, the same techniques as used in a nondissipative wave-packet propagation. The only additional complication is the noise term, which is propagated by the simple Euler scheme.[34] The Wiener process $d\xi(t)$ has been generated by two (the real and imaginary part) discrete Gaussian random variables with variance $2dt$. To speed up simulation and convergence, we used a smaller grid points $N_x=256$ and a smaller time step $\Delta t=2.5$ a.u. in the following simulation. All quantities, such as the population on eigenstates and the desorption rate, are calculated independently from each stochastic realization. They are then summed up to give the averaged ones for a set of realizations.

Figure 5 shows the vibrational temperature as a function of time for two sets of M, the number of stochastic realizations. The temperature obtained from SDE converges quickly to that given by the density matrix, the averaged one. With $M=2500$, the two temperatures almost coincide as shown in Fig. 5.

Figures 6 and 7 show the desorption rate as a function of time for $M=500$ and 10 000, respectively. The desorption rate converges much slower than the vibrational temperature because of the quantum jump behavior of desorption. As shown by Fig. 7, the desorption rate does not fully converge for M as large as 10 000. Much more realization is needed to get better converged rate and yield.

Apart from the slow convergence of the desorption rate, SDE provides a qualitatively different picture of desorption from that given by the density matrix. In a stochastic realization, one typically sees a series of discrete jumps in the desorption rate. In other words, bond breaking occurs as discrete jumping event in SDE instead of a smooth function as described by the density matrix, although they are equivalent in ensemble average. This picture of bond breaking is closer to the experimental one if an ensemble of systems are measured individually one by one, which should record discrete jumps/spikes in an individual sysytem each time. This feature is important and interesting. Recent progress in experimental techniques has made it possible to probe the local dynamics of individual quantum systems, like single molecules, and to directly observe quantum jumps in the time domain.[35,36] In this perspective, the wave-function approach based on the Lindblad functional represents a promising scheme to describe such individual systems.
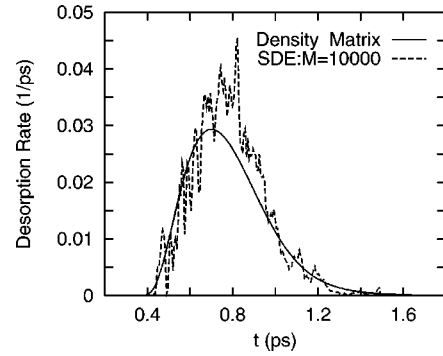
V. CONCLUDING REMARKS

We have presented a Lindblad approach to describe quantum open systems by constructing a single Lindblad operator from the microscopic Caldeira-Leggett model for linear dissipation. Its functional form has been uniquely determined based on the high-temperature master equation and its generalization to low temperatures. This has led to a new master equation, which preserves positive density evolution on short times and asymptotically approaches equilibrium within a wide range of temperatures. This master equation has been applied to a model problem in surface physics, vibrational heating and relaxation of a Morse oscillator induced by electrons. The equilibrium and positivity shown by the numerical results demonstrates that it provides a promising scheme for ultrafast dynamics of open systems in the framework of the density matrix.

We have also shown that the Lindblad master equation, when solved with stochastic wave functions, provides a more physical description of quantum jumps of individual systems. Such jumps cannot be described by the density matrix approach, but do exist in reality in individual open systems. This is particularly encouraging indeed, since recent experiments with ultrasmall spatial and time resolution tend to reveal the underlying properties of indvidual systems, like single adsorbed molecules,[36] and their jump events directly in the time domain. In this perspective, our Lindblad approach constructed from the microscopic model represents a promising scheme to describe such systems and properties. It may bring completely new insight into the dynamics of individual process, which may be different from those measured on an ensemble of systems.

While the approach presented here has been restricted to the case of linear coupling, it is possible to extend it to nonlinear coupling. We have recently worked out a model with a nonlinear coupling between a system and an Ohmic bath, which will be given elsewhere. It is also highly desirable to extend this scheme to the zero-temperature limit by going beyond the harmonic oscillator approximation used at $T=0$.

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