Dissipative quantum dynamics at surfaces: A nonlinear-coupling model

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The recently developed Lindblad approach for quantum dynamics of an open system with linear dissipation has been extended to a model of nonlinear coupling. The coupling term $H_i = \sum_{k} C_{ik} f(x) q_k$ is an arbitrary function of the system coordinate, but remains to be linear in bath coordinates. A Lindblad master equation and its associated stochastic differential equation have been obtained. To study dissipative surface dynamics, a general form of $f(x)$ has been proposed. It is shown that such a nonlinear-coupling model is crucial to qualitatively describe gas-surface dynamics, when a gas molecule impinging or leaving a surface goes beyond the linear-coupling regime. [S0163-1829(99)05343-6]

Quantum dynamics of an open or a dissipative system is a subject of general interest in quantum mechanics. So far, the description of open-system dynamics has largely been based on a model of bilinear coupling between the system and its environment (linear dissipation) with few exceptions. The linear-coupling model, derived usually from a linear expansion of the interaction potential at small bath-system coordinates, is valid only for systems with small deviation from their equilibrium configuration. In reality, there are many situations in which a system can go beyond the linear-coupling regime. In gas-surface dynamics, for example, a gas particle impinging or leaving a surface may be located at very small and very large distances from a surface, where the linear-expansion approximation does not apply. In the asymptotic limit of large separation, the particle should be completely decoupled from the surface degrees of freedom. It is thus highly desirable to devise models that incorporate nonlinear coupling to the system in order to describe dissipative dynamical processes at surfaces.

In the literature, there are several theoretical treatment of nonlinear effects in dissipative quantum tunneling and Brownian motion in condensed phases. In particular, Hu, Paz, and Zhang (HPZ) studied a number of models for a system with nonlinear coupling to a general environment, and obtained several generalized master equations. These master equations, though derived in a first-principle way from model Hamiltonians, have two major drawbacks when applying to surface systems: (i) they are not in the Lindblad form, and thus do not ensure positive evolution of the reduced density matrix. Nonpositive diagonal density matrix is unphysical and often leads to dynamical behaviors that counter our intuition and experimental observations; and (ii) they were only derived in the high-temperature regime, i.e., the physical regime for quantum Brownian motion in condensed matter; and (iv) it preserves the quantum-mechanical fluctuations of the system at all times and at all temperatures, i.e., $\langle \Delta x^2 \Delta p^2 \rangle \geq h^2/4$. These features have not been concurrently reproduced by other master equations before and are all essential for dissipative quantum dynamics at low temperatures.

Here, this Lindblad approach is extended to a model of nonlinear coupling with the goal to describe surface dynamical systems. The coupling term $H_i = \sum_{k} C_{ik} f(x) q_k$ is taken to be an arbitrary function of system coordinate $x$ but remains to be linear in bath coordinates $\{q_k\}$. A Lindblad master equation and its associated stochastic differential equation have been obtained based on the HPZ model. When choosing $f(x) = x$, this model reduces to the case of linear dissipation obtained earlier. For application in surface dynamics, a general form of $f(x)$ is also proposed. This nonlinear model is then applied to study vibrational damping and desorption for a model system, $O_2/Pt(111)$. It is demonstrated that the nonlinear-coupling model is essential to qualitatively describe the reaction dynamics at surfaces.

The model I start with is a localized oscillator nonlinearly coupled with an Ohmic phonon bath,

$$\mathcal{H} = \frac{p^2}{2m} + U(x) + \sum_{k} C_{ik} f(x) q_k + \sum_{k} \left( \frac{p_k^2}{2M} + \frac{1}{2} M \omega_k^2 q_k^2 \right),$$

(1)

where $x$ and $p$ are position and momentum of the open system, the oscillator, and $\{q_k, p_k\}$ are those for the harmonic oscillators of the phonon bath. The coupling term remains to be linear in the bath coordinates but is an arbitrary function of $x$. This model Hamiltonian was intensively investigated by HPZ, using both path-integral and field-theoretic methods.

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In coordinate space, the master equation for the reduced density matrix $\rho$ can generally be written as

$$\frac{\partial \rho(x,x',t)}{\partial t} + i \hbar \left( H(x) - H(x') \right) \rho(x,x',t) = \langle x | L_D | x' \rangle,$$

(2)

where the dissipation Liouville (Lindblad functional) $L_D$ describes the effect of the bath and was obtained in the high-temperature regime,

$$\langle x | L_D | x' \rangle = -\frac{\gamma}{\hbar} \left( \frac{2m k T}{\hbar} \right) \left( f(x) - f(x') \right)^2 + \left( f(x) - f(x') \right) \times \left( f'(x) \partial_x - f'(x') \partial_{x'} \right) \rho(x,x',t),$$

(3)

where $\gamma = \eta/(2m)$ is the damping rate of the oscillator with mass $m$, while $\eta$ and $T$ are the friction coefficient and bath temperature, respectively. By convention, I have used $\partial_x = \partial_r \partial x$, and $f'(x) = df(x)/dx$. There are two assumptions in deriving this equation: (i) an ohmic spectral representation of the bath, and (ii) the high-$T$ approximation of the correlation functions, which leads to Markovian dynamics of the system. It should be mentioned that extension to treat an electronic bath is straightforward. The overall modification needed is equivalent to replace the phonon spectral function and the friction coefficient by those of the electronic bath. Equation (3) also holds for an ohmic electron bath except that the damping rate attains a different physical meaning.

In the following, I construct a Lindblad functional, $L_D = \sum \left( V_f, \rho V_f \right] + \left[ V_f, \rho, V_f \right)$, with a single operator $V$ based on the nonlinear-coupling model of HPZ and the Lindblad theory of positive dynamic semigroup. The criteria for such a phenomenological construction are the following: (i) it should recover Eq. (3) in the high-temperature limit, for Eq. (3) is the exact equation derived from the model Hamiltonian; (ii) at low temperatures, it should (at least) lead to the correct equilibrium with the bath; and (iii) it should be simple in form in order to be useful for practical application. Having these in mind, a generalized combination of coordinate $x$ and momentum $p$ can be constructed with a single operator $V$,

$$\begin{align*}
V &= \mu f(x) + ivg(x) \\
V^\dagger &= \mu f(x) - ivg(x),
\end{align*}$$

(4)

here $\mu$ and $v$ are the combination coefficients, and $f(x)$ and $g(x)$ are two real functions determined later on. I should mention that a similar combination has also been considered by Gallis before. However, the explicit form of the functional was not determined in the way it is in this work.

Inserting operator $V$ into the Lindblad functional, the explicit form of $L_D$ can be worked out,

$$L_D = \left[ V, \rho V \right] + \left[ V, \rho, V \right] = \mu^2 \left( 2f^2 - f^2 p^2 - f^2 \rho^2 \right) + \nu^2 \left( 2ggpp - pg^2p - pg^2 \rho^2 \right) - i \mu v \left( 2fpp \rho \right) - 2gppf + \rho (fgp - pgf) + (fgp - pgf) \rho. \tag{5}$$

In order to compare Eq. (5) with the high-temperature master equation (3), one can project $L_D$ into the coordinate space, and it should recover Eq. (3):

$$\langle x | L_D | x' \rangle = -\mu^2 \left( f(x) - f(x') \right)^2 \rho(x,x',t) - 2\mu \nu \hbar \left( f(x) - f(x') \right) \left[ g(x) \partial_x - g(x') \partial_{x'} \right] \rho(x,x',t) - \hbar^2 \nu^2 \left[ g(x) \partial_x + g(x') \partial_{x'} \right]^2 + \left[ g(x) g'(x) \partial_x + g(x) \partial_{x'} \right] \rho(x,x',t). \tag{6}$$

In arriving at Eq. (6), a minor counterterm, $- (i\hbar) \left[ H_x, \rho \right]$ with $H_x = \mu \nu \hbar \left( fgp + pgf \right)$, has been added to $L_D$. This counterterm cancels two renormalization terms arising from Eq. (5), and ensures that the evolution of the mean position $\langle x \rangle$ and momentum $\langle p \rangle$ obeys the Ehrenfest theorem in the linear-coupling limit. It should be pointed out that the effect of the counterterm is negligible for most physical systems due to $\gamma < \Omega$. For a localized motion in condensed phases, for example, the damping rate is typically a few percent (or less) of the vibrational frequency.

It is worthwhile to mention that, for the general nonlinear-coupling model discussed in this paper, the equations of motion for the mean position and momentum become

$$\langle x \rangle = \frac{\langle p \rangle}{m} + \hbar^2 \nu^2 \langle \kappa(x) \rangle \tag{7}$$

$$\langle p \rangle = \langle \partial_x V \rangle - \gamma \langle g^2 p + pg^2 \rangle, \tag{8}$$

where $\kappa(x) = \partial_r \kappa^2(x)$. These relations differ from the conventional Ehrenfest theorem with additional (quantum) corrections. Only in the linear-coupling limit, namely, $f(x) = x, g(x) = 1$, are the two the same. In this sense, the conventional Ehrenfest theorem is merely a result of the linear-coupling model. Some other discussions on this point can be found in Ref. 18.

In order to recover Eq. (3) from Eq. (6) in the high-$T$ regime, it is obvious that $g(x)$ should take the following form:

$$g(x) = \frac{df(x)}{dx}. \tag{9}$$

The remaining difference between Eqs. (3) and (6) are the additional terms proportional to $\nu^2$ in Eq. (6). These terms are vanishing in the high-temperature regime, but become important for positivity requirement at low temperatures. Equation (2) together with (6) is the Lindblad master equation for the nonlinear-coupling model that we sought.

The two coefficients $\mu$ and $\nu$ can be determined in a way similar to the linear dissipation, for the coupling term of Eq. (1) is still linear in the bath coordinates as in the linear-coupling model. One can therefore apply the same approximations to the fluctuation $\alpha(x,t)$ and dissipation kernel $\alpha_r(t)$ as done previously. This in turn gives the following coefficients:

$$\nu^2(T) = \frac{\gamma m \Omega}{2h} \tanh \left( \frac{\hbar \Omega}{4k T} \right), \tag{11}$$

$$2\mu \nu = \gamma / h, \tag{12}$$

where $\Omega$ is the oscillator frequency of the system. These coefficients reduce to those contained in Eq. (3) in the high-temperature limit, and is consistent with the quantum
The evolution of the system is determined by a stochastic differential equation (SDE). The master equation can be equivalently represented by an ensemble of stochastic wave functions \( \{ \psi \} \), whose evolution are determined by a stochastic differential equation (SDE). Using the linear-unraveling scheme\(^\text{21}\) of the master equation, the SDE for the nonlinear-coupling model becomes

\[
\frac{d\psi}{dt} = -\left( \frac{i}{\hbar} [H + F] \right) \psi + G \xi d\xi, \tag{13}
\]

\[
F = \mu^2 f(x)^2 + i\frac{\gamma}{\hbar} f(x) g(x) p + \nu^2 p g(x)^2, \tag{14}
\]

\[
G = \mu f(x) + i \nu g(x) p, \tag{15}
\]

where \( d\xi \) is a complex Wiener process. By a sufficient number of stochastic realizations, the ensemble average of the wave functions gives an equivalent solution to the density matrix. Different from the Schrödinger wave functions, each \( \psi \) of Eq. (13) contains quantum transitions (jumps) induced by its bath, an important feature of open-system dynamics. Technically, the unraveling of the density matrix into wave functions is very useful for numerical solution of the wave-packet dynamics using the grid method, for the dimension of the wave function is half of that of the density matrix. Moreover, different stochastic wave packets can easily be propagated in parallel.

For practical application of this model, it is necessary to specify the coupling function \( f(x) \) for a physical system. In their earlier study, HPZ have considered\(^\text{21}\) various series functions, such as quadratic, cubic, and higher-order terms. For surface systems, a particularly interesting function is the one with exponential decay, for most interactions at surfaces decay exponentially at large particle-surface distance. This universal feature results from the electronic properties of a solid surface. Therefore, it is useful to consider the following \( f(x) \) with a single parameter \( a \):

\[
f(x) = a^{-1}[1 - \exp(-ax)], \tag{16}
\]

\[
g(x) = \exp(-ax). \tag{17}
\]

Here \( x \) is measured from the equilibrium position of the system. It is obvious that \( f(x) \) always approaches the linear coupling at small \( |x| \) or at \( a \to 0 \), while it decays exponentially at large \( x \) in the asymptotic region. Parameter \( a \) measures the nonlinearity of the coupling function. Without losing generosity, \( a \) can be chosen as the Fermi wave vector, \( a = k_F \), of the surfaces. For metals, it is between 0.5–1.0 a.u. In Fig. 1, \( f(x) \) is plotted as a function of \( x \) for three cases: \( a = 0 \) (linear), 0.5, and 1.0 a.u., respectively. For comparison, a Morse potential, \( U(x) = \exp(-2x^2) - 2 \exp(-x) \), is also shown to indicate the range of adiabatic and dissipative interactions for a typical surface system. The nonlinear function captures the decoupling behavior of the particle-surface interaction at large \( x \), where the adiabatic potential vanishes. The linear-coupling model \((a=0)\) is incorrect in the outer region, for it assumes a uniform force \( f(x) = x \) for all \( x \) at all distances.

As an example of application, I apply Eq. (13) to study vibrational damping of a molecule-surface bond, the \( \text{O}_2\)-Pt(111), induced by surface electrons at \( T = 200 \) K, a model problem that has been studied earlier by the linear-coupling model. The potential of the \( \text{O}_2\)-Pt(111) bond is represented by a Morse potential. The vibrational dynamics has been numerically solved with the same technique used before.\(^\text{13}\) Figure 2 shows the temperature relaxation of the bond from the \( n = 1 \) initial state with linear \((a = 0)\), and nonlinear coupling \((a = 1.0)\) to the electrons. The vibrational damping rate has been chosen as \( \gamma = 3.33 \times 10^{11} \) s\(^{-1}\). The population and thus the temperature relaxation does not seem to depend on the nonlinearity of the coupling. This is be-
cause the relaxation of the $n = 1$ excited state proceeds dominantly at the bottom of the potential well, where the coupling function $f(x)$ is almost linear.

The desorption rate, i.e., the rate of escaping from the potential well, depends sensitively on the nonlinearity of the coupling term, as shown in Fig. 3. The rate given by linear coupling [$a = 0$, Fig. 3(a)] is orders of magnitude smaller than the rate given by the nonlinear coupling [$a = 1.0$, Fig. 3(b)]. This is because the desorption dynamics depends on both the short- and long-range interaction of the potential. The linear-coupling model assumes a uniform force at all distances even if the molecule is far away from the surface. As a result, it should give no desorption because a desorbing molecule will sooner or later lose all of its kinetic energy to the surface and get trapped onto the surface. In fact, it gives no desorption because a desorbing molecule will sooner or later lose all of its kinetic energy to the surface and get trapped onto the surface. This unrealistic description of the linear-coupling model at large molecule-surface distances. With nonlinear coupling, the desorption rate increases substantially, for the molecule becomes gradually decoupled from the surface as it moves outwards, and thus has a finite chance to escape from the surface. Figures 2 and 3 indicate that the linear-coupling model, though correctly describes the vibrational damping, gives a completely incorrect picture of the desorption rate. The result shown in Fig. 3, though demonstrated for the desorption process, has general implication to other reactive processes, such as inelastic scattering, sticking, diffusion, and chemical reactions at surfaces.

In conclusion, I have given a simple nonlinear-coupling model for dissipative quantum dynamics, based on the Lindblad theory of open-system dynamics. Application to a model surface process, vibrational damping and desorption, indicates that the nonlinear-coupling model is essential to correctly describe the surface reaction dynamics in even a qualitative manner.

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1. For a recent review, see for example, S. Goldstein, Phys. Today 51 (3), 42 (1998); 51 (4), 38 (1998), and references therein.
19. G. W. Ford and R. F. O’Connell, Phys. Rev. Lett. 82, 3376 (1999). In addition to the incorrect coefficients, which violate the principle of detailed balance, the question of form invariance discussed by this comment is completely out of question for (i) a general oscillator and (ii) a general model of nonlinear coupling like the HPZ model we discuss in this work. Although the form of a quantum-mechanical equation can change under a unitary transformation, different mathematical forms of an equation should describe the same physical law. See a more detailed discussion by S. Gao, ibid. 82, 3377 (1999).