Dissipative Quantum Dynamics with a Lindblad Functional

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(Received 15 April 1997; revised manuscript received 28 July 1997)

A Lindblad operator is proposed to describe quantum dynamics of an open system with linear dissipation. Its functional form is determined based on the microscopic Caldeira-Leggett model. It yields a new master equation which preserves positive density evolution on short times and approaches equilibrium at high and low temperatures. The new master equation is applied as an example to study the femtosecond dynamics of vibrational relaxation and desorption at a metal surface. [S0031-9007(97)04383-4]

PACS numbers: 05.30.–d, 05.40.+j, 68.35.Ja

Dissipation and fluctuation in an open quantum system play an important role in a variety of phenomena in physics and chemistry. While dissipation in classical mechanics can be well described by the Langevin or the Fokker-Planck equation, quantum dynamics of an open system remains to be a challenging field [1–3], and is of general concern in many different areas such as quantum noise in tunneling junctions, quantum theory of measurement [3], and reaction rate theory in condensed phase [4].

The description of quantum dissipation of an open system has largely been based on the reduced density matrix formalism [5,6], 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 [7] and more recently to derive in a first-principle way the dissipation functional from microscopic Hamiltonians [8–10]. A quantum master equation, in analog with the Fokker-Planck equation, for the dynamics of the open system can be obtained in the high temperature or Markovian limit [8–12]. As given by Caldeira and Leggett in their pioneering work [8], the reduced density matrix ρ of a harmonic oscillator, linearly coupled to an Ohmic environment (linear dissipation) at temperature T, obeys the following master equation:

$$\frac{d\rho}{dt} + \frac{i}{\hbar}[H,\rho] = -\frac{\gamma}{\hbar}\left\{\frac{2mkT}{\hbar}[x,[x,\rho]] + i[x,[p,\rho]_+]\right\}. \quad (1)$$

Here $\gamma = \eta/2m$ is the characteristic damping rate of the oscillator with mass m and Hamiltonian H, and η is the friction coefficient. Similar master equations have been obtained along this line for a particle in a general environment [9–11]. Unfortunately, master equations like Eq. (1) are known to violate the positivity requirement of the density operator [11–14], and therefore lead, in certain cases, to unphysical results, particularly on a time scale comparable with the characteristic damping time γ^{-1}.

This problem does not exist in an alternative approach of open quantum systems, namely, the theory of quantum dynamical semigroups by Lindblad [15] and Kossakowski and colleagues [16]. In particular, Lindblad showed that the generator [15] for a positive dynamical map should be of the following form:

$$L_D = \sum_m \{[V_m, \rho V_m^\dagger] + [V_m \rho, V_m^\dagger]\}, \quad (2)$$

where the V_m's are the Lindblad dissipation operators. However, these operators are in general unknown and do not assure equilibrium with the bath. The Lindblad theory, albeit its neat and concise layout, remains to be more like a formal structure than an approach of practical applications, although a few constructions of such operators have been available in the literatures [17–19].

Here we propose a Lindblad operator to describe quantum dynamics of an open system with linear dissipation. Its explicit form is so determined as to reproduce the dissipation terms of the Caldeira-Leggett model at high temperatures and their generalizations to low temperatures. We arrive at a new master equation which 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-principle quantum master equations. Moreover, it provides an efficient scheme to study dissipative quantum dynamics, since 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 packets [18] $\{\Psi_k(x,t)\}$ with the given Lindblad operator. As a first example of application, the new master equation is used to study the femtosecond dynamics of vibrational relaxation for a Morse oscillator induced by a bath of metal electrons.

Our proposal of the Lindblad operator is motivated partly by the known functional of a damped harmonic oscillator, where the simplest dissipation operator is an annihilation and/or a creation operator [16]. We thus look for a single Lindblad operator V which is a linear combination of coordinate x and momentum p [19],

$$\begin{cases} V = \mu x + i\nu p \\ V^{\dagger} = \mu x - i\nu p \end{cases}, \tag{3}$$

where coefficients μ and ν are arbitrary c numbers that will be determined below. The equation of motion for ρ, $\frac{d\rho}{dt} + \frac{i}{\hbar}[H,\rho] = L_D[\rho]$, can be written out explicitly according to Eqs. (2) and (3),

$$\begin{aligned} \frac{d\rho}{dt} + \frac{i}{\hbar}[H',\rho] = &- \mu^2[x,[x,\rho]] - 2i\mu\nu[x,[p,\rho]_+] \\ &- \nu^2[p,[p,\rho]], \end{aligned} \tag{4}$$

$$H' = H - 2\mu\nu\hbar xp\,,$$

where $[A,B]_+$ represents an anticommutation relation between operators A and B. In obtaining Eq. (4), the identity $[x,p] = i\hbar$ has been used to rearrange the cross terms of x and p. The three terms on the right-hand side and the last one on the left are all traceless (due to the cyclic property of trace), which guarantees $\frac{d}{dt}\,\mathrm{Tr}\,\rho = 0$, i.e., the norm conservation of the reduced density matrix. In fact, the general form Eq. (2) is traceless and thus the Lindblad approach is generally norm conserving.

To determine coefficients μ and ν, one easily realizes that the first two terms on the right-hand side of Eq. (4) are essentially the same terms as in the Caldeira-Leggett master equation (1). The latter was exactly derived from a microscopic Hamiltonian in the high-temperature limit, or equivalently the classical limit $\hbar \to 0$, where the force-force correlation function becomes localized in time. This comparison suggests the following conditions for choosing μ and ν:

$$\begin{cases} \mu^2 = \gamma 2kTm/\hbar^2 \\ 2\mu\nu = \gamma/\hbar\,, \qquad \text{as } T \to \infty\,, \\ \nu^2 = 0 \end{cases} \tag{5}$$

which yields straightforwardly $\nu^2 = \gamma/8mkT$ in the high-temperature regime. The latter is different from $D_{qq} = \gamma/6mkT$, a diffusion coefficient that has recently been derived by Diósi by going beyond the lowest order Markovian approximation at high and medium temperatures [11].

To extend the functional to low temperatures, we point out that the two dissipation terms in Eq. (1) have different physical origin. The second term, which is given by the imaginary part of the force-force correlation function $\alpha(t) = \langle F(t)F(0)\rangle$, describes the dissipation effect and is temperature independent [8,10,11]. This indicates that $2\mu\nu = \gamma/\hbar$ is valid at all temperatures. On the contrary, the first term, which is given by the real part of the same correlation function, results from environment-induced fluctuation (noise) and depends on temperature T as $\alpha_R(t,T) = \int_0^{\Omega_c} I(\omega)\coth(\frac{\hbar\omega}{2kT})\cos(\omega t)\,d\omega$. Here $I(\omega) = \eta\omega/\pi$ is the spectral function for the Ohmic environment, and Ω_c is the bandwidth of the spectrum. At low T, $\omega\coth(\frac{\hbar\omega}{2kT})$ is a smooth function of ω while $\cos(\omega t)$ is fast oscillating. This observation leads us to the following approximation:

$$\begin{aligned} \alpha_R(t,T) &\simeq \frac{\eta}{\pi}\,\omega_c\coth\!\left(\frac{\hbar\omega_c}{2kT}\right)\int_0^{\Omega_c}\cos(\omega t)\,d\omega \\ &= \eta\omega_c\coth\!\left(\frac{\hbar\omega_c}{2kT}\right)\tilde{\delta}(t)\,, \end{aligned} \tag{6}$$

where $\tilde{\delta}(t) = \frac{1}{\pi}\int_0^{\Omega_c}\cos(\omega t)\,d\omega$, 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 $\Omega_c \to \infty$ and thus $\tilde{\delta}(t)$ approaches $\delta(t)$ [20]. This approximation is different from the earlier ones [8,10,11], which are all based on a temperature expansion of the noise kernel. It leads to a replacement of $2kT \to \hbar\omega_c\coth(\frac{\hbar\omega_c}{2kT})$ in the first diffusion term of Eq. (1) and thus in our choice of μ^2. In fact, this is a simple replacement from the classical to quantum representation of the fluctuation-dissipation relation in the narrow band 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 the potential minimum. The Lindblad operator V then reduces to the annihilation operator of the harmonic oscillator, giving $\mu/\nu = m\Omega$ and in turn $\omega_c = \Omega/2$, i.e., half of the oscillator frequency. The temperature dependence of the two coefficients then reads

$$\mu^2(T) = \frac{\gamma m\Omega}{2\hbar}\coth\!\left(\frac{\hbar\Omega}{4kT}\right), \tag{7}$$

$$\nu^2(T) = \frac{\gamma}{2\hbar m\Omega}\tanh\!\left(\frac{\hbar\Omega}{4kT}\right), \tag{8}$$

with the accompanying relation $2\mu\nu = \gamma/\hbar$. Both expressions reduce to Eq. (5) in the high-temperature regime, and have their physical bases on the quantum fluctuation-dissipation theorem. They thus bring the equilibrium behavior into the Lindblad formalism through their temperature dependence.

In coordinate space, the master equation (4) takes the following form:

$$\begin{aligned} \frac{\partial\rho(x,x',t)}{\partial t} + \frac{i}{\hbar}[\tilde{H}(x) - \tilde{H}^{\star}(x')]\rho(x,x',t) = -\Big\{&\mu^2(T)(x-x')^2 + \gamma(x-x')\left(\frac{\partial}{\partial x} - \frac{\partial}{\partial x'}\right) \\ &- \nu^2(T)\hbar^2\left(\frac{\partial}{\partial x} + \frac{\partial}{\partial x'}\right)^2\Big\}\rho(x,x',t)\,, \end{aligned} \tag{9}$$

$$\tilde{H}(x) = H(x) + i\hbar\gamma x\frac{\partial}{\partial x} + i\,\frac{\hbar\gamma}{2}\,. \tag{10}$$

The last two terms of Eq. (10) come from H' of Eq. (4), namely, $\langle x|[-2\mu\nu\hbar xp, \rho]|x'\rangle = -2\mu\nu\hbar \times \langle x|xp\rho - \rho px - i\hbar\rho|x'\rangle = i\hbar\gamma(x\frac{\partial}{\partial x} + x'\frac{\partial}{\partial x'} + 1) \times \rho(x,x',t)$. This master equation differs from all previous ones in two aspects: (1) A renormalized Hamiltonian with a frictional force and an imaginary term and (2) an additional diffusion term (the ν^2 term) with temperature-dependent diffusion coefficient. This new term, which is vanishing in the high-temperature limit as in Eq. (1), is important to preserve intrinsic quantum fluctuation [21] at low temperatures. In addition, as Eq. (9) is directly constructed from the Lindblad functional, it is therefore norm conserving (which can be explicitly proved [18]) and guarantees the positivity of the density matrix even on short time scales. This is extremely important for the description of dissipative quantum dynamics involved in a variety of transient phenomena.

As an example of application of the new master equation (9), we study the dynamics of vibrational relaxation of a Morse oscillator induced by electrons at a metal surface. This is a problem of high current interest in surface physics and can be described by a model of linear dissipation [22]. To be specific, we simulate O_2 on a Pt(111) surface. Nonadiabatic electron-hole pairs are believed to be the dominant mechanism for the damping of vibration on Pt(111) with a lifetime $\gamma^{-1} = 3$ ps [22]. The Hamiltonian of the free oscillator takes the following form:

$$H = -\frac{\hbar^2}{2m}\frac{d^2}{dx^2} + D[e^{-2\alpha x} - 2e^{-\alpha x}], \qquad (11)$$

with parameters ($\hbar\Omega = 0.049$ eV, $\alpha = 2.545$ a.u., and $D = 0.4$ eV) chosen to represent those of the adsorbed O_2 molecule on Pt(111) [22]. The relaxation dynamics is obtained by propagating an initial wave packet corresponding to the first vibrationally excited state of the oscillator, $\rho(x,x',0) = \Psi_1(x)\Psi_1(x')^\dagger$. Equation (9) is solved numerically using the splitting operator technique, where the terms with only x or p operators are propagated in the coordinate and momentum space, respectively, with the help of the fast Fourier transform (FFT) [23]. The terms containing both x and p operators are propagated by the two-step Wendroff-Lax scheme for the flux-conservative differential equations [23]. We used a time step $\Delta t = 10$ a.u. and 512 grid points sampled on a length of $L_x = 3$ a.u.

Figure 1 shows the wave packet evolution as a function of time. Without dissipation, i.e., $\gamma = 0$, the initial wave packet would remain in the excited pure state for an infinitely long time. Because of coupling to electrons, any nonthermal distribution relaxes and approaches equilibrium with its environment. Figure 1 shows the dynamical process during the first 500 fs. The wave packet evolves from the excited state to a thermalized Gaussian wave packet. Figure 2 shows the development of the vibrational temperature, $T_v = \hbar\Omega/[k\ln(P_0/P_1)]$ with $P_i(t) = \int dx \int dx' \Psi_i(x)^\dagger \rho(x,x',t)\Psi_i(x')$, at longer times for different bath temperatures. The wave packet approaches the electron temperature within the vibrational lifetime $\gamma^{-1} = 3$ ps, even in the low temperature $kT \ll \hbar\Omega$ regime. The final equilibrium that the wave packet reaches does not depend on the initial density distributions.

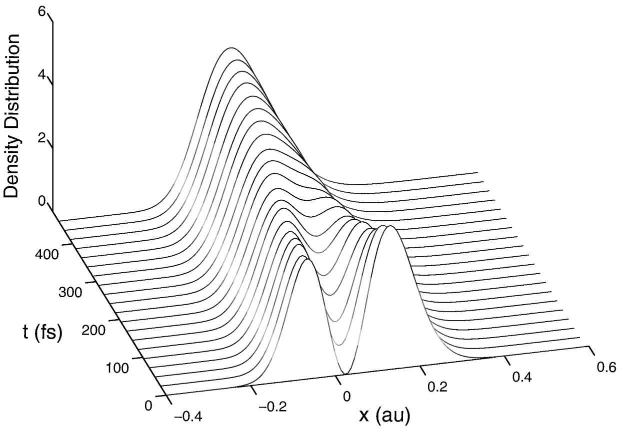

FIG. 1. The diagonal density evolution $\rho(x,x,t)$ of a Morse oscillator as a function of time at $T = 200$ K. The parameters are chosen to represent an O_2-Pt(111) bond with a damping rate $\gamma = 3.3 \times 10^{11}$ s^{-1} due to coupling to electrons at the metal surface. The initial density matrix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

To illustrate the importance of positivity of the density matrix, we plot in Fig. 3 the desorption rate (current), $j(t) = -\frac{i\hbar}{2m}(\frac{\partial}{\partial x} - \frac{\partial}{\partial x'})\rho(x,x',t)|_{x=x'=x_d}$, at the desorption boundary x_d 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. (1) does not have the correct sign in

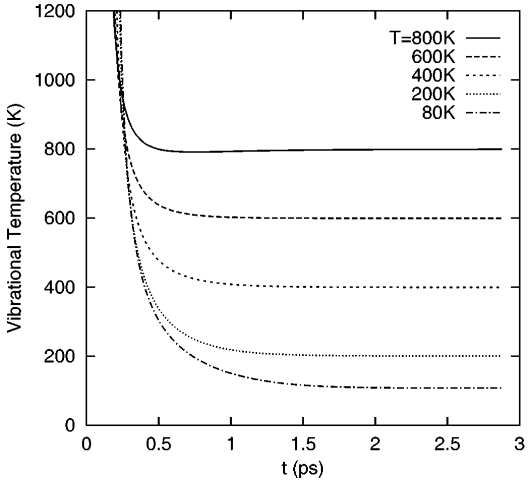

FIG. 2. The development of the vibrational temperature for the same initial wave packet shown in Fig. 1 at different bath temperatures (T). Initially the wave packet has a nonthermal distribution and the temperature is not well defined. Note that the vibrational quantum of the oscillator corresponds to a temperature of $\hbar\Omega/k = 570$ K. The wave packet approaches equilibrium with the electron bath at both high and low temperatures.

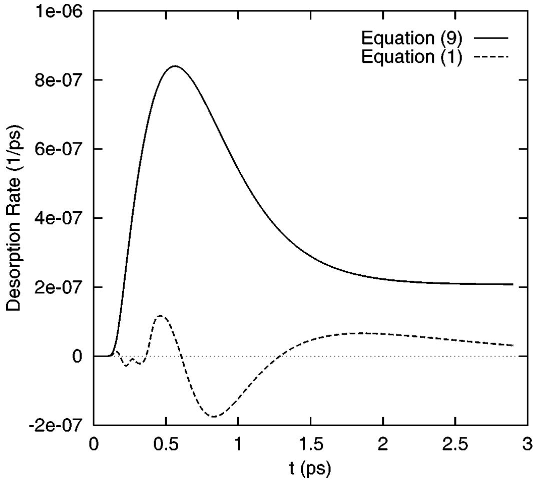

FIG. 3. The calculated desorption rate as a function of time before absorbing boundary at $T = 200$ K. The rate given by Eq. (1) does not have the right sign in the subpicosecond regime due to the unphysical negative density distribution. This problem does not exist in the rate given by the new master equation (9).

the subpicosecond regime due to the unphysical negative density distribution at the desorption boundary. In comparison, the new master equation (9) correctly describes the desorption rate as a function of time during relaxation.

Finally, we point out that Eq. (9) becomes poor in the zero-temperature limit for a particle in an anharmonic potential due to the harmonic oscillator approximation. Nevertheless, it is applicable to most physical systems at nonzero temperatures.

In summary, we have proposed a Lindblad operator for describing dissipation in quantum regime based on the microscopic Caldeira-Leggett model, and obtained a new quantum master equation. This approach, though demonstrated here for linear dissipation, can be generalized to systems with nonlinear couplings to more general environment.

This work is supported by the Swedish Natural Science Research Council (NFR). I would like to thank Mats Persson and Jari Kinaret for helpful discussions. Critical comments from Bengt Lundqvist are also gratefully acknowledged.

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[1] E. B. Davis, *Quantum Theory of Open Systems* (Academic, London, 1976).
[2] C. W. Gardiner and M. J. Collett, Phys. Rev. A **31**, 3761 (1985).
[3] W. H. Zurek, Phys. Today **44**, No. 10, 36 (1991), and references therein.
[4] P. Hanggi, P. Talkner, and M. Borkovec, Rev. Mod. Phys. **62**, 251 (1990).
[5] K. Blum, *Density Matrix Theory and Applications* (Plenum, New York, 1981).
[6] R. P. Feynman and F. L. Vernon, Jr., Ann. Phys. (N. Y.) **24**, 118 (1963).
[7] For a review of the various phenomenological models, see, for example, H. Dekker, Phys. Rep. **80**, 1 (1980).
[8] A. O. Caldeira and A. J. Leggett, Physica (Amsterdam) **121A**, 587 (1983); Ann. Phys. (N. Y.) **149**, 374 (1983).
[9] W. G. Unruh and W. H. Zurek, Phys. Rev. D **40**, 1071 (1989).
[10] B. L. Hu, Juan Pablo Paz, and Yuhong Zhang, Phys. Rev. D **45**, 2843 (1992); **47**, 1576 (1993).
[11] L. Diósi, Europhys. Lett. **22**, 1 (1993); Physica (Amsterdam) **199A**, 517 (1993).
[12] V. Ambegaokar, Ber. Bunsen-Ges. Phys. Chem. **95**, 400 (1991).
[13] A. Tameshtit and J. E. Sipe, Phys. Rev. Lett. **77**, 2600 (1996).
[14] R. Karrlein and H. Grabert, Phys. Rev. E **55**, 153 (1997).
[15] G. Lindblad, Commun. Math. Phys. **48**, 119 (1976).
[16] A. Kossakowski, Rep. Math. Phys. **3**, 247 (1972); V. Gorini, A. Kossakowski, and E. C. G. Sudarshan, J. Math. Phys. (N.Y.) **17**, 821 (1976).
[17] R. Alicki and K. Lendy, *Quanum Dynamical Semigroups and Applications,* Lecture Notes in Physics Vol. 286 (Springer-Verlag, Berlin, 1987).
[18] N. Gisin and I. C. Percival, J. Phys. A **25**, 5677 (1992); S. Gao, Phys. Rev. B (to be published).
[19] A general linear combination has been discussed by A. Sandulescu and H. Scutaru, Ann. Phys. (N.Y.) **173**, 277 (1987); A. Isar, A. Sandulescu, and W. Scheid, J. Math. Phys. (N.Y.) **34**, 3887 (1993); **32**, 2128 (1991). See also M. R. Gallis, Phys. Rev. A **48**, 1028 (1993); **53**, 655 (1996). The present paper looks for a particular but unique combination for a general oscillator, whose functional form is determined by a microscopic Hamiltonian model, the Caldeira-Leggett model.
[20] Please note the order between the factorization in Eq. (6) and the Markovian approximation. The former is physical. The narrower the bandwidth of $I(\omega)$ (smaller Ω_c), the better the approximation in Eq. (6). The second step $\Omega_c \rightarrow \infty$ is mathematical, and is consistent with the Lindblad formalism, which itself is based on the Markovian approximation.
[21] H. Dekker and M. C. Valsakumar, Phys. Lett. **104A**, 67 (1984).
[22] S. Gao, D. G. Busch, and W. Ho, Surf. Sci. **344**, L1252 (1995); S. Gao, Phys. Rev. B **55**, 1876 (1997).
[23] W. H. Press, S. A. Teukolsky, W. T. Vetterling, and B. P. Flannery, *Numerical Recipes* (Cambridge University Press, Cambridge, 1992).